

CRANFIELD UNIVERSITY

Erin Losty

**Investigating the Importance of Emerging Disinfection by-products
Formation Through Traditional Flowsheets and Advanced Treatment
Technologies.**

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

Cranfield Water Science Institute

PhD

Academic Year: 2015 - 2019

Supervisor: Dr Emma Goslan and Prof. Bruce Jefferson

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ABSTRACT

Chlorine was first used to disinfect drinking water in the US as early as 1908 with other disinfectants, ozone, chlorine dioxide to follow. However, it wasn't until the 1970's that Rook discovered a possible link to higher levels of chloroform in drinking water treated with chlorine and inadvertently linked the possibility of precursor material to products of the disinfection process. While the introduction of chlorine to disinfect water has been significant in eliminating pathogens for safe drinking water, it becomes important to safeguard the public against disinfection by-product (DBP) exposure. This thesis intends to give an understanding into the relationship between the control pathway and total DBP formation, giving an insight to the occurrence and the formation for DBPs in drinking water. Emphasis is placed on the natural organic matter characteristics and precursors involved in the formation of DBPs through the treatment process with the use of 3 surface waters. Analysis of 27 traditional and emerging DBPs seek to give a better understanding of the composition of the DBP mixture as a whole, their formation and subsequent minimisation. Comparing two advanced treatment methods, Advanced Oxidative Processes and Nanofiltration with optimal and sub optimal conditions and provide operational advice on minimising DBP formation. AOPs reduced the DBPs and HI more efficiently than nanofiltration but only when high H_2O_2 levels are used. At lower H_2O_2 doses, DBPs increased where as nanofiltration reduced the DBP precursors considerably under optimal and sub-optimal conditions, becoming important in waters with high seasonal variability.

Minimising DBPs, specifically THM concentrations has been a priority of water treatment to date, but to reduce the hazard index associated to DBPs would be more beneficial. WHO *in vivo* generated guideline values exists for only 19 of the 27 DBPs measured, this could potentially limit the ability to understand the impact of the broadest range of emerging DBPs. Over 600 have been discovered and more research is needed to define this mixture and stipulate DBP interactions impacting the hazard index. The key emerging DBPs impacting the HI, using the guideline values, are the brominated and nitrogenated species, BDCAA, BCAA, DCAN and BCAN. Recommendations to

monitoring and regulation would be to add these to the current regulatory list by extending HAA5 to HAA9 or as a minimum to include the Br-HAAs. Bromine removal and its subsequent formation of Br-DBPs when not removed effectively, can impact the HI dramatically and, therefore, emphasis for removal is needed. Traditionally upland waters have been the focus due to its high formation of THMs, but it has the lowest HI throughout. Lowland lake, with the highest bromine levels generated the highest HI, consideration is needed to better minimise DBP formation.

Keywords: Natural Organic Matter, Advanced Oxidative Processes, Nanofiltration, Emerging DBPs, Hazard Index

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LIST OF ABBREVIATIONS

•OH	Hydroxyl radical
1,2 DE	1,2 dibromoethane
ADWG	Australian Drinking Water Guidelines
AOP	Advanced oxidation process
AOX	Adsorbable organic halogen
BCAA	Bromochloroacetic acid
BCAM	Bromochloroacetamide
BCAN	Bromochloroacetonitrile
BCIM	Bromochloriodomethane
BDCAA	Bromodichloroacetic acid
BDCAM	Bromodichloroacetamide
BDCM	Bromodichloromethane
BDIM	Bromodiiodomethane
BF	Bromoform
Br/Cl-DBP	Brominated/chlorinated disinfection by-product
Br-DBP	Brominated DBPs
Br-HAA-FP	Brominated Haloacetic acid Formation potential
Br-HAAs	Brominated Haloacetic acid

Br-THMs	Brominated Trihalomethane
BSF	Bromine substitution factor
C1 Solv6	1,2dibromoethane,tetrachloroethylene, dibromochloropropane, carbon tetrachloride, 111 trichloroethane and trichloroethylene
CH	Chloral hydrate
CHO	Chinese hamster ovary
CIAM	Chloroiodoacetamide
Cl-DBP	Chloro-organic DBPs
CO ₂	Carbon Dioxide
COOH	Carboxylic acid functional group
CP	Cholorpicrin
CS	Chlorinated chemical
CS6	Sum of: 1,2 dibromoethane, tetrachloroethylene, dibromochloropropane, carbon tetrachloride, 111 trichloroethane and trichloroethylene
CT	Carbon tetrachloride
CT HI	Carbon tetrachloride Hazard Index
DBAA	Dibromoacetic acid
DBAM	Dibromoacetamide
DBAN	Dibromoacetonitrile
DBCAA	Dibromochloroacetic acid
DBCAM	Dibromochloroacetamide

DBCM	Dibromochloromethane
DBCP	Dibromochloropropane
DBIM	Dibromoiodomethane
DBP	Disinfection by-product
DBP/GV	Disinfection by-product Guideline value
DBP27	List of 27 DBPs measured in this PHD
DBP-FP	Disinfection By-products Formation Potential
DCAA	Dichloroacetic acid
DCAAFP	Dichloroacetic acid formation potential
DCAM	Dichloroacetamide
DCAN	Dichloroacetonitrile
DCBAA	Dichlorobromoacetic acid
DCIM	Dichloroiodomethane
DCP	1,1-Dichloropropanone
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
Dp	Diffusion coefficient
DWI	Drinking water inspectorate
EC	Effective concentration
EPA	Environmental Protection Agency

EU	European Union
FP	Formation potential
GAC	Granular activated carbon
GAC	Granular activated carbon
GC	Gas Chromatography
GC/ECD	Gas chromatography with electron capture detection
GC/MS	Gas chromatography with mass spectrometry
GC-ECD	Gas Chromatography-electron capture detector
GDWQ	Guidelines for Drinking-water Quality
GV	Guideline value
H ₂ O	Water
H ₂ O ₂	Hydrogen peroxide
HA	Humic acid
HAA	Haloacetic acid
HAA5	Sum of monochloroacetic acid (MCAA), trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA).
HAA6	Sum of Monochloroacetic acid, Dichloroacetic acid, Bromochloroacetic acid, Dibromoacetic acid, Trichloroacetic acid and Bromodichloroacetic acid.
HAA9 acids	Sum of 9 chlorine- and bromine-containing haloacetic acids
HAA-FP	Haloacetic acid formation potential

HAL1	Haloacetaldehyde, chloral hydrate.
HALs	Haloacetaldehyde
HAN	Haloacetonitrile
HAN2	Dichloroacetonitrile and Dibromoacetonitrile
HAN4	Sum of dichloro-, trichloro-, dibromo- and bromochloro-acetonitrile
HAN-FP	Haloacetonitrile formation potential
HF	Halofuranones
HI	Hazard Index
HK	Haloketone
HK2	Sum of 1,1,1-trichloro- and 1,1-dichloropropanone
HNM	Halonitromethane
HNM1	Halonitromethane, chloropicrin
HOBr	Hypobromous acid
HOCl	Hypochlorous acid
HPI	Hydrophilic
HPLC	High performance liquid chromatography
HPO	Hydrophobic
HPSEC	High performance size exclusion chromatography
IAs	Iodoacids
IC	Inorganic carbon
ICP-MS	Inductively coupled plasma- mass spectroscopy

IPCS	International Programme on Chemical Safety
LC50	Lethal concentration ₅₀
LOD	Limit of Detection
log K _{ow}	Hydrophobic interactions
LOQ	Limit of quantification
MAC	Minimum acceptable concentration
MAVs	Maximum acceptable values
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MCL	Minimum containment level
MDL	Method detection limit
MRL	Method reporting level
MS	Mass Spectrometry
MtBE	Methyl tert-butyl ether
MW	Molecular weight
MWCO	Molecular weight cut-off
MWD	Molecular weight distribution
N-DBP	Nitrogen-containing disinfection by-product
NDMA	Nitrosodimethylamin
NF	Nanofiltration
NF270	NF270 membrane (Dow-Filmtec)
NF70	NF70 membrane (Dow-Filmtec)

NF90	NF90 membrane (Dow-Filmtec)
NH ₂ Cl	Monochloramine
NHMRC	National health and medical research council Australia
NOAEL	No-observed-adverse-effect level
NOM	Natural organic matter
NPOC	Non purgeable organic carbon
O ₃	Ozone
-OH	Hydroxyl functional group
Other DBPs	Monobromoacetic acid, chlorodibromoacetic acid, tribromoacetic acid, trichloroacetonitrile and bromochloroacetonitrile
PAC	Powdered activated carbon
pKa	Acid dissociation constant
polyDADMAC	Polydiallyldimethylammonium chloride polymer
RO	Reverse Osmosis
SEC	Size exclusion chromatography
SEQ	South East Queensland
SP1	Sampling point 1 in November
SP2	Sampling point 2 in May
SPE	Solid phase extraction
SUVA	Specific UV absorbance at 254 nm
TBAA	Tribromoacetic acid
TBAM	Tribromoacetamide

TBM	Tribromomethane
TBNM	Tribromonitromethane
TC	Total Carbon
TCAA	Trichloroacetic acid
TCAAFP	Trichloroacetic acid formation potential
TCAM	Trichloroacetamide
TCAN	Trichloroacetonitrile
TCE	Trichloroethylene
TCM	Trichloromethane
TCNM	Trichloronitromethane
TCP	1,1,1-Trichloropropanone
TDI	Tolerable daily intake
TETCE	Trichloroethylene
THAA	Trihaloacetic acids
THM	Trihalomethane
THM4	Sum of Trichloromethane, Bromodichloromethane, Dibromochloromethane and Tribromomethane.
THM-FP	Trihalomethane formation potential
TIE	111 trichloroethane
TN	Total nitrogen
TOC	Total organic carbon
TON	Total organic nitrogen

TOX	Total organic halide
TPI	Transphilic
TTE	Tetrachloroethylene
UK	United Kingdom
UQ	University of Queensland
US	United States
US EPA	United States Environmental Protection Agency
US	Unites States of America
UV	Ultraviolet
UV Vis	Ultraviolet & Visible
UV/H ₂ O ₂	Ultraviolet hydrogen peroxide
UV/TiO ₂	Ultraviolet titanium dioxide
UV-AOP	Ultraviolet advanced oxidative processes
UVC	Ultraviolet band 200-280nm (λ 254nm used)
WHO	World Health Organization
WTP	Water treatment plant
X	Halide, Chlorine/bromine/Iodine
X-DBPs	Halide, Chlorine/bromine/Iodine containing DBP

1 Introduction

Introduction

1.1 Introduction

Disinfection by-products (DBPs) are unintentionally formed during the disinfection stage of drinking water production which is used to reduce microbial pathogens, rendering water safe to drink. Raw waters before treatment, contain organic and inorganic materials which can react with the disinfectant (chlorine, chloramine, chlorine dioxide and ozone) forming DBPs. To date over 600 individual DBPs have been discovered, grouped into over 32 categories (Richardson, 2003). The most prevalent by weight are the trihalomethanes (THMs) and the haloacetic acids (HAAs) such that current focus of both research and operational practice is towards these. For instance, current regulations in Europe requires management of the treatment works to ensure the sum of four THMs (THM4) remains below 100 µg/L. In the US this is extended to include HAA5 reflecting knowledge that the THMs and HAAs form from different precursors/pathways. Either way, the regulated DBPs are being used as proxy for the whole, enabling simple and affordable monitoring and management practices. For instance, the World Health Organisation (WHO) guidelines in 2011 suggest if chlorination is practised, the THMs and HAAs will be the main DBPs and by keeping these below the guidance levels, will provide adequate control of all DBPs.

The current regulation assumes that the higher the concentration of the regulated DBPs, the greater the risk involved and as such they act as a proxy for not just the concentration of the other DBPs but their formation and removal as well as in terms of human exposure and associated risk (Bond, *et al*, 2011; Ding *et al.*, 2018; EPA, 2006; EPA, 1998; Li & Mitch, 2017; WHO, 2011). The emerging DBPs typically exist at relatively low concentrations and so can be viewed as less significant. However, their toxicity may be substantially greater such that even at low concentrations they may be important. Accordingly, it is suggested that the relative significance of both traditional and emerging DBPs be re-examined through a toxicological lens.

1.1.1 Hazard index and guideline values

Consideration of the relative toxicity is described through a hazard index (HI). The HI is the sum of the hazard quotients (HQ) for each chemical within the mixture, in this case the individual DBP chemicals people are exposed to. It is the ratio between the individual DBP exposure concentration ([DBP_x]) and the corresponding reference guideline value (GV_x). To determine the HI for a mixture, a hazard quotient is calculated for each component by dividing the exposure level or DBP concentration for each component with its corresponding guideline value. The individual hazard quotients are then added to give an overall HI according to equation 1.1, where HI is the hazard index; [DBP] represents the exposure concentration of each individual DBP chemical; and GV represents the reference guideline value for each individual DBP. Equation 1.1 represents a generalised form of HI derived from the HQs summed, each HQ is represented in this case by DBP chemicals 1-n, depending on the number of chemical species within the test mixture (1-n), their concentration and corresponding GVs available (1-n).

$$HI = \sum HQ = \frac{DBP_1}{GV_1} + \frac{DBP_2}{GV_2} + \dots + \frac{DBP_n}{GV_n}$$

Equation 1.1

For instance, WHO have suggested a component-based approach to THMs where the concentrations of each individual DBP concentration ([DBP]) is divided by their respective WHO guideline value (GV_x) and summed, giving a hazard index for the mixture, and should be less than 1 as seen in equation 1.2.

$$HI = \frac{[CF]}{GV_{CF}} + \frac{[BDCM]}{GV_{BDCM}} + \frac{[BF]}{GV_{BF}} + \frac{[DBCM]}{GV_{DBCM}}$$

Equation 1.2

For example, a concentration of 20, 25, 30 and 35 µg/L of CF, BDCM, BF and DBCM respectively and using the guideline values of 300, 120, 100 and 100 µg/L found in Table 1.1, the result can be seen in equation 1.3.

$$HI = \frac{20}{300} + \frac{25}{120} + \frac{30}{100} + \frac{35}{100} = 0.925$$

Equation 1.3

Providing a qualitative assessment of the hazardous properties of chemicals within a mixture, the HI value is interpreted according to whether or not it exceeds unity. Having a HI less than 1 indicates that exposure is below the reference level chosen, in this instance the guideline value, and is therefore exposure is considered low risk. If the HI is above or equal to 1, exposure to the mixture of chemicals are at or above the reference level, signalling there may be risk of exposure to this mixture of chemicals, indicating greater concern (Mumtaz *et al.*, 1992; U S EPA, 1986; WHO, 2017a). This approach is a modification of initial work by Mumtaz *et al.*, who used a weighted approach to assess interactions in chemical mixtures (Mumtaz *et al.*, 1992; Mumtaz *et al.*, 2010). It generates a risk indicator for a group chemical groups to improve risk indication estimates for the entire mixture and was suggested for use for the THM mixture by Teuschler *et al.*, in a research report on mixtures of DBPs in drinking water (Mumtaz *et al.*, 1992; Teuschler *et al.*, 1999). New Zealand has adopted this health based approach for THM regulation, using the WHO guideline values for the individual THMs and summing their concentration to the guideline value. They also have maximum acceptable values (MAVs) for the individual THMs (Ministry of Health, 2017; WHO, 1993). In equation 1.3, example of the HI of THM4, the resulting HI is below 1, therefore considered low risk. This is an achievable, case by case hazard index which takes the potency of each individual DBP in to account. This method can be used for monitoring but also to elucidate the toxicity driver with the DBP mixture (WHO, 2017a). There is currently no ‘regulatory-applicable’ method for the risk assessment of mixtures in drinking waters but it is widely accepted that the components act in an additive manor at low environmental concentrations (WHO, 2017a). When there is evidence to prove otherwise, the interaction occurs in an antagonistic or synergistic fashion (Boobis *et al.*, 2011; Brack *et al.*, 2015).

The GVs used in such assessments are developed by the International Programme on Chemical Safety (IPCS), through which the WHO works to establish the scientific basis for the management of chemical safety. GV are derived from the best available toxicological data and are independently reviewed and updated periodically from relevant studies on toxicity in animals and humans as well as available literature showing exposure in people to the individual chemical/DBP. A tolerable daily intake (TDI) is derived using the most sensitive end point in the most relevant study, preferably using drinking water to administer the chemical. Uncertainty factors are incorporated and the no observed adverse effect level (NOAEL) found in the relevant toxicological studies to allow for ambiguity or data deficiencies. The guideline value is then derived from the TDI considering default assumptions such as the body weight of

individuals, the proportion of total intake attributed to drinking water, and daily drinking water consumption volume. In the absence of adequate data on concentrations in appropriate media, the TDI can also be derived using mathematical models, estimating the risk at a specific exposure level. Consideration may also need to be given to other sources of the chemical, such as inhalation of volatile DBPs in the shower or while cleaning, as exposure from drinking water consumption may be a minor contributor. The guidance values are not set regulation and are set to be adapted at national and local levels as appropriate for local circumstances (Grellier *et al.*, 2015; United Nations Environment Programme *et al.*, 1994; WHO, 1993, 2017, 2018).

The overall process of deriving a guideline value for a given chemical/DBP requires expert judgement and careful consideration of the available scientific evidence. International risk assessments need to be considered, along with the published, peer-reviewed scientific literature. *In vivo* assays using experimental animals are given a higher priority to derive health-based values DBPs as they are considered the gold standard for toxicology. Only relevant studies meeting high criteria levels are used, because of this they are used as a guidance worldwide to set maximum contaminant levels, regulations and general acceptance DBP concentrations (Hrudey *et al.*, 2015; Plewa, *et al.*, 2017; WHO, 2017a). Although *in vivo* testing is considered the gold standard for regulations, these currently apply to a relatively small fraction of the overall DBPs currently discovered. These include the regulated DBPs which accounts for only a small proportion of the overall toxicity. Adding to *in vivo* research is restricted by time, scientific and financial constraints as *in vivo* testing is costly and can take years to complete (Itoh *et al.*, 2011). These constraints are acknowledged in the WHO Guidelines for Drinking-water Quality and a shift in favour of preventive risk management rather than increasing the number of chemical parameters monitored is recommended. Because of this, studies have focused on the overall toxicity of drinking water trying to take the DBP mixture in to account but as the DBP mixture is partially defined, a smaller defined mixture acts as a proxy for the whole mixture (WHO, 1993, 2017a, 2018).

Whilst robust, GVs exists for only 19 DBPs potentially limiting the ability to understand the impact of the broadest range of emerging DBPs. Alternative approaches exist utilising *in vitro* bioassays with different end points such as the use of LC50 data from Hamster ovary studies. These studies seek to elucidate the toxicity of individual DBPs by examining genomic DNA damage in Chinese hamster ovary cells using chronic cytotoxicity and acute genotoxicity (also known as the single cell gel electrophoresis (SCGE) or comet assay) assays. The chronic cytotoxicity assay measures the reduction in cell density as a function of the concentration, and

the acute genotoxicity assay quantitatively measures the level of genomic DNA damage induced in individual cells (Wagner *et al.*, 2017). Over 100 individual DBPs were tested revealing unregulated DBP classes, particularly N-DBPs and Br-DBPs, may be more cytotoxic and genotoxic than the regulated THM4 (and HAA5 in the US). However, according to a review by Cortés (2018), the comet assay, detects damage which is generally repaired by the cells, due to this more relevant genotoxicity studies to include persistent mutations, such as chromosomal or gene mutations, are needed for these DBPs (Cortés *et al.*, 2018). Thus, translation of such data into human health concerns is difficult raising concerns as to the applicability of any findings derived through such an approach, revealing its limitations (EPA, 2006; WHO, 2017a).

Accordingly, within the current thesis the assessment of hazard index follows the approach outlined by the WHO and utilises the available GV's including two suggested amendments (Table 1.1).

Table 1.1: Summary of guidance values used throughout this thesis

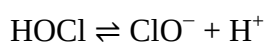
DBP group	Compound	Guideline value (µg/L)
Trihalomethanes (THMs)	Trichloromethane (CF)	300
	Tribromomethane (BF)	100
	Dibromochloromethane (DBCM)	100
	Bromodichloromethane (BDCM)	120
Haloacetic acids (HAAs)	Dibromoacetic acid (DBAA)	12
	Bromochloroacetic acid (BCAA)	1
	Bromodichloroacetic acid (BDCAA)	1
	Monochloroacetic acid (MCAA)	20
	Dichloroacetic acid (DCAA)	50
	Trichloroacetic acid (TCAA)	200
Haloacetonitriles (HANs)	Dichloroacetonitrile	20
	Dibromoacetonitrile	12
Haloaldehyde (HAL)	Trichloroacetaldehyde/ Chloral Hydrate (CH)	100
Chlorinated solvents (CS)	Carbon tetrachloride	4
	1,2-Dibromo-3-chloropropane	1
	1,2-Dibromoethane	0.4
	Tetrachloroethene/ tetrachloroethylene	40
	Trichloroethene	20
	1,1,1-Trichloroethane	2000

1.1.2 DBP management through precursor removal

The organic matter within surface waters comprises of a complex mixture of organic with inorganic moieties, originating from natural (allochthonous), algal (autochthonous- AOM) and

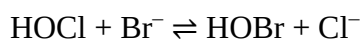
anthropogenic (human pollution – commonly referred to effluent organic matter - EfOM) sources (Egeberg *et al.*, 2002). Surface waters are commonly separated into three categories: Upland, lowland lakes and lowland rivers which contain different fractions of NOM, AOM and EfOM as well as inorganic components and other water quality parameters such as turbidity. Upland sources are known to be rich in NOM and especially organics which are characterised as larger MW compounds, rich in aromatic moieties which are hydrophobic and are known to be result in high THM formation levels. In contrast, lowland sources contain smaller MW organics which are less aromatic and more hydrophilic than their upland counterparts and form much lower levels of THMs. Both EfOM and AOM are comparatively nitrogen rich and so are associated with the formation of greater amounts of N-DBPs (Bond *et al.*, 2011). Bromine level vary considerably across all source water types but are expected to occur more prevalently in the lowland sources suggesting these waters may also form more Br-DBPs. Consequently, it is suggested that the different water sources will generate different distributions of DBPs and that when N-DBPs and Br-DBPs are considered lowland source water may become more important with respect to DBP management than currently perceived on a THM basis.

The main approaches to manage DBP formation is by removing precursor material before the disinfection process and this has been shown to be successful in managing THM formation level and meeting regulatory requirements. In addition, some site switch disinfectant away from chlorine to alternative forms such as chloramine which are known to form less THMs. However, such disinfectants have been shown to form higher concentrations of the emerging and so may not be suitable in the long term (Goslan *et al.*, 2009). Chlorine, in the form of hypochlorite (OCl^-) acts as an oxidizing agent reacts with a wide range of compounds including inorganic precursors, bromide and iodide naturally found in many source waters and can form brominated and iodinated DBPs (Zhang *et al.*, 2018). Hypochlorous acid, from the addition of hypochlorite, dissociates into hydrogen ions (H^+) and hypochlorite ions as seen in the reversible reaction equation 1.4



Equation 1.4

Hypochlorous acid is a weak acid with a pKa of approximately 7.5 at 25 °C, it is dominant at pH levels below 7.5 and is a more effective disinfectant than hypochlorite ion, which dominates above pH 7.5. In waters containing high levels of the inorganic bromide ion, with the addition of hypochlorite disinfectant, hypobromous acid is produced shown in equation 1.5



Equation 1.5

Unlike the reaction with hypochlorite, this reaction is irreversible, and the product hypobromous acid is a better halogenating agent than hypochlorous acid but can produce high bromate. Hypobromous acid is a weak acid with a pKa of 8.7 at 25 °C, and under alkaline conditions can decompose to bromate and bromide (WHO, 2011; Zhang *et al.*, 2018). Once formed, hypobromous acid reacts with NOM to form brominated DBPs, their concentration formed indigenous to the amount of bromine in the water available for substitution, and the amount of chlorine added. The DBPs formed depend on the NOM present in the water, bromine incorporation in to NOM has been shown to rise with increasing bromine to organic carbon ratios (Liang *et al.*, 2003; Westerhoff *et al.*, 2004). pH can have a significant effect on the formation of DBPs during chlorination, as the pH decreases, the concentration of THMs decrease and HAAs increases. pH can also play an important role in determining the concentration and speciation of DBPs formed, with lower, more acidic, pHs resulting in the formation of less chloroform, lowering THMs (Hung *et al.*, 2017). When the pH is increased, the formation of THMs also increases, with a large increase in the reaction rate occurring at pH 7-9, but this effect was weakly pronounced in the 6-8 pH range. Looking at HAA speciation, decreasing the pH, increased the formation of di- and trihalogenated HAA species, with the addition of bromide as compared to species with chlorine addition, but showed little difference in HAA speciation at pH 8 and pH 6 (Cowman and Singer, 1996). Chlorination of aspartic acid found an increase of DCAN when pH was increased from 5 to 6 but when pH was increased from 6 to 9 the DCAN formation decreased, while the dichloroacetamide and trichloronitromethane formation increased with increasing pH from 5 to 8 (Chen *et al.*, 2017). Chu *et al.* (2010) found increasing the pH from 5-7 decreased the DCAN significantly but increased the dichloroacetamide and DCAA formations (Chu *et al.*, 2010).

NOM Precursor material can be removed by coagulation, ion exchange, activated carbon adsorption, ozone, biotreatment and is known to be effective for upland catchment sites with these sites set up to reduce THM formation potential (Bond *et al.*, 2010). Lowland sites, which typically form much less THMs report much lower organics removal, but this has not been of concern due to the focus on THMs. Accordingly, it is suggested that broadening the range of DBPs considered may change this situation and require better precursor control at lowland

sites. This will be difficult to achieve with traditional technologies such as coagulation and adsorption and so advanced treatments such as nanofiltration membranes and advanced oxidation processes may well be required.

1.1.3 Research Development

The work presented in this thesis was developed as part of an EPSRC case award in conjunction with UKWIR. The ambition of the project was to ascertain the impact of considering emerging DBPs on the overall management of DBPs across UK water treatment catchment types (Figure 1.1). To achieve this 27 individual DBPs were measured, from 7 different categories sampled from 14 surface water treatment works based on traditional technologies. In addition, three works were chosen to represent an upland, lowland lake and lowland river for more detailed investigation. This included tracking the DBPs from the raw water to the final product through formation potential tests and applying nanofiltration and advance oxidation processes to these three waters to ascertain the potential impacts. In all cases, the measured mass concentrations were converted into a hazard index form the 19 DBPs that had available GVs.

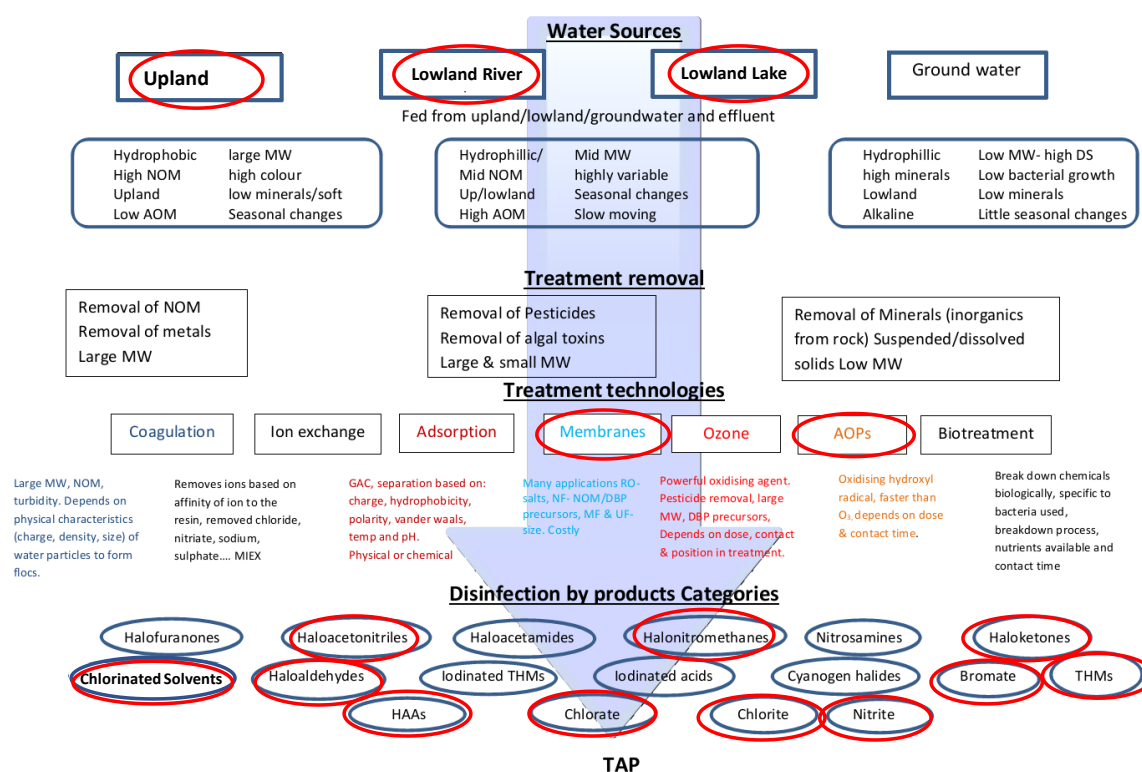


Figure 1.1 Illustration of water sources, properties and water treatments for precursor removal

1.2 Aims and Objectives

Disinfection by-products are an unintended consequence of the disinfection process, and the high variability of NOM in water sources makes DBP formation difficult to predict. This leads to the challenge of assessing the risk involved in their exposure which is currently based on total THM4 concentrations below 100µg/L in the UK/EU and total HAA5 below 60 µg/L. Emerging DBPs are also formed during disinfection which have shown to have higher cytotoxicity and genotoxicity than their regulated counterparts, with higher potency at lower concentrations. Regulation has focussed on minimising the THM/HAA concentration but a shift towards reducing the risk involved in DBP exposure leads to the currently unanswered question of which DBPs sufficiency act as a proxy for the load, and how to minimise risk of their exposure. Measuring a wide range of DBPs and water characteristics from existing traditional existing flow sheets, with different water source characteristics, will fill this knowledge gap. This is covered in chapters 2 and 3 where the concentration is converted to a hazard index to determine the exposure risk. The impact of adding emerging treatment technologies in reducing DBPs and their associated risk investigated in chapter 4 and 5 using advanced oxidative processes and nanofiltration under different conditions to show their impact on DBP formation and the associated hazard. Major drawbacks of both are their instillation and operational costs, due to this, investigating whether they may be effective in reducing traditional and emerging DBPs and their associated HI would be advantageous to filling this knowledge gap.

Aim: To understand how to minimise the overall hazard associated with disinfection by-products using advanced oxidation processes and nanofiltration.

The main objectives of this thesis were:

1. To understand the concentration and hazard index associated with emerging DBPs formed when using traditional flowsheets (Chapters 1 & 2)
2. To understand the impact of considering hazard Index over mass concentration when applied to traditional flowsheets (Chapters 1 & 2)
3. To understand the impact of advanced treatment (AOPs and nanofiltration) and different source waters on minimising the hazard index associated with disinfection by-products (Chapters 3 & 4)
4. To provide a recommendation on a way forward to minimise the hazard index associated with disinfection by-products (Implication of the work).

1.3 Thesis Structure

This thesis takes the form of a series of chapters formatted as papers for publication. All papers were written by the first author, Erin Losty and have been edited by Dr Bruce Jefferson. All experiments have been carried out in Cranfield University laboratory undertaken by Erin Losty with the help of placement students Erwan Gingat, Morganne Lavillaugouet who stayed for 3 months in the summer of 2016 and Marlène Ribeiro Marques and Malek Kridene in the summer of 2017.

Chapter 1: Introduction

Introduces the background to the thesis and the minimisation of DBPs

Chapter 2: Disinfection by-products from surface waters: A comparison of 14 water treatment works in terms of the mass concentration and hazard index associated with regulated and emerging DBPs

Traditional and emerging DBPs were tested from a range of 14 surface waters final waters and the associated hazard index explored using guideline values and LC50 toxicity values. The DBP speciation was explored in terms of concentration and associated hazard index. Correlations between bulk water parameters and DBPs were explored using pearson moment correlation coefficient.

Chapter 3: Regulated and Emerging Disinfection by-products formation from surface waters: A comparison of upland and lowland source waters

Surface waters from 3 drinking water treatment plants were sampled before treatment as raw water, after treatment, before chlorination and final waters after disinfection and their DBP precursors explored using formation potential tests to understand to impact of source water type and the use of FP tests on the hazard index profile generated.

Chapter 4: Minimisation of traditional and emerging Disinfection by-products formed in surface waters using Nanofiltration

The impact of treating raw water with nanofiltration membranes was explored to understand the impact of surface hydrophilicity of the membrane and the source water type (upland, lowland lake, lowland river) on their efficiency in removing traditional and emerging DBP precursors to minimise their concentration and hazard index.

Chapter 5: Minimisation of Disinfection by-products using Advanced Oxidation Processes UV/H₂O₂

The impact of treating raw water with an advanced oxidative process was explored with 3 surface waters at various doses (H₂O₂/UV) to determine the reduction of each water type and the reduction of the concentration and associated hazard of traditional and emerging DBPs.

Chapter 6: Discussion: Implications for the Treatment of Drinking Water

Discussion of the findings within the thesis and their implications in drinking water treatment were framed around a way forward to minimise DBPs in terms of their concentration and hazard index

Chapter 7: Conclusions and Further work

This outlines the results of the study and suggests recommendations for future investigations

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**2 Disinfection by-products from surface waters: A comparison of
14 water treatment works in terms of the mass concentration
and hazard index associated with regulated and emerging
DBPs**

Disinfection by-products from surface waters: A comparison of 14 water treatment works in terms of the mass concentration and hazard index associated with regulated and emerging DBPs

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2.1 Abstract

DBP regulation focuses on concentration of THM4 as a surrogate for exposure to the DBP mixture, but are the appropriate DBPs being monitored, in terms of hazard and exposure? To explore this the final water from fourteen surface water treatment works in the UK were tested for traditional and emerging DBPs. THM4 and HAA9 were the most abundant with the traditional DBPs represents 57-92% of the total DBPs. However, they showed no correlation between the concentrations of each other or the remaining emerging DBPs. The traditional and emerging DBPs have been measured in this study across 7 categories and the concentration of 13 individual DBPs translated to a hazard index ratio using *in vivo*, WHO GV and *in vitro*, LC50 values. Both methods are compared for their viability as a surrogate of exposure. When using the *in vivo*, WHO GV the Br-HAAs become significant and represent 4%-6% of the DBP concentration, but in terms of hazard index this becomes 75-96% (0.2-18% using LC50) of the total. Whereas with the *in vitro*, LC50 the HANs become important, representing 1-30% of the concentration compared to 51-98% (1-4% using GV) of the total HI, giving very different pictures. A pearson moment correlation coefficient with an r^2 of 0.97 was found between HAA4 (BCAA, BDCAA, DBAA and MCAA, with guideline values), and the HI, suggesting the inclusion of HAAs to regulation

Keywords Disinfection by-products (DBPs), toxicity, hazard index

2.2 Introduction

Disinfection by-products (DBPs) form during the disinfection process through the reaction of the disinfectant with organic matter presents within the water. There are over 600 individual DBPs discovered to date, grouped into over 32 categories (Richardson *et al.*, 2003). The most prevalent by weight are trihalomethanes (THMs) and haloacetic acids (HAAs) accounting for up to 70% of the total. Accordingly, regulations have focussed on these with the sum of four THMs (THM4) needing to remain below 100 µg/L in the UK. In comparison, in the US, THM4 and HAA5 are regulated to 80 µg/L and 60 µg/L respectively. In both cases, regulated DBPs are utilised as a proxy of the whole, enabling relatively simple and affordable monitoring. For instance, the World Health Organisation (WHO) guidelines in 2011 suggest if chlorination is practised, the THMs and HAAs will be the main DBPs and by keeping these below the guidance levels, will provide adequate control of all DBPs.

Previous consideration of correlations between water quality parameters, measures of specific groups of DBPs (i.e. THM4) and the whole have revealed a complex, inconsistent response (Ates, *et al.*, 2007; Bond *et al.*, 2015; Bull *et al.*, 2009; Bull, *et al.*, 2009; Hua, *et al.*, 2015; Jeong *et al.*, 2016; Rice *et al.*, 2009; Richardson *et al.*, 2005; Villanueva *et al.*, 2012). However, a number of general observations can be derived. For instance, at lower temperatures, less THMs are formed than at higher temperatures, contributing to seasonal differences with the same water (Serrano *et al.*, 2015; Uyak, *et al.*, 2008). Further, the relative ratio of bromine to chlorine impacts the speciation of the DBPs with elevated bromide concentrations associated to increased amounts of brominated DBPs. Importantly, THMs and HAAs are known to have different precursors and their formation pathways are not thought to be linked (Ates *et al.*, 2007), thus adding evidence to challenge whether THM4 is a suitably representative surrogate of the whole (Bull *et al.*, 2009a; Bull *et al.*, 2009b). In response a number of authors have switched to using the sum of the THM4 and HAA5 as a proxy of the whole (Weinberg *et al.*, 2002)

The current regulation of DBPs is concentration focussed, which assumes the higher the concentration of the regulated THM4 (+HAA5), the greater the risk involved. Because of this, the THM4 is acting as a proxy, not only in terms of concentration, formation and removal, but

also in terms of human exposure and risk (Bond *et al.*, 2011; Ding *et al.*, 2018; EPA, 2006; EPA, 1998; Li & Mitch, 2017; WHO, 2011). Whilst the other known DBPs, referred to as the emerging DBPs, tend to occur at relatively low concentrations, their toxicity may be substantially greater indicating the appropriateness of THM4 with or without HAA5 as a proxy requires re-examination. Consideration of the relative toxicity is best described through a hazard index which is equal to the sum of the concentration of the individual DBP divided by its respective guideline values (GV) (WHO, 2017). There is currently no 'regulatory-applicable' method for the risk assessment of mixtures in drinking waters but it is widely accepted the components act in an additive manner at low environmental concentrations (WHO, 2017a). When there is evidence to prove otherwise, the interaction occurs in an antagonistic or synergistic fashion (Boobis *et al.*, 2011; Brack *et al.*, 2015). To solve this, WHO have suggested a component-based approach to THMs, which they suggest is transparent and easy to implement. The concentrations of each individual DBP is divided by their respective WHO guideline value and summed, giving a hazard index for the mixture, and should be less than 1. This is an achievable, case by case hazard index and takes the potency of each individual DBP into account (WHO, 2017a). This method can be used for monitoring but also to elucidate the toxicity driver within the DBP mixture.

Toxicological data can be taken from both *in vivo* and *in vitro* bioassays with different endpoints which generate different values (Hanigan *et al.*, 2017; Jeong *et al.*, 2016; Parvez *et al.*, 2017; Stalter *et al.*, 2016; Wagner & Plewa, 2017). For example, tribromoacetic acid tested with two *in vitro* bioassays gave a low reading of 4.40×10^4 for a bioassay with the oxidative stress response pathway endpoint compared to a higher reading of 7.0×10^6 for a bioassay with a genotoxicity endpoint (Stalter *et al.*, 2016). In comparison, the WHO guideline values (GV) are based on many years of *in vivo* animal studies of each specific chemical and are generally considered the most appropriate and robust approach to understanding potential hazard levels (Li & Mitch, 2017). Whilst robust, the GVs are limited to 13 DBPs restricting the ability to assess the greatest possible range of emerging DBPs. There is currently a paucity of information concerning comparison of the different toxicity data restricting understanding as to the potential impacts of using *in vitro* over *in vivo* data. Further, the limited toxicological and epidemiological data associated to emerging DBPs coupled with a partially characterised DBP mixture further complicates the consideration of THM4 (or HAA5) as a proxy for the whole.

It has been suggested that the hazard profile of the overall mixture may be governed by a few of its components, raising questions as to: are the correct components being monitored and regulated? (Li and Mitch, 2017; Plewa *et al.*, 2008; Plewa *et al.*, 2017; Richardson *et al.*, 2008; Simmons *et al.*, 2002). The current paper responds to this question by measuring 26 DBPs formed at 14 different drinking water sites in the UK. The concentration data is transformed into a hazard index through both *in vivo* (WHO GV values -13 DBPs) and *in vitro* (The Lethal concentration 50 with Chinese hamster ovary cells – 18 DBPs) data to understand the potential links to DBP concentration and HI as well as re-examining the appropriateness of using THM4 as a surrogate for DBP monitoring and control.

2.3 Materials and Methods

2.3.1 Analytical methods

All standards, reagents and chemicals were purchased from Sigma Aldrich (Gillingham, UK) and Fisher (Loughborough, UK). Chlorinated final water samples were collected from fourteen active drinking water works in the UK including eight works treating raw waters from upland catchments and six treating either lowland lake or river water (Figure 2.2). Final water samples were collected in glass vials and bottles, preserved and transported to the laboratory with ice packs. All samples were analysed for THM4, Haloacetonnitriles (HAN4), haloketons (HK2), halonitromethanes (HNM), haloacetaldehydes (HAL) and chlorinated chemicals (CS) according to EPA Method 551.1. HAA9 was analysed according to EPA method 552.3. All DBPs were analysed according to a gas chromatography-electron capture detector (GC-ECD) method using an Agilent HP 6890 Series GC System with a modified GC method (Milton Keynes, UK), column DB-1 and quantified using OpenLab software. Total organic carbon (TOC), Non purgeable organic carbon (NPOC) and Total Nitrogen (TN) was performed using Shimadzu TOC-V VWP (Milton Keynes, UK). Bromide, Bromate and Chloride concentrations were determined according to EPA method 300.1 and run on Thermo-Scientific ICS-1600 (Milton Keynes, UK). Total bromine and Iodine were measured using Perkin Elmer Elan 9000 Inductively coupled plasma- mass spectroscopy (ICP-MS) (Beaconsfield, UK). All occurrence samples were taken in duplicate, extracted and measured in triplicate on each instrument. The internal standard bromofluorobenzene was added to each sample for the analysis of method

EPA Method 551.1. 1,2,3 trichloropropane was used as an internal standard and 2-bromobutanoic acid was used as a surrogate, derivatised during the methylation step in EPA method 552.3. 8. Calibration standards of 0-200 µg/L were extracted and run with each set of samples, with a low calibration point within a factor of 2 of the minimum reporting level for each sample batch. As per method 300.1, dichloroacetate was used as the internal standard in each calibration and sample, and a calibration from 0-5 mg/L was used, sample dilution with ultrapure water was used if necessary. Within each sample batch, a calibration point was run after each 8-10 samples and again at the end for quality control for each instrument used. The limit of quantification (LOQ) for GC-ECD methods was 0.5 µg/L, with MCAA at 2 µg/L, IC was 50 µg/L for chloride and 0.25 mg/L for remaining ions measured. The Shimadzu TOC-V VWP had a limit of detection (LOD) of 0.5 µg/L, with automatic dilution where necessary and the LOD of bromine using Perkin Elmer Elan 9000 ICP-MS was 0.2 µg/L.

2.3.2 Toxicity Calculations

To establish a priority list within the DBP mixture, two methods were compared taking the concentration and potency of each individual DBP.

The first method used World Health Organisation derived guideline values (GV) based on no-observed adverse effect level (NOAEL) and tolerable daily intake (TDI) values, from long term laboratory *in vivo* studies, including carcinogenic and mutagenic end points (WHO, 2011, 2017b). GV's are worldwide guidelines based on robust animal studies but have a limited DBP set, therefore restricting the inclusion of emerging DBPs. The GV dataset includes 13 DBPs measured here: THM4, HAA6, HAN2 and HAL1. THM4 consisting of Trichloromethane (CF), Bromodichloromethane (BDCM), Dibromochloromethane (DBCM) and Tribromomethane (BF). HAA6 consists of Monochloroacetic acid (MCAA), Dichloroacetic acid (DCAA), Bromochloroacetic acid (BCAA), Dibromoacetic acid (DBAA), Trichloroacetic acid (TCAA) and Bromodichloroacetic acid (BDCAA). HAN2 consisted of Dichloroacetonitrile (DCAN) and Dibromoacetonitrile (DBAN) and HAL1 is chloral hydrate (CH).

The second method utilised LC50 values from *in vitro* studies by Wagner and Plewa (2017), where the lowest concentration of 31 individual DBPs were shown to cause a 50% reduction in the growth of Chinese hamster ovary cells. 18 of these DBPs overlapped with those measured in this study, the 13 with GV values and an extra 5 known as other DBPs. These were, Monobromoacetic acid (MBAA), Chloro-dibromoacetic acid (CDBAA), and

Tribromoacetic acid (TBAA) from the HAA category, and Trichloroacetonitrile (TCAN) and Bromochloroacetonitrile (BCAN) from the HAN category. The measured concentrations were divided by the corresponding LC50 or Guideline value providing a ratio, to elucidate toxicity drivers and as a basis of comparison.

The hazard index was calculated for each individual DBP by dividing the occurrence concentration by either the GV or the LC50 data (Figure 2.1). The total HI was calculated as the sum of the individual as can be seen in

$$HI = \sum HQ = \frac{DBP1}{GV1} + \frac{DBP2}{GV2} + \dots + \frac{DBPn}{GVn}$$

Equation 2.1

Table 2.1 Toxicity data for individual DBPs

DBP	GV (µg/L)	LC50 (µg/L)	DBP	GV (µg/L)	LC50 (µg/L)
THM4			HAN4		
CF	300	1.15E+06	BCAN	*	1.3E+03
BDCM	120	6.49E+05	DBAN	12	5.7E+02
DBCM	100	1.12E+06	DCAN	20	6.3E+03
BF	100	1.00E+06	TCAN	*	2.3E+04
HAA9			HNH		
BCAA	1	1.19E+05	TCNM	*	8.81E+04
BDCAA	1	1.96E+05	HAL1		
CDBAA	*	5.10E+04	CH	100	1.92E+05
DBAA	12	1.29E+05	CS		
DCAA	50	9.41E+05	TCE	20	*
MBAA	*	1.33E+03	1,2 DBE	0.4	*
MCAA	20	7.65E+04	TETCE	40	*
TBAA	*	2.52E+04	CT	4	*
TCAA	200	3.92E+05	1,1,1 TCE	2000	*
HK2			1,2 DBCP	1	*
1,1-DCP	*	*			
1,1,1- TCP	*	*			

*Denotes no available value

2.4 Results

2.4.1 Water Characteristics and DBP concentrations

The NPOC varied between 0.13 mg/L and 4.32 mg/L across the 14 sites with a higher average level observed in the lowland sites at 3.2 mg/L compared to the upland sites at 1.2 mg/L (Table 2.2). The lower residual levels occurred at the upland sites despite them typically having higher raw water NPOCs and reflects the characteristics of the organics which are known to be amenable to removal. In contrast, the lowland sites typically have lower raw water NPOCs but the organics tend to be significantly more recalcitrant to removal by traditional treatment technologies such as coagulation (Philippe *et al.*, 2010). The upland sites were all characterised by containing a low TN concentration which ranged between 0.28-0.57 mg/L compared to 1.21-4.61 mg/L for the lowland sites. Total bromine levels were more distributed across the sites although uplands sites 1-5 contained very low levels at between 2.3-5.4 µg/L. In comparison two lowland sites were observed to contain high levels of total bromine at 77.2 and 193 µg/L for sites 10 and 9 respectively. All other sites had intermediate levels between 11.2 and 28.7 µg/L across both upland and lowland sites. Overall the range of carbon, nitrogen and total bromine levels observed indicated that a broad distribution of DBPs could form with an expectation that sites 1-5 should predominately form chlorinated over brominated or nitrogenous DBPs.

Table 2.2: List of sites, treatment and final water measurements

Source Type	Coagulant Type	Secondary Filtration	GAC	Ozone	UV	Final Water			
						TOC* (mg/L)	NPOC* (mg/L)	TN* (mg/L)	Total Br ^{-**} (µg/L)
1 UR ^a	Iron	Yes	No	No	No	1.1 ± 0.219	1.3 ± 0.092	0.5 ± 0.07	5.4 ± 0.017
2 UR ^a	None	No	Yes	Yes	Yes	1.5 ± 0.102	1.4 ± 0.265	0.3 ± 0.06	3.1 ± 0.153
3 UR ^a	None	Yes	Yes	Yes	Yes	2.0 ± 0.379	1.7 ± 0.003	0.5 ± 0.03	3.7 ± 0.051
4 UR ^a	Al	Yes	Yes	No	Yes	0.0 ± 0.077	0.1 ± 0.105	0.3 ± 0.08	2.3 ± 0.178
5 UR ^a	Al	RGF	No	No	No	2.0 ± 0.205	1.3 ± 0.205	0.6 ± 0.02	4.3 ± 0.018
6 U ^b	Iron	RGF	No	No	Yes	0.8 ± 0.304	1.8 ± 0.192	0.4 ± 0.01	22.6 ± 0.093
7 U ^b	Iron	RGF	No	No	Yes	0.8 ± 0.136	1.8 ± 0.225	0.4 ± 0.04	22.6 ± 0.001
8 U ^b	Iron	RGF	No	No	Yes	1.3 ± 0.051	1.8 ± 0.089	0.5 ± 0.13	24.0 ± 0.109
9 LL ^c	Iron	RGF	Yes	Yes	No	6.1 ± 0.202	4.1 ± 0.058	2.3 ± 0.02	193.0 ± 0.199
10 LL ^c	Iron	RGF	Yes	Yes	No	4.6 ± 0.181	3.8 ± 0.051	3.1 ± 0.09	77.2 ± 0.072
11 LR ^d	Al	Yes	Yes	No	No	1.8 ± 0.321	1.3 ± 0.019	4.6 ± 0.05	21.5 ± 0.017
12 LR ^d	Al	Yes	Yes	No	No	1.7 ± 0.059	1.7 ± 0.174	1.2 ± 0.04	28.7 ± 0.038
13 IR ^e	Iron	No	Yes	No	No	1.2 ± 0.336	4.3 ± 0.017	3.9 ± 0.1	11.3 ± 0.002
14 R ^f	Al	No	Yes	No	No	1.9 ± 0.146	4.2 ± 0.042	2.5 ± 0.04	11.2 ± 0.015

^a Upland Reservoir^b Upland^c Lowland Lake^d Lowland Reservoir^e Impounding Reservoir^f River

*Duplicate samples with triplicate injections and an instrument LOD of 0.5 µg/L

** Duplicate samples with duplicate injections and an instrument LOD of 0.2 µg/L

2.4.2 Concentration and speciation of the DBPs

The total DBP concentration ranged from 35.0 µg/L in site 13 to 146.7 µg/L in site 3 with no obvious difference in the levels formed between the upland and the lowland sites (Figure 2.1). The corresponding reactivities ranged between 35.6-295.7 µg/mg for the upland catchment and between 8-86 µg/mg for the lowland sites. Whilst varied, the reactivity of the organic residuals in the upland sites was generally more reactive than that residing in the lowland waters. To illustrate, sites 8 and 10 had similar total DBP levels at 77.0 µg/L and 76.6 µg/L respectively but NPOC levels of 1.83 mg/L and 3.06 mg/L such that their respective reactivities were 42 and 20.4 µg/mg. Comparing this to the EPA DBP occurrence study which covers an extensive range of DBPs measured, including emerging DBPs, over different water types with reactivities with the current study. The reactivities of the surface varied widely and can be seen in Table

2.3. The waters with higher TOC gave the highest reactivities of carbon in both the literature and the current study. There was no significant correlations between the DBP sum and the TOC/NPOC with the literature, the overall r^2 correlations with TOC and the DBP sum in the literature was 0.01 and in the current study with the DBP sum of final waters from traditional flow sheets, the r^2 value was 0.06. When comparing literature for DBP-FP, higher r^2 values between 0.45 and 0.9 for THM-FP and 0.43 and 0.84 for HAA-FP for raw and treated surface waters (Golea *et al.*, 2017).

Table 2.3 Comparison of organic carbon reactivity after treatment with literature and current study

Source water		TOC/ NPOC (mg/L)	DBP sum (µg/L)	Reactivities (µg/mg C)
EPA DBP Occurrence study, 2002				
overall N=58	min	0.3	7.4	3.3
	max	5.1	192.9	390.4
	Avg	2.6	91.3	53.9
Groundwater N=17	min	1.4	23.2	9.9
	Max	4.4	144.1	390.4
	Avg	1.4	64.7	97.7
Surface water N=41	min	1.4	23.2	9.9
	max	5.1	192.9	102.7
	Avg	3.1	102.5	35.3
Current study				
overall N=14	min	0.1	35.0	8.1
	max	4.3	146.7	295.7
	Avg	2.2	68.8	57.2
Upland N=8	min	0.1	38.1	35.6
	Max	1.8	146.7	295.7
	Avg	1.4	70.3	76.9
Lowland N=6	min	1.3	35.0	8.1
	max	4.3	109.7	85.7
	Avg	3.2	66.8	30.9

*DBP sum includes the sum of THM4, HAA9, HAN4, HAL1, HNM1, HK2 and Cl Chem.

Analysis of the different DBP groups that made up the total revealed that the THMs and HAAs represented between 24.5-77% and 13-55% of the total. The next most significant group was the HANs which contributed between 1-24% to the total. Overall the sum of the three main categories, consisting of 16 DBPs in total, made up an average of 93.2% of total DBP concentration with roughly an even contribution from both the THMs (41.7%) and the HAAs

(44%). However, the ratio of HAAs:THMs varied considerably between 2:1 and 1:6, consistent with the two groups being formed through different pathways/precursors (Bond *et al.*, 2011).

The THM4 levels in all sites was below the 100 µg/L target level and ranged from a maximum of 63.5 µg/L for the upland site 3 and a minimum of 7.1 µg/L for the upland site 2, equating to only 13% of the total DBP measured for that site. Speciation of the THMs revealed a split between upland and lowland sites with chloroform (CF) constituting an average of 83% of the THM in the upland sites and 38% in the lowland sites. The difference was based on higher levels of Br-THMs in the lowland sites congruent with the higher levels of bromine observed. Overall across the lowland sites Br-THM averaged 65% of the total THM with a high of 80% for site 9 which had a bromine level of 193 µg/L.

The maximum HAA9 concentration was again observed at site 3 (as for the THMs) at 68.3 µg/L, equating to 44% of the total, and compares to the minimum level of 13.5 µg/L observed in the lowland site 9 which accounted for only 24.5% of the total DBP. Speciation of the HAAs within the upland sites revealed predominately chlorinated HAA and in particular DCAA and TCAA. For instance, in site 3 which had the highest overall HAA concentration, 91% of the total came from DCAA and TCAA. In contrast, the distribution of the HAA species was more heavily oriented toward Br-HAAs with the lowland sites. To illustrate, Br-HAAs accounted for 71% and 72% of the total HAA for sites 9 and 10 which had bromine levels of 193.0 and 72.2 µg/L. A similar trend was not seen with total nitrogen whereby the levels of nitrogen containing DBPs (N-DBPs) did not mirror the THM of the respective waters. For instance, the highest HAN concentrations were observed at sites 6-9 at levels of 13.3 µg/L but had low TN levels of between 0.4-0.7 mg/L (Table 2.1).

Previously reported surveys of multiple sites have revealed larger variations in the THM4 and HAA9 than observed here, with ranges of 0.8-98.1 µg/L and 0.9-86.9 µg/L (Villanueva *et al.*, 2012) and 11.4-120.4 µg/L and 12.9-22.3 µg/L (Huang, *et al.* 2015). In the latter study, the DOC of the waters from 14 sites in Taiwan was in the same range observed here (0.26-4.78 mg/L) such that the reactivity was higher than observed here and is consistent with high levels of humic acids in those waters. In both published studies, the proportion of brominated DBP mirrored, at least to a reasonable degree, the level of bromine in the water confirming the results presented here and highlighting the importance of monitoring bromine levels.

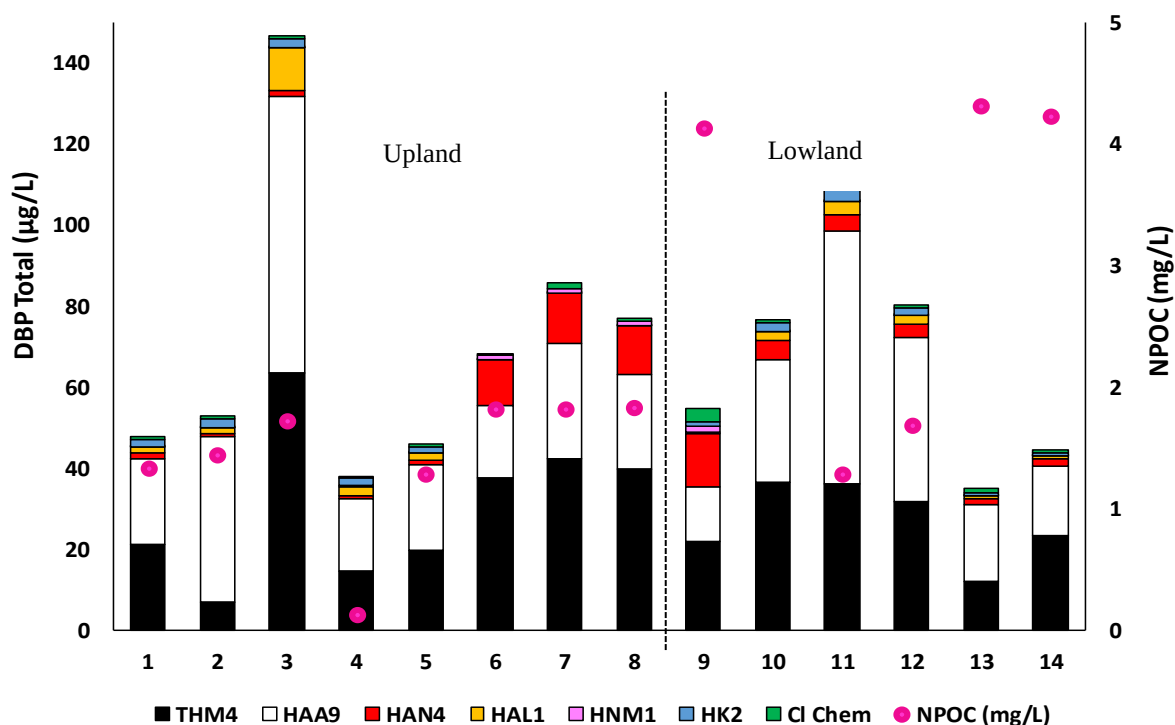


Figure 2.1: DBP concentration measured from sites 1-14 and corresponding NPOC value

2.4.3 Correlations between DBP

The data from the 14 sites was utilised to look for possible correlations within DBPs (total, groups or individuals) as well as against water quality parameters (Table 2.4). The total mass concentration of DBP measured in the survey correlated with the mass of THM4 and HAA9 with r^2 values of 0.81 and 0.75 respectively congruent with them being the predominant DBPs to form. Accordingly, the relationship can be viewed as an artefact and not a true reflection of changes in the other DBPs. For example, THM4 correlated well with CF with a r^2 of 0.74, but this was due to CF being a high proportion of the overall THM concentration, with an average of 63% and as high as 99% in upland waters. Further, combining HAA9 and THM4 as one group and correlating against total DBP results in a r^2 value of 0.95. However, correlating the combined THM4 and HAA9 group against the other DBPs yields a r^2 value of 0.55 (Figure 2.2). Consequently, the use of THM4 and HAA9 as a surrogate of the total does not offer a robust indication of the likely formation levels of the other DBPs. This is also mirrored in a study correlating THM4 against HAA9, with a coefficient of 0.6 at a p value <0.001 (Villanueva *et al.*, 2012). Previously published r^2 values from Ates *et al.* (2007) and Goslan *et al.* (2009) were 0.68 and 0.17, concluding they have limited capacity for predicting formation and so are an inadequate surrogate for the formation of other DBPs

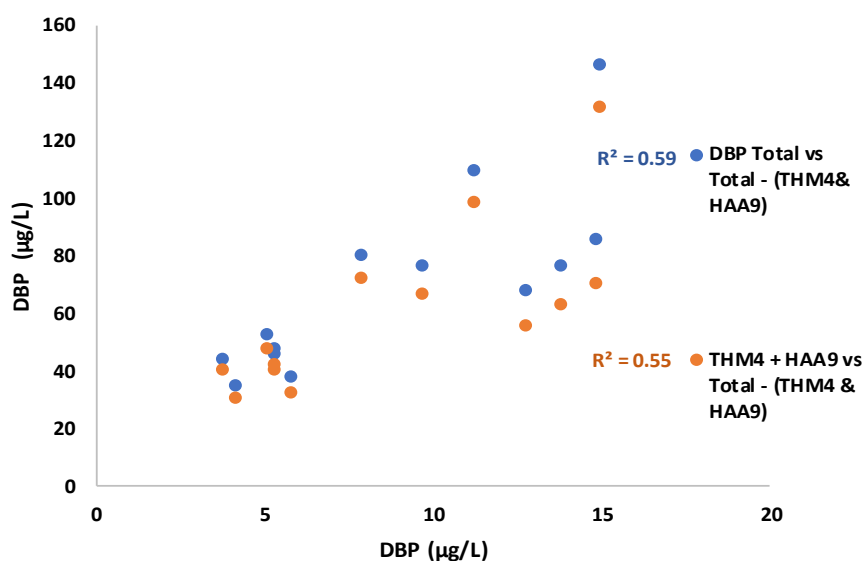


Figure 2.2:Correlation between the sum of the other DBPs (non THM4+HAA9) against the sum of THM4+HAA9

Significant correlations were observed between individual DBPs within the same overall group suggesting similarities in formation pathways and precursors across all the waters. For instance, r^2 values above 0.8 occurred in the HAA category between DBAA vs TBAA, DBCM vs DBAA, and MBAA vs DBAA with values of 0.89, 0.88 and 0.80. a similar relationship was found within the THM group between BDCM and DBCM with an r^2 value of 0.71. A previous study found equivalent links between DBCM and DBCAA, TBAA, and DBAA with r^2 values of 0.87, 0.73 and 0.71 respectively (Villanueva *et al.*, 2012). A commonality across the majority of these is the inclusion of bromine within the DBP congruent with the highly reactive hypobromous acid or hypobromite ion competing with chlorine to form Br-DBPs (Farkas *et al.*, 1949).

Further significant correlations, above 0.9, were observed between individual DBPs across categories with the highest at 0.99 between TCAN, in the HAN group, and CP, in the HNM group. Both are N-DBPs with structures $\text{Cl}_3\text{-C}\equiv\text{N}$ and $\text{Cl}_3\text{-C-N=O}_2$, respectively and have been shown to form from similar precursors such as L-aspartic acid, a free amino acid, and ala-ala, a dipeptide sequence (Bond *et al.*, 2009; Bond *et al.*, 2014; Hu *et al.*, 2010). Importantly, no significant relationship was observed between bromine or nitrogen and the respective Br-DBPs or N-DBPs with r^2 values of 0.05 and 0.58 respectively. Accordingly, the type of bromine and nitrogen reactive species present in the water are therefore important in forming the corresponding Br-DBPs and N-DBPs.

Table 2.4 Pearson moment correlation coefficients between DBPs and DBP categories

	CF	BDCM	DBCM	BF	MB	DC	BC	TC	DB	BDC	CDB	TB	TCAN	DCAN	BCAN	DBAN	CH	CP	TCP	DCP	TCE	1,2 DBE	TETCE	CT	111, TCE	1,2 DBCP	THM4	HAN4	HA1	HNM1	HK2	HAA9	Cl solv	DBP total	TOC	NPOC	TN	Br	
CF	1.00																																						
BDCM	0.07																																						
DBCM	0.17	0.71																																					
BF	0.16	0.43	0.42																																				
MB	0.28	0.54	0.69	0.40																																			
DC	0.15	0.01	0.01	0.09	0.02																																		
BC	0.20	0.76	0.88	0.31	0.79	0.01																																	
TC	0.61	0.03	0.01	0.10	0.03	0.54	0.00																																
DB	0.33	0.55	0.80	0.54	0.89	0.02	0.79	0.07																															
BDC	0.04	0.54	0.68	0.09	0.58	0.00	0.78	0.02	0.45																														
CDB	0.16	0.00	0.06	0.04	0.02	0.08	0.00	0.00	0.02	0.09																													
TB	0.17	0.49	0.77	0.75	0.61	0.04	0.61	0.06	0.83	0.30	0.08																												
TCAN	0.14	0.30	0.28	0.04	0.05	0.11	0.30	0.01	0.13	0.11	0.22	0.15																											
DCAN	0.06	0.76	0.58	0.23	0.30	0.10	0.70	0.06	0.35	0.49	0.02	0.38	0.63																										
BCAN	0.30	0.23	0.08	0.04	0.05	0.09	0.17	0.00	0.09	0.01	0.70	0.05	0.68	0.38																									
DBAN	0.16	0.41	0.36	0.94	0.46	0.08	0.31	0.08	0.57	0.11	0.04	0.68	0.01	0.18	0.02																								
CH	0.18	0.22	0.02	0.00	0.00	0.53	0.07	0.76	0.00	0.05	0.08	0.00	0.18	0.28	0.17	0.00																							
CP	0.11	0.26	0.28	0.04	0.03	0.09	0.27	0.01	0.11	0.10	0.16	0.15	0.99	0.60	0.58	0.00	0.16																						
TCP	0.06	0.47	0.20	0.02	0.22	0.10	0.38	0.08	0.21	0.30	0.14	0.05	0.20	0.38	0.32	0.06	0.34	0.15																					
DCP	0.17	0.25	0.21	0.11	0.12	0.29	0.33	0.00	0.19	0.15	0.12	0.18	0.61	0.56	0.47	0.07	0.12	0.56	0.19																				
TCE	0.22	0.28	0.35	0.13	0.42	0.07	0.29	0.07	0.47	0.21	0.00	0.22	0.01	0.03	0.04	0.20	0.00	0.01	0.32	0.00																			
1,2 DBE	0.05	0.37	0.18	0.08	0.03	0.06	0.17	0.03	0.09	0.08	0.10	0.09	0.53	0.44	0.39	0.06	0.22	0.51	0.38	0.41	0.10																		
TETCE	0.10	0.01	0.01	0.03	0.15	0.03	0.01	0.04	0.06	0.00	0.07	0.00	0.19	0.04	0.01	0.13	0.00	0.28	0.10	0.04	0.15	0.04																	
CT	0.13	0.01	0.01	0.03	0.17	0.08	0.01	0.07	0.05	0.00	0.06	0.00	0.20	0.04	0.00	0.11	0.03	0.28	0.06	0.07	0.10	0.07	0.95																
111, TCE	0.25	0.12	0.03	0.00	0.01	0.02	0.06	0.00	0.02	0.00	0.70	0.00	0.51	0.15	0.78	0.01	0.10	0.43	0.33	0.17	0.13	0.34	0.00	0.00															
1,2 DBCP	0.06	0.31	0.18	0.58	0.07	0.01	0.15	0.00	0.17	0.04	0.00	0.37	0.24	0.37	0.19	0.52	0.07	0.22	0.08	0.38	0.02	0.32	0.01	0.03	0.03														
THM4	0.74	0.06	0.01	0.00	0.01	0.14	0.00	0.65	0.02	0.03	0.24	0.00	0.02	0.04	0.14	0.00	0.37	0.01	0.00	0.03	0.04	0.00	0.10	0.12	0.17	0.01													
HAN4	0.15	0.16	0.12	0.00	0.01	0.13	0.15	0.00	0.04	0.03	0.43	0.04	0.94	0.43	0.79	0.01	0.17	0.90	0.18	0.52	0.01	0.45	0.13	0.14	0.67	0.13	0.06												
HA1	0.18	0.22	0.02	0.00	0.00	0.53	0.07	0.76	0.00	0.05	0.08	0.00	0.18	0.28	0.17	0.00	1.00	0.16	0.34	0.12	0.00	0.22	0.00	0.03	0.10	0.07	0.37	0.17											
HNM1	0.11	0.26	0.28	0.04	0.03	0.09	0.27	0.01	0.11	0.10	0.16	0.15	0.99	0.60	0.58	0.00	0.16	1.00	0.15	0.56	0.01	0.51	0.28	0.28	0.43	0.22	0.01	0.90	0.16										
HK2	0.14	0.50	0.28	0.07	0.23	0.25	0.49	0.04	0.28	0.32	0.18	0.14	0.50	0.64	0.54	0.09	0.31	0.42	0.76	0.67	0.16	0.54	0.01	0.00	0.35	0.27	0.00	0.44	0.31	0.42									
HAA9	0.12	0.27	0.16	0.00	0.11	0.64	0.29	0.58	0.09	0.34	0.01	0.06	0.13	0.39	0.03	0.00	0.62	0.13	0.26	0.28	0.00	0.11	0.03	0.06	0.00	0.05	0.35	0.07	0.62	0.13	0.38								
Cl solv	0.07	0.01	0.03	0.02	0.11	0.10	0.00	0.08	0.02	0.01	0.01	0.00	0.35	0.13	0.02	0.08	0.08	0.45	0.00	0.15	0.05	0.30	0.83	0.89	0.02	0.06	0.10	0.27	0.08	0.45	0.04	0.09							
DBP total	0.49	0.15	0.05	0.00	0.02	0.40	0.08	0.77	0.01	0.17	0.12	0.02	0.00	0.14	0.03	0.00	0.57	0.00	0.09	0.02	0.01	0.02	0.02	0.05	0.09	0.02	0.81	0.01	0.57	0.00	0.07	0.75	0.06						
TOC	0.09	0.17	0.03	0.40	0.25	0.04	0.07	0.03	0.17	0.01	0.01	0.12	0.07	0.01	0.01	0.54	0.00	0.11	0.04	0.00	0.10	0.00	0.63	0.60	0.01	0.12	0.01	0.09	0.00	0.11	0.02	0.00	0.51	0.00					
NPOC	0.07	0.01	0.00	0.26	0.09	0.15	0.00	0.10	0.05	0.02	0.00	0.10	0.03	0.00	0.00	0.21	0.06	0.03	0.15	0.02	0.03	0.12	0.14	0.23	0.03	0.01	0.03	0.03	0.06	0.03	0.10	0.10	0.28	0.06	0.38				
TN	0.07	0.19	0.32	0.22	0.53	0.15	0.42	0.03	0.32	0.34	0.41	0.31	0.01	0.16	0.33	0.20	0.05	0.01	0.03	0.00	0.00	0.22	0.01	0.06	0.45	0.01	0.00	0.11	0.05	0.01	0.03	0.00	0.09	0.01	0.10	0.34			
Br	0.07	0.02	0.00	0.20	0.19	0.14	0.00	0.09	0.10	0.00	0.00	0.03	0.32	0.05	0.02	0.35	0.05	0.41	0.01	0.08	0.12	0.07	0.82	0.81	0.05	0.00	0.03	0.33	0.05	0.41	0.01	0.07	0.79	0.02	0.79	0.28	0.08	1.00	

No other parameter correlated well with the total DBP concentration apart from the TCAA concentration. Previous investigations into correlations have shown links between THMs and DOC, UV254, SUVA and the hydrophobic fraction (Ates *et al.*, 2007a; Ates, *et al.*, 2007b; Roccaro *et al.*, 2014; Villanueva *et al.*, 2012) but where not seen here. Further, the coefficients identified in the different studies vary considerably indicating no universal linkage.

2.4.4 Hazard Index based on WHO Guideline Values

The mass concentration data (Figure 2.1) was utilised to calculate a hazard index based on the WHO GV which includes 13 of the measured DBPs (Figure 2.3). The overall HI varies across the sites from a low of 0.97 for site 6 to a high of 23.5 for site 11. In general, the higher HI were associated with the lowland sites (9-14) and the lower HI values with the upland sites (1-8). Across all sites, HAAs were the dominant DBP in terms of the HI contributing between 87% in site 6 and 98% in site 11, of the total. In contrast, whilst THM contributed up to 55% of the mass concentration of total DBPs, the impact on the HI was relatively minor with a maximum contribution of 13% with site 6. This further queries the role of monitoring THMs in minimising the risk associated to DBPs.

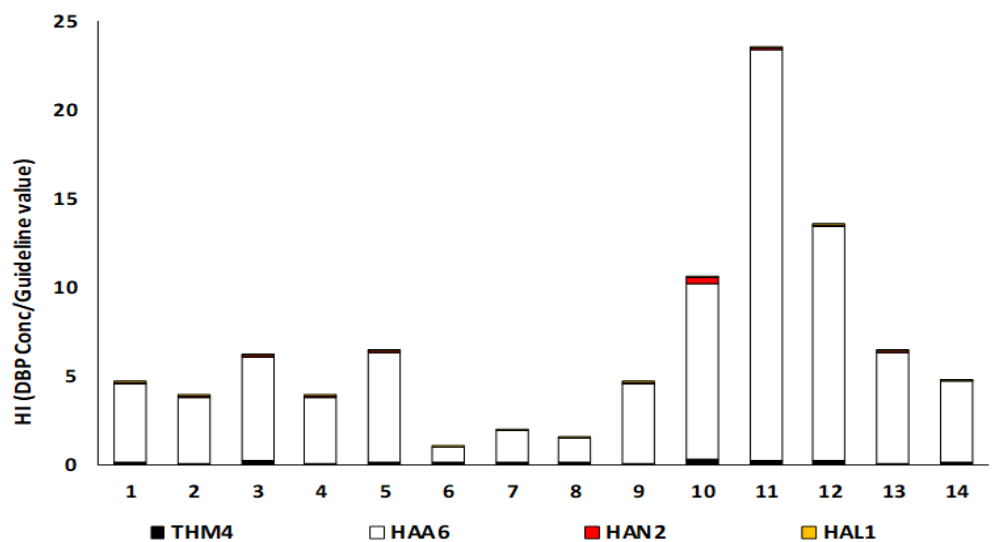


Figure 2.3: Hazard Index of sites 1-14 using the concentration of 13 DBPs within 4 DBP categories and corresponding WHO guideline values

Analysis of the individual species within the HAA group revealed that the majority of the HI was generated from two individual HAAs: BCAA and BDCAA with a small contribution from DBAA and DCAA (Figure 2.4). Overall the Br-HAAs contributed between 76-98% in all waters. Consequently, Br-HAAs can be viewed as the most important group in defining the hazard index of any water. Further, this means that concentration, even of HAAs, does not necessarily indicate HI. For instance, site 3 with the highest overall DBPs of 146.7 µg/L, has a corresponding HI of 6.2 compared with site 11 which has a total DBP of 109.7 µg/L and a HI of 23.5, nearly 4 times more than site 3. The difference between the two is the bromine levels in the water which were 0.28 mg/L for site 3 and 3.06 mg/L for site 11.

The sum of the remaining DBPs (THM4, HAN2 and HAL1) contributed between 0.08 and 0.58 to the HI indicating they are not significant drivers of toxicity from DBPs (Figure 2.5). The highest HI from THMs was observed for site 10 with a value of 0.28 such that all sites had a HI-THM well below a value of 1. The major difference between the speciation of the remaining groups is within the water types, the lowland waters which contain more bromine have a higher HI from contributing Br-DBPs which corresponded to a maximum of 97% of the HI for sites 10,11,12 and 13. The average contribution from non HAA Br-DBPs was 68% in the lowland waters compared to 19% in the upland waters. In the upland sites CF dominated the HI, contributing between 32-99% of the total from the THM component.

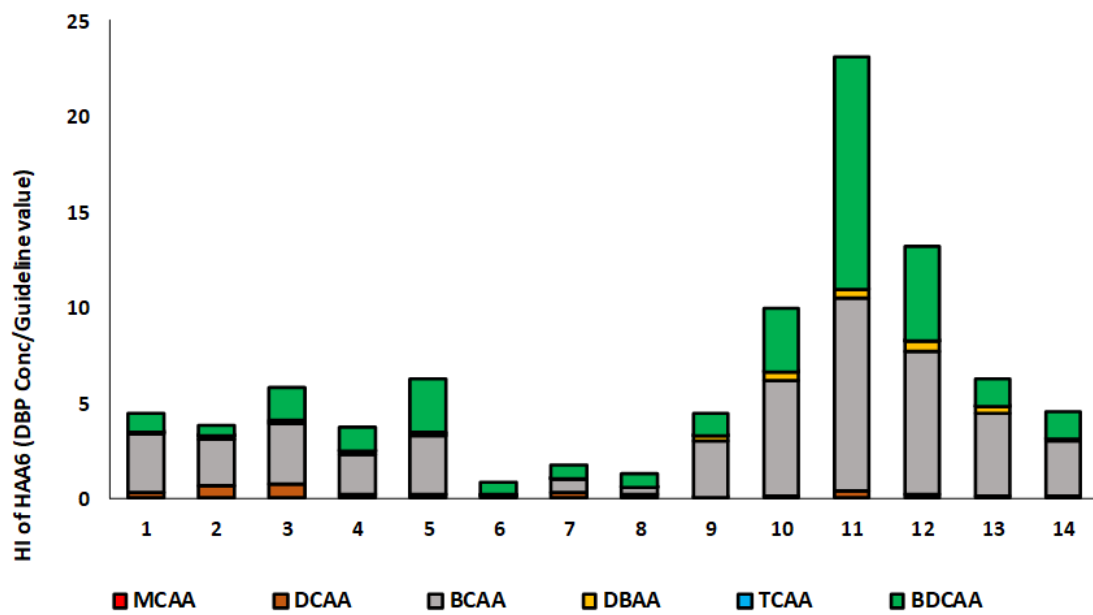


Figure 2.4: Hazard Index of sites 1-14 using the concentration of 6 HAAs and corresponding WHO guideline values

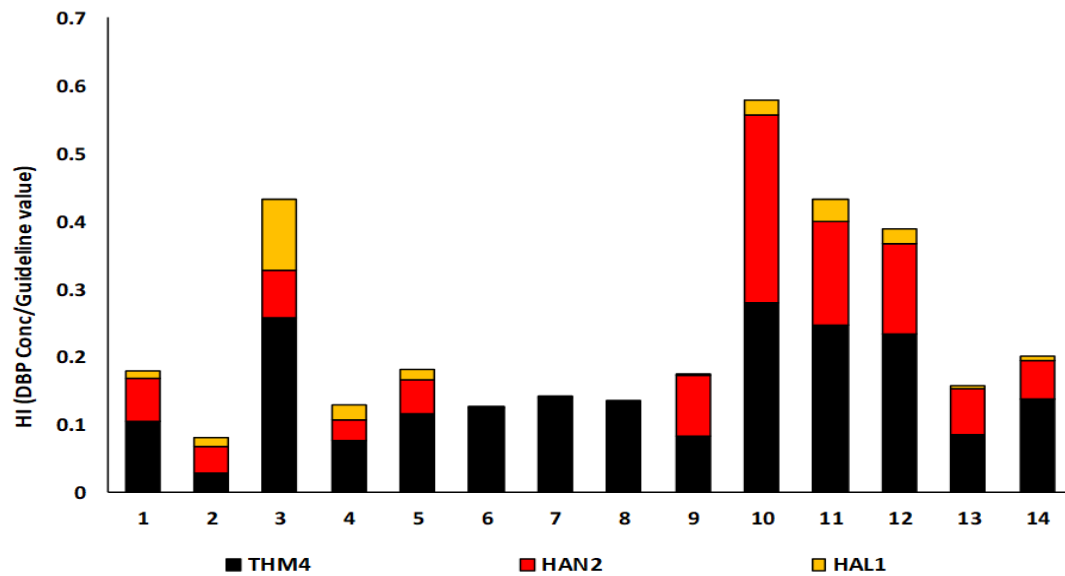


Figure 2.5 Hazard Index of sites 1-14 using the concentration of 3 DBP categories and corresponding WHO guideline values

2.4.5 Hazard Index Values using LC50 toxicity potency values

The HI derived from the LC50 toxicity data ranged between 6.1×10^{-5} and 4.5×10^{-3} across the 14 sites tested (Figure 2.6). However, a very different picture is developed compared to the use of GV values in that HAAs, that have GVs, no longer dominate the overall HI. The use of LC50 data enables five DBPs to be assessed that do not have GVs labelled collectively as “Other DBPs5” and includes the missing HAAs (MBAA, CDBAA and TBAA) and the missing HANs (TCAN and BCAN). This group added a significant amount to the overall HI of all sites and is the dominant component of sites 6-8. Overall, the use of LC50 data broadens the identification of critical DBPs to the nitrogenous and brominated DBPs. However, this is also true when only considering the DBPs that also have GV values, *DBP-13*, where HAN2 becomes the most important group. The speciation within this alters between the upland and lowland waters with DBAN making up an average of 42% of the HAN2 HI in upland sources and 85% in the lowland sources (Figure 2.6). For instance, in site 9, DBAN contributes 96% of the HI associated to the *DBP-13* with a concentration of $1.07 \mu\text{g/L}$. The highest DBAN concentration was observed at site 10 at $2.32 \mu\text{g/L}$ generating the highest HI from which 94% was associated with DBAN. Importantly neither HAA6 or THM4 contribute significantly to the total HI with for instance THM4 contributing between 0.4-7.0% of the overall HI.

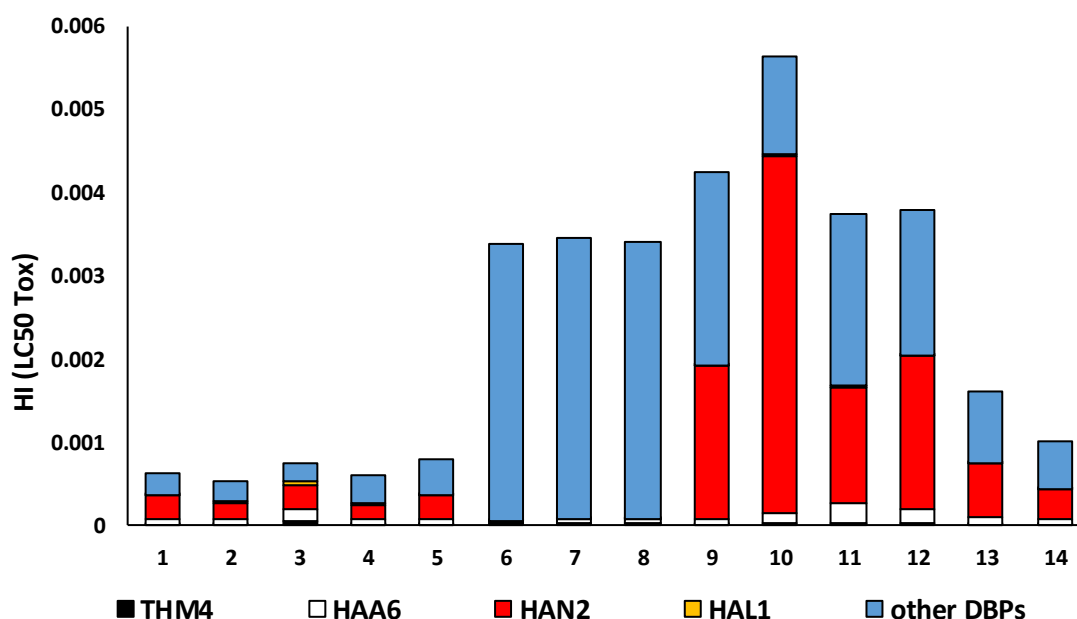


Figure 2.6: Hazard Index of sites 1-14 using the concentration of 6 DBP categories and corresponding LC50 potency values

More detailed analysis of the other DBPs⁵, with no GV value, revealed they contributed significantly to the overall HI ranging from between 20% and 98% across all sites (Figure 2.6). Speciation of the five additional DBPs revealed the two most impactful to be BCAN and MBAA, both brominated DBPs (Figure 2.7). The most impacted were sites 6-8, where 89-90% of the HI from the HAN category came from BCAN and accounted for 86-87% of the total DBP HI. These are upland sources, with low TN and bromine, giving BCAN concentrations of 3-4.0 µg/L. The influence of BCAN in the remaining sites ranged from 10-40% of the overall HI. The other major contributor was MBAA which was observed to impact the lowland site more significantly than the upland sites contributing up to 26% of the overall HI, the main influence in sites 9-13, ranging from 14.2×10^{-4} - 8.6×10^{-4} .

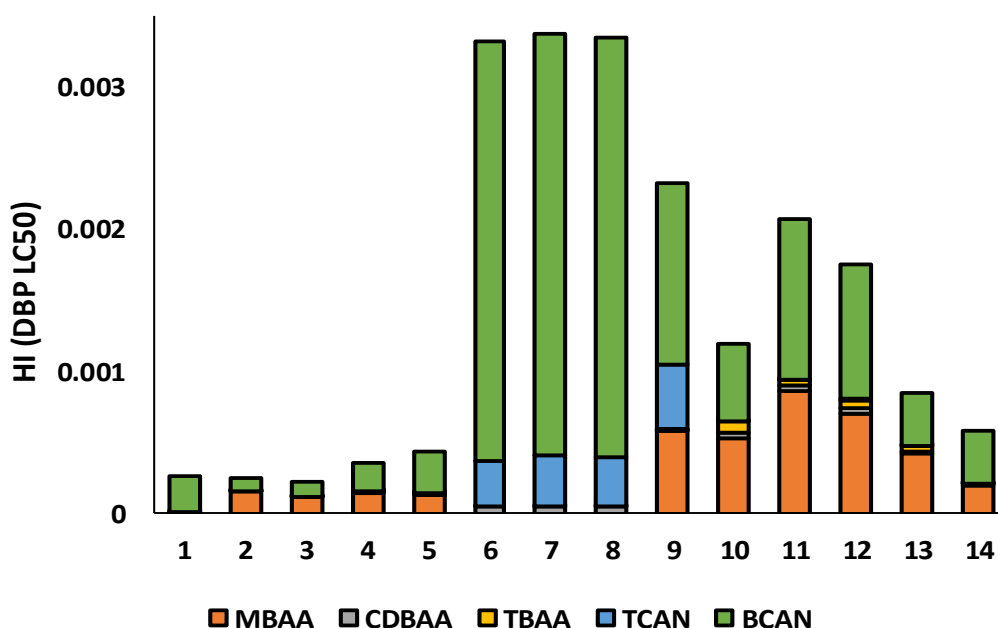


Figure 2.7: Hazard Index of sites 1-14 using the concentration of the other DBPs⁵ and corresponding LC50 potency values

2.5 Discussion

The survey of 14 sites has revealed differences in how the different DBPs impact the perception of the water depending on whether mass concentration is used or the data is converted into a hazard index through either *in vitro* (LC50 values) or *in vivo* (GV values) toxicological data. This is manifest in terms of which DBPs are considered of most risk and ultimately the overall interpretation of the water quality from the different sites. To illustrate, the data from two lowland sites is compared across the three measures using only DBP co-existing in both toxicological data sets (i.e. DBP-13) (Figure 2.8).

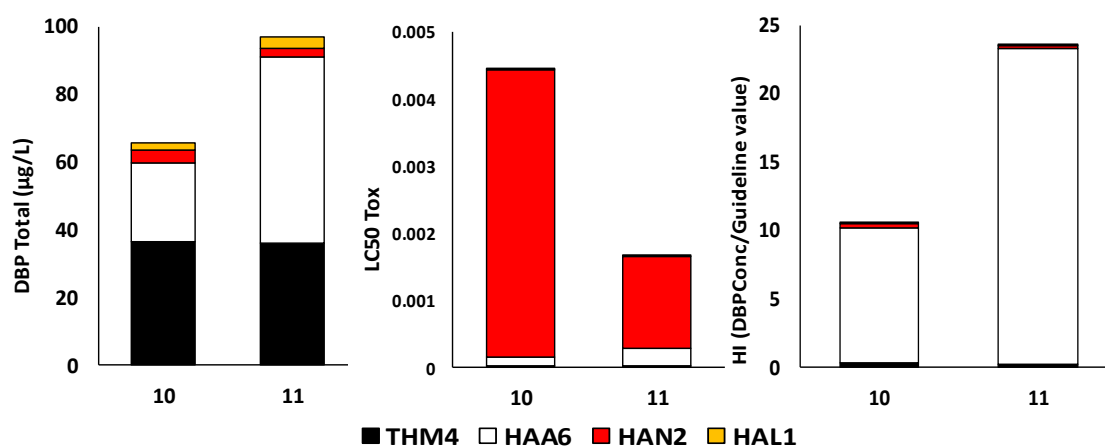


Figure 2.8 illustration of the different profile observed by considering mass concentration, hazard index (LC50) and hazard index (GV) for two lowland waters.

Site 11 had the highest concentration of DBPs within the lowland sites and lowest NPOC such that the organics were the most reactive across the survey. Site 10 and 11 is used as a comparison as it contains a similar level of THMs at 36.4 µg/L and 36.1 µg/L respectively and hence would be currently viewed as similar based on current regulations in the UK. The total DBPs for the two sites were 76.6 and 109.7 µg/L for sites 10 and 11 respectively and based on current US regulation (THM4+HAA5) would be 51 and 70. Accordingly, if viewed as either total DBP or THM4+HAA5, site 11 would be viewed as the higher risk. However, when viewed through a LC50 lens, the picture is reversed with

site 10 generating the higher hazard index. This is due to the concentration and make-up of the HANs within the two waters. Neither the HAA nor THMs made any significant contribution to the overall HI with instead the N-DBP associated to the HANs dominating the overall HI. This trend can be seen in many studies using LC50 values to compare waters under different treatment and conditions (Furst *et al.*, 2018; Li *et al.*, 2017; Plewa *et al.*, 2017; Le Roux *et al.*, 2017; Szczuka *et al.*, 2017; Zeng *et al.* 2016). Inclusion of the otherDBPs5 group, where only LC50 data exists, increases the HI of sites 10 and 11 by 79% and 45% respectively but does not change the overall picture. The additional HI is associated to predominately BCAN and MBAA in roughly equal proportions. Considering the data using GV values, the picture is altered again with the greater HI being generated from site 11 (Figure 2.8). In this case the HAAs contribute most to the HI and especially the Br-HAAs. Specifically, BDCAA and BCAA although the relative contribution of the two differs between the two sites.

Accordingly, the choice of toxicological data has a significant impact on how the different DBPs are viewed. If LC50 data is used, N-DBP and Br-DBPs will be viewed as significant with those associated with the category HAN dominating how the DBPs within a water are viewed. This places much greater emphasis towards waters rich in nitrogen bearing precursors such as AOM or EfOM, typically found in lowland catchments. In contrast, if based on GV values, focus is solely towards Br-HAAs as they contribute the vast majority towards the HI. This means much greater consideration should be given the bromine levels within waters and methods to manage its incorporation during DBP formation. Both approaches had one commonality in that THMs generated a minor contribution to the total HI. Accordingly, monitoring THMs as a guide to the minimisation of the hazard associated to DBPs appears insufficient as it will not provide insight into variation in the DBPs which contribute most to the HI. Including HAAs improves the ability to predict HI, at least the GV version of HI. However, the current HAA5 regulation in the US does not contain key species, specifically BCAA and BDCAA, and so it is recommended that HAA9 should be monitored to ensure the most effective understanding concerning potential hazard. Further, inclusion of the HANs as well (HAAs + HANs) provides a robust picture irrespective of the toxicological datasets used. Illustration of this is provided by plotting the HI (DBP13-GV) against the concentration of HAAs and HANs (Figure 2.10). In particular, comparison is made between the regulated HAAs in the US

(MCAA, DCAA, TCAA and DBAA, excluding MBAA as it has no GV) described as HAA4(US) and the four most significant HAAs seen in this study (BCAA, BDCAA, DBAA and MCAA) in combination with the two HANs (DBAN and DCAN). Switching the HAA species that are monitored improved the regression coefficient from 0.14 to 0.97.

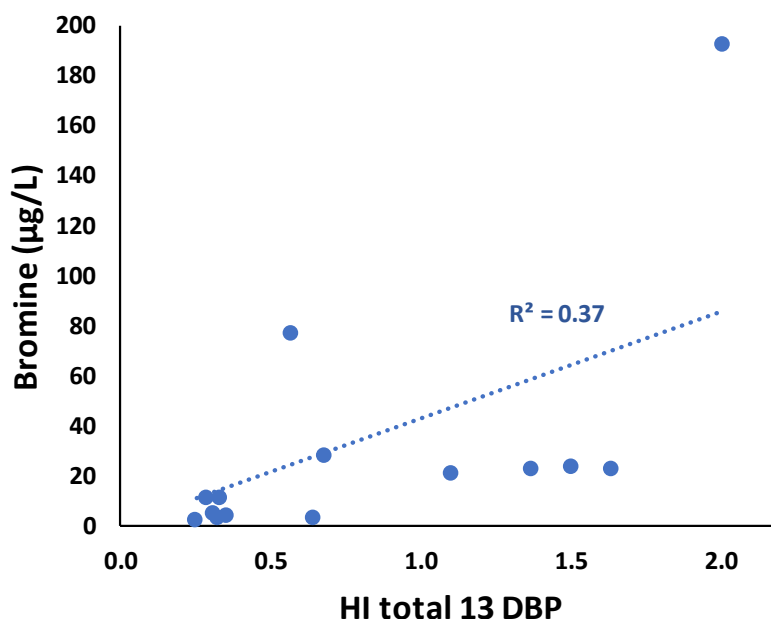


Figure 2.9 HI vs total bromine concentration

A correlation between the HI using the GV values and total bromine gave an r^2 value of 0.37 ($y=42.85x$), indicating a low correlation. Six waters with similar total bromine concentrations between 11 and 29 µg/L differed highly when translated to HI, with a range of 0.3-1.6, indicating the bromine speciation within the DBPs is important for the HI. This can be achieved practically by switching to a HAA9 method which has become more routine through improvements in analytical capability.

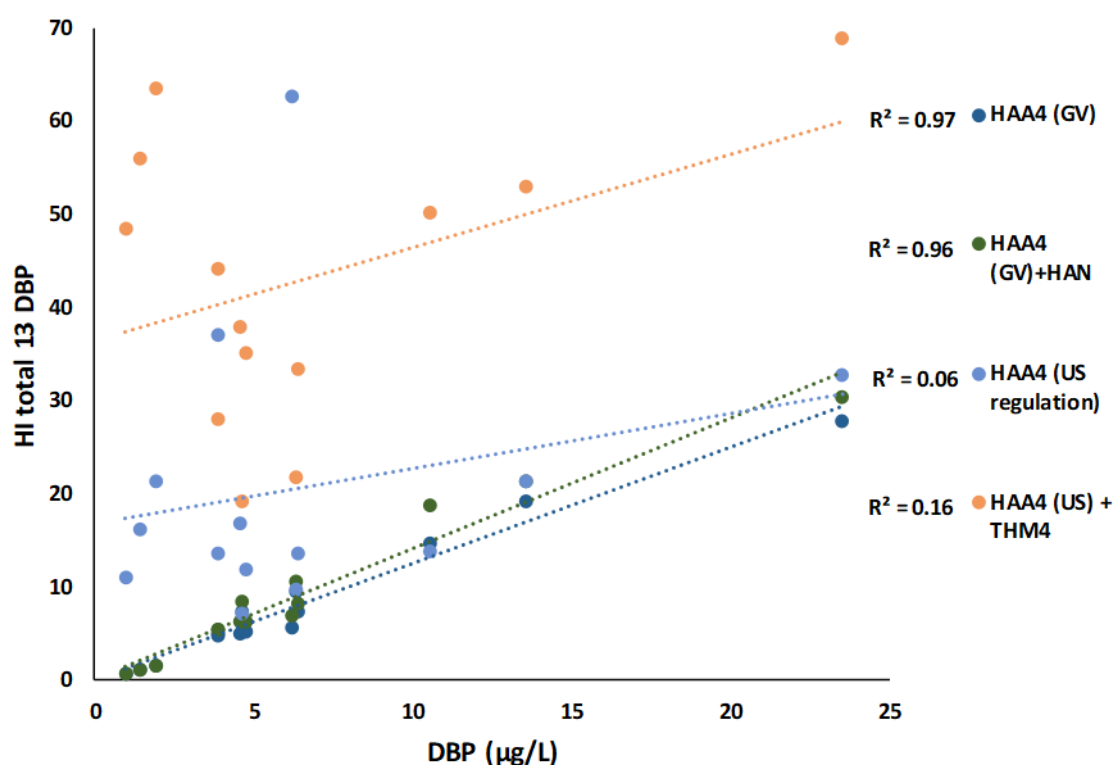


Figure 2.10: HI plotted against DBP concentration of HAAs and HANs

2.6 Conclusions

Measurement of THM4 and HAA9 provides a reasonable estimate of the total DBP concentration that may form as they represent the major species by mass. However, they do not correlate to the concentration of the other DBPs making them insensitive to understand the importance of emerging DBPs. The impact of converting to a hazard index depends on the toxicological dataset used. When viewed through the lens of the WHO GVs, the emerging DBPs are not particularly significant, Instead Br-HAAs become the key marker of the impact of the DBPs and this is effectively monitoring with a HAA9 methods. In contrast, if LC50 datasets are used, N-DBPs from the emerging DBP group HANs become the most important and the significance HAA are greatly reduced. Either way, THMs were observed not to impart a significant impact nor where they are seen as a good proxy for either the HAAs or the HANs and as such the use of THMs monitoring

alone requires re-consideration. It is proposed that monitoring be extended to either HAA9 or with also HAN4 to provide the most robust consideration of the potential risks associated with DBPs.

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3 Regulated and Emerging Disinfection by-products formation from surface waters: A comparison of upland and lowland source waters.

Regulated and Emerging Disinfection by-products formation from surface waters: A comparison of upland and lowland source waters.

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3.1 Abstract

Three surface water sources (upland, lowland river, lowland reservoir) with a range of organic and inorganic moieties were surveyed to show DBP formation and distribution that can form. Traditional and emerging DBP-FP were measured in raw waters, treated waters and then compared to the DBPs from the corresponding final waters, chlorinated onsite. They were compared in terms of concentration and HI with *in vivo*, WHO GV. The amount of both traditional and emerging DBPs formed, their speciation and associated HI is highly source dependant. The Br-HAAs dominated the HI, with waters containing high levels of bromine having an impact on their formation and hence the HI. A group of 6 emerging DBPs, chlorinated chemicals also were shown to be impact the HI due to low associated GV and increased during the formation potential tests. Upland waters with the lowest bromine and nitrogen concentrations formed the lowest Br-DBPs and N-DBPs and had the lowest HI. Overall, the findings demonstrated that when considering the hazard index of the formed DBPs, lowland surface waters become more of a concern than when only considered in terms of THM mass concentration.

Keywords Disinfection by-products (DBPs), Surface waters, hazard index

3.2 Introduction

During the disinfection process, chlorine reacts with organic matter (OM) present in the water forming unwanted disinfection by-products (DBPs). The first DBPs to be reported were in the 1970s with the discovery of trihalomethanes (THMs) and this was followed by the addition of haloacetic acids (HAAs) (Rook, 1974; Richardson, 2004). These two groups of DBPs represent the majority of the known DBP by mass and so are commonly used as a proxy for the whole. For instance, current regulation requires that waters contain less than 100 µg/L of THM4 in the UK and 80 µg/L and 60 µg/L for THM4 and HAA5 in the US (Rook, 1974; DWI, 2012; WHO, 2018). Today, with advances in analytical chemistry, an additional 600 *emerging* DBPs (non THM or HAA) have been identified in drinking water (Richardson, 2004; Krasner *et al.*, 2006). Emerging DBPs are typically formed in relatively low mass concentrations but are reported to be more toxic than THMs and so, even at low concentrations may pose a concern (Muellner *et al.*, 2007; Richardson *et al.*, 2007; Yang *et al.*, 2014; Wagner *et al.*, 2017). In addition, the incorporation of other halogens such as bromine and iodine into the resultant DBPs increases their toxicity. Accordingly, understanding the level of inorganic components such as nitrogen, iodine, and bromine in the water becomes important. For instance, with increasing bromine in the water there is a shift towards mixed Cl- Br- containing DBPs and eventually to Br-DBPs (Ates *et al.*, 2007; Huang *et al.*, 2013; Bond *et al.*, 2014b).

The total amount and relative distribution of the different DBPs that form is a consequence of differences in the organic make-up of the source water, the type and efficacy of treatment processes ahead of the disinfection step and the disinfection conditions applied. OM comprises of a complex mixture of organic material originating from natural and anthropogenic (human pollution) sources from contact with dead and living organic matter and is found in all water sources (Egeberg, *et al.*, 2002; Thurman *et al.*, 1985; Tian *et al.*, 2013). Typically, surface waters are defined into three different categories: Upland, lowland river and lowland reservoir (or lake) as the types of organic matter found in each group exhibit similarities. For instance, upland sources are known to contain high levels of natural organic matter characterised as larger MW compounds,

rich in aromatic moieties which are hydrophobic and are known to result in high THM formation levels (Gough *et al.*, 2014; Ritson *et al.*, 2014). In contrast, lowland sources tend to be richer in lower MW compounds which are less aromatic and more hydrophilic EfOM and form much lower levels of THMs. In cases where algae can predominate such as lakes and reservoirs, AOM becomes important and is the most variable as it depends on which algal species is abundant at the given time (Goslan *et al.*, 2017; Pivokonsky *et al.*, 2016). Both EfOM and AOM are richer in nitrogen containing organics, known to form relative low levels of THMs but have been associated to the formation of higher concentrations of emerging DBPs (Bond *et al.*, 2011).

Accordingly, it is posited that the different source water types are likely to form different levels of emerging DBPs. This requires further examination to ascertain the relative significance this may have on the assessment of risk associated to consumption of the trace levels of DBPs in drinking water. The paper responds by comparing the DBPs that formed from three source waters (upland, lowland river, lowland reservoir) over two sampling periods including traditional (THM and HAA) and emerging (HK2, HNM, HAL, CS) DBPs in raw, treated and final water. The significance of the emerging DBPs was assessed through the calculation of the resulting hazard index utilising World Health Organisation (WHO) guideline values (GV). To the authors knowledge this is the first study to directly compare the full range of surface water types in terms of emerging DBP formation and assess the significance of the levels found with respect to the WHO GV values.

3.3 Methods and Materials

3.3.1 Analytical methods and Sampling

All standards, reagents and chemicals were purchased from Sigma Aldrich (Gillingham, UK) and Fisher UK (Loughborough, UK). Samples were collected from the raw water, treated water prior to disinfection and the disinfected water from three active drinking water sites in the UK to represent a typical upland lake, lowland river and lowland lake

catchment. Samples were collected at two time points in SP1 in November 2016 and SP2 in May 2017 and were preserved and buffered on collection, stored below 5°C and analysed within 7 days. Upland water is treated with coagulation with iron, UV and chlorine disinfection. Lowland lake is pre-ozonated before iron coagulation, followed by GAC and disinfection with chlorine. Lowland river is iron coagulation, filtration and disinfection with chlorine.

DBP formation potential tests were performed on raw waters and waters treated on site before chlorination on the day of collection. Extraction and analysis of the resultant DBPs was carried out within 3 weeks of sampling. Samples were disinfected in glass vials with sodium hypochlorite at 5 times the TOC concentration to make sure all organic content had reacted with the chlorine. Sodium hypochlorite was tested using a Hach Ltd., (Manchester, UK) chlorine test kit diluted with deionised water to bring the chlorine levels within the test kit range to measure the chlorine each day before use. After adding chlorine to 5 times the TOC, the samples were stored at 20°C ± 2°C for 7 days to ensure chlorine has reacted with the DBP precursors present. The DBPs were analysed for THM4, HAN4, HK2, HNM, HAL and CS according to EPA Method 551.1. HAA9 was analysed according to EPA method 552.3. All DBPs were analysed according to a gas chromatography-electron capture detector (GC-ECD) method using an Agilent HP 6890 Series GC System with a modified GC method, column DB-1 and quantified using OpenLab software. Samples above the calibration range were diluted with MTBE to bring the sample concentration within the linear part of the calibration range.

The internal standard bromofluorobenzene was added to each sample for the analysis of method EPA Method 551.1. 1,2,3 trichloropropane was used as an internal standard and 2-bromobutanoic acid was used as a surrogate, derivatised during the methylation step in EPA method 552.3. 8 Calibration standards of 0-200 µg/L were extracted and run with each set of samples, with a standard within a factor of 2 of the minimum reporting level for each sample run. As per method 300.1, dichloroacetate was used as the internal standard in each calibration and sample, and a calibration from 0-5 mg/L was used, sample dilution was used if necessary. Within each sample run, a mid range standard was run after each 10 samples and again at the end for instrument quality control. The limit of quantification (LOQ) for GC-ECD methods was 0.5 µg/L, with MCAA at 2 µg/L, IC was

50 µg/L for chloride and 0.25 mg/L for remaining ions measured. The Shimadzu TOC-V VWP had a limit of detection (LOD) of 0.5 µg/L, with automatic dilution where necessary and the LOD of bromine using Perkin Elmer Elan 9000 (ICP-MS) (Beaconsfield, UK) was 0.2 µg/L.

Total organic carbon (TOC), Non-purgeable organic carbon (NPOC) and Total Nitrogen (TN) was performed using Shimadzu TOC-V (VWP). Ion concentrations were analysed using Thermo-Scientific (ICS-1600) according to EPA method 300.1. Bromine and Iodine were measured using Perkin Elmer Elan 9000 inductively coupled plasma-mass spectroscopy (ICP-MS) (Beaconsfield, UK). All occurrence samples were taken in duplicate with each individual sample then extracted and measured in triplicate on each instrument.

3.3.2 Toxicity Calculations

The hazard index calculations used were based on World Health Organisation derived guideline values (GV) based on No-observed adverse effect level (NOAEL) and tolerable daily intake (TDI) values. Resulting from long term laboratory *in vivo* studies, including carcinogenic and mutagenic end points. GV's are worldwide guidelines based on robust animal studies but have a limited DBP set, therefore restricting the inclusion of emerging DBPs. The GV dataset includes 19 DBPs measured here, THM4, HAA6, HAN2, HAL1 and 6 chlorinated chemicals. The 6 chlorinated chemicals are; 1,2-dibromoethane, tetrachloroethylene, dibromochloropropane, carbon tetrachloride, 1,1,1-trichloroethane and trichloroethylene. THM4 consisting of Trichloromethane, Bromodichloromethane, Dibromochloromethane and Tribromomethane. HAA6 consists of Monochloroacetic acid, Dichloroacetic acid, Bromochloroacetic acid, Dibromoacetic acid, Trichloroacetic acid and Bromodichloroacetic acid. HAN2 is Dichloroacetonitrile and Dibromoacetonitrile and HAL1 is chloral hydrate.

3.4 Results

3.4.1 Water Characteristics

The average NPOC for the three raw water sources were 18.8 mg/L, 5.7mg/L and 4.7mg/L for the upland, lowland lake and lowland river respectively (Table 3.1). The corresponding specific UV absorbance levels (SUVA) were 5.4, 1.2 and 3.9 respectively indicating the expected difference in the hydrophobicity of the organics contained within each water source. Further, as expected, the upland source contained minimal nitrogen as illustrated by a total nitrogen concentration of 0.04-0.11mg/L. This compares to levels of 0.25-2.45mg/L for the lake and 1.98-2.48mg/L for the river congruent with the presence of EfOM and AOM in the respective sources. Bromine concentrations followed a similar pattern with concentrations of 108.7 µg/L in the river and 185 µg/L in the lake compared to 39 µg/L in the upland source. Iodine levels were low in all samples ranging from 2-5 µg/L.

Overall, the upland source is characterised as low alkalinity, low inorganic water containing a high level of organic matter which is amenable to removal through traditional technologies. This is confirmed by the average NPOC removal efficiency which was 89% during the first sampling period and 87% during the second sampling period. In contrast, the two lowland sites contained more inorganic ions, a higher alkalinity and less organic matter but which was more recalcitrant to removal with average levels of 29-40% for the river water and 20-34% for the lake water. The consequence was that the treated waters from the lowland sources contained more organic matter at the point of disinfection than from the sites treating water from the upland catchment. To illustrate, average NPOC in the treated waters were 1.8-2.0mg/L for the upland site compared to 4.14 and 2.9-3.2mg/L for the lowland lake and river respectively. Overall, the water characterisation supports the notion that the lowland source waters should produce more emerging DBPs, especially those containing nitrogen and bromine, than water from the upland site.

Table 3.1 Water sources and averaged water characteristics

Source Water	Sample	Raw Waters						Treated Waters					
		NPOC (mg/L)	TN (mg/L)	TOC (mg/L)	IC (mg/L)	UV ₂₅₄ cm ⁻¹	Br ⁻ (µg/L)	NPOC (mg/L)	TN (mg/L)	TOC (mg/L)	IC (mg/L)	UV ₂₅₄ cm ⁻¹	Br ⁻ (µg/L)
Lowland Lake	SP1	5.21	0.25	4.71	39.09	0.06	184.50	4.14	2.33	6.15	35.88	0.02	177.45
	SP2	6.25	2.45	6.24	39.39	0.08	198.00	4.14	2.33	2.31	39.57	0.02	193.00
Upland	SP1	16.09	0.11	21.50	0.67	0.89	39.45	1.83	0.44	2.21	1.23	0.14	28.20
	SP2	15.64	0.04	15.28	0.26	0.83	39.10	2.02	0.42	2.29	1.16	0.14	24.00
Lowland River	SP1	5.38	1.98	6.13	37.67	0.20	116.50	3.25	2.49	2.89	39.95	0.09	107.00
	SP2	4.07	2.48	4.17	41.67	0.17	101.00	2.90	2.57	3.93	37.48	0.20	113.00

3.4.2 Disinfection By-Product Formation Potential of Raw Waters

The DBP-FP formed with the raw water from the upland site showed the highest concentration and variance of total DBPs measured with a range of 2000-3500 µg/L and an average of 2500 µg/L. In comparison, the average total DBP for the lowland river and lake were 1200 µg/L and 1670 µg/L respectively (Figure 3.1a). The corresponding formation potential normalised to the amount of carbon (NPOC) was 132µg/mg, 255 µg/mg and 292 µg/mg for the upland, river and lake waters respectively. This demonstrates that the upland source waters are not more reactive overall but have the potential to form more DBP than the lowland sources waters because of their higher NPOC. Traditional perceptions are that upland source waters exhibit the highest reactivity based on THM-FP (Brooks *et al.*, 2015). The current data shows that by considering a broader range of potential DBPs, the established perception may need re-examination. Converting the DBP-FP data to a hazard index reveals a different picture whereby the upland source water is observed to exhibit the lowest average and range of HI (Figure 3.1b). To illustrate, average HIs were 43, 68 and 143 for the upland, lowland river and lowland lake respectively. The absolute values of HI are expected to be elevated as the measurement is based on raw water using a formation potential test and so cannot be used to judge the potential risk associated with these water types. However, comparison of the data is appropriate and demonstrates that the water from the lowland sources potentially offers more cause for concern when viewed in terms of the tradition and emerging DBPs combined.

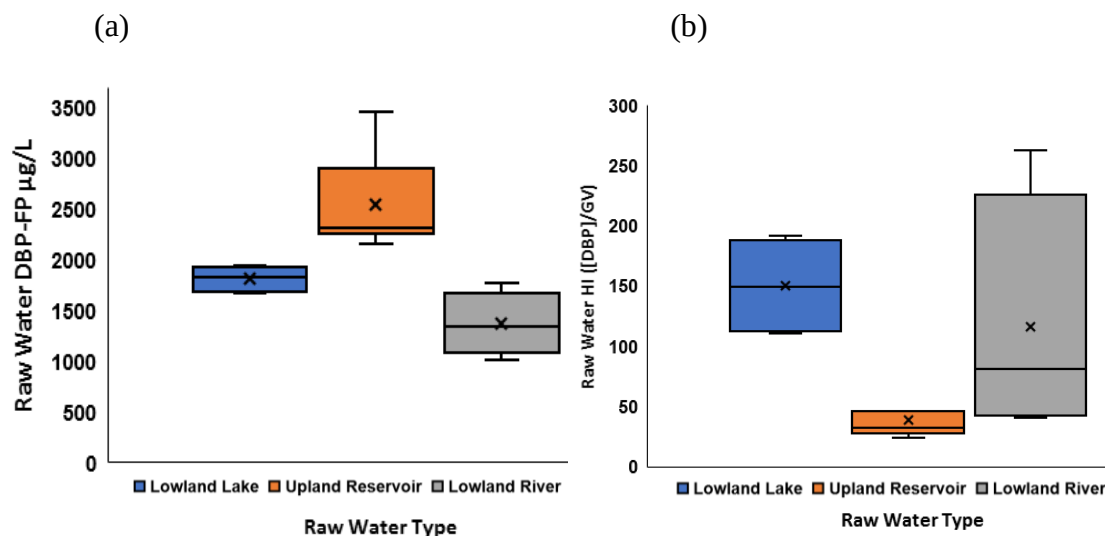


Figure 3.1 Total DBP-FP concentration(a) and the hazard Index(b) based on Guideline Values of 3 surface Raw Waters (n =12) (sampled before treatment)

Speciation of the DBPs into the main groups confirmed that by mass the THM and HAA were the predominate species. To illustrate, the mass percentage of THM and HAA was 79-87% for the upland source water, for the lowland lake and 24% and 63% for the lowland river (Figure 3.2). Further, across all source waters the HAAs represented the predominate DBP fraction constituting 62%, 57% and 58% for the lowland lake, upland and lowland river respectively for the two sampling periods. The two predominate emerging DBP groups were the HAL and HK which contributed between 4-11% and 0.6-8.6% respectively across all waters. The highest absolute values of HAL were observed in the case of the upland source water where the HAL-FP was 306 and 124 µg/L for the two sampling periods. In comparison the equivalent ranges were 156-78 µg/L and 61-67 µg/L for the lowland lake and river respectively. The remaining emerging DBP constituted minor contribution to the total with ranges across all water sources of 0.4-1.8%, 0.1-0.7% and 0.1-0.5% for the HAN4, CS6 and HNM1 respectively. As expected, higher levels of N-DBPs were formed from the lowland source waters which were richer in nitrogen containing organics. For instance, the HAN4-FP was 23-24 µg/L for the lowland river, 8-34 µg/L for the lowland lake compared to 10-14 µg/L for the upland source. Previous consideration of the relative contribution of different groups supports these findings but reports a higher contribution from the HANs. For instance, Roccarco *et al.*, (2014) reported DBP-FP proportions of 66-75% HAA-FP, 22-28% THM-FP and 3-7% HAN-FP, with the specific levels depending on the water.

Conversion of the data to HI reveals a shift in the consideration of the most important DBPs. Across all waters, THM contribute only between 0.7-9.4% to the total HI compared to 70-90% for the HAA6. Indeed, CS6 contributed more to the total HI than THM with between 0.1-23% across all waters. The HAL1 and HAN2 groups combined contributed a high of 5.7% and a low of 1.8% in the upland and river raw waters respectively. Comparison across the source water types revealed the highest HI coming from the lowland lake sources due to the very high levels of HAA-FP congruent with the precursor compounds commonly associated with lowland lakes such as AOM (Goslan *et al.*, 2017).

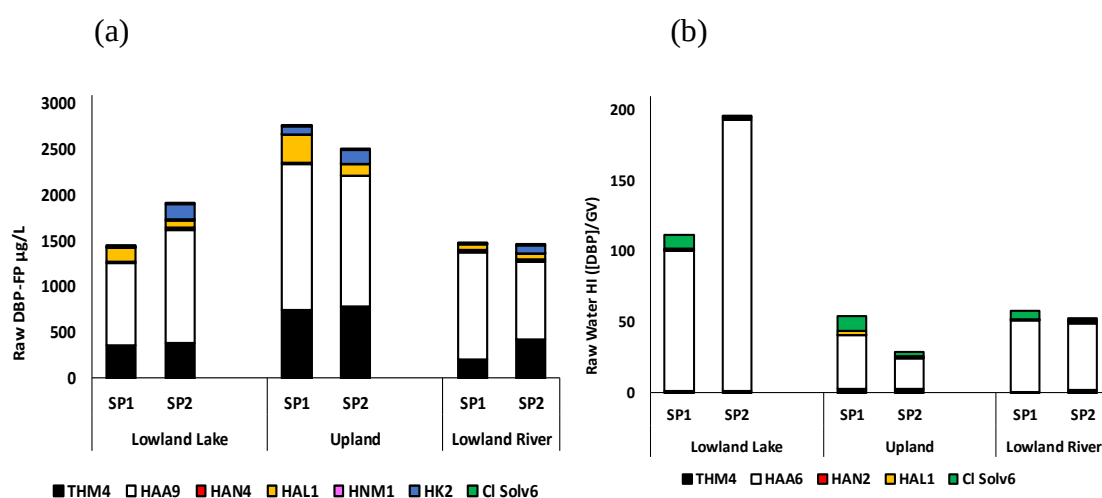


Figure 3.2: DBP-FP speciation of categories for their concentration (a) and hazard Index (b) of Raw Waters (n=12) (sampled before treatment)

Analysis of the speciation with the HAA and THM groups revealed the cause of the differences observed above. In the case of THM-FP, all waters were dominated by the chlorinated DBP CF which constituted 98%, 95 and 90% of the total THM-FP on average for the upland, lowland river and lowland lake respectively. In the case of the lowland source waters, a small amount of a brominated THM, BDCM was also apparent at concentrations of 4-8 $\mu\text{g/L}$ for the lowland lake and 2-4 $\mu\text{g/L}$ for the lowland river (Figure 3.2). THMs have relatively low potency levels with the GV for CF and BDCM of 300 and 120 respectively. In comparison, HAA have lower GV values making the impact on the HI more significant. For instances, the GV for the three more significant HAA in relation to the HI are 50 for DCAA and 1 for both BCAA and BDCAA. The later showing the significance of brominated HAA on the assessment of the overall HI.

In terms of mass concentration, the most significant HAAs were the chlorinated HAAs: DCAA and TCAA consistent with the use of formation potential test were the chlorine is provided in excess and so favours the formation of chlorinated by-products (Symons, *et al.*, 1993). Comparison across the source water types revealed that the upland source formed the most HAA in total which was predominated by TCAA and DCAA. To illustrate, TCAA concentrations from the upland source water were 167-182 µg/L compared to 105-223 µg/L for the lowland lake and 30-90 µg/L for the lowland river. Brominated HAAs were split across the range of possible products but a higher total level of Br-HAA was formed in the lowland lake samples at 200-273 µg/L including the highest levels of BCAA and BDCAA at 62 µg/L and 40 µg/L, respectively. In comparison, the upland source water formed lower levels of Br-HAA with substantially lower levels of BCAA and BDCAA. When viewed in terms of the HI, two HAA become the most important, BCAA and BDCAA with DCAA and BDAA providing the majority of the remaining contribution to the HI.

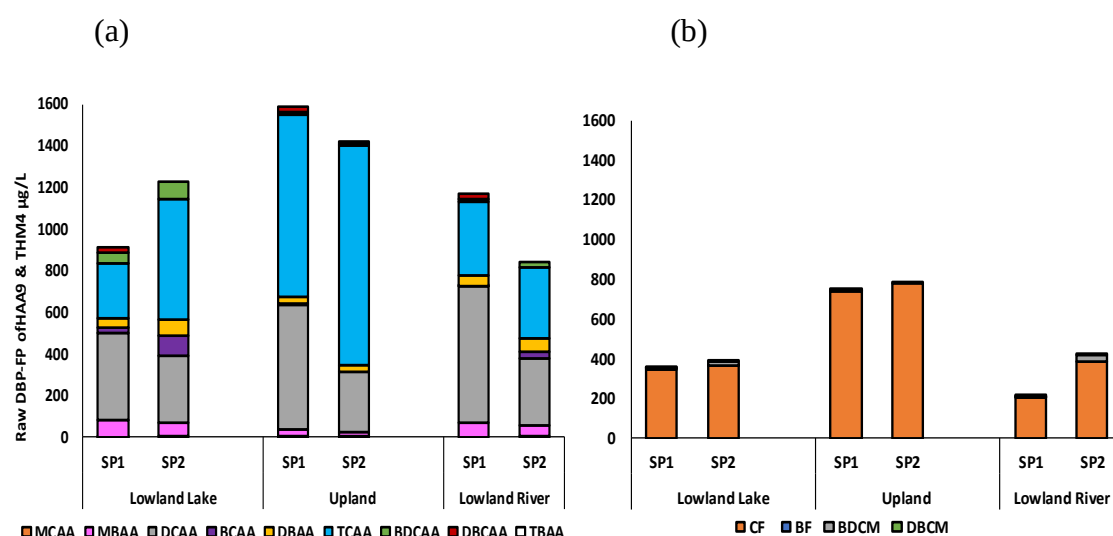


Figure 3.3 Speciation of HAA (a) and THM (b) categories of Raw Waters (sampled before treatment) as DBP27-FP concentrations.

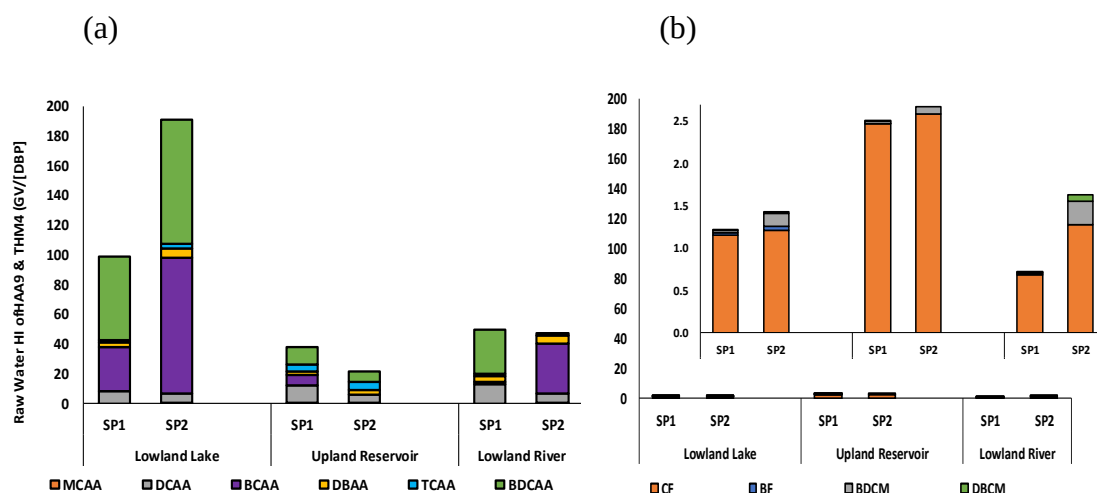


Figure 3.4 Speciation of HAA (a) and THM (b) categories of Raw Waters (sampled before treatment) as DBP19 as Hazard Index

3.4.3 Disinfection By-Product Formation Potential of Treated Waters

Removal of the precursor compounds through the treatment processes resulted in a reduction of the DBP-FP to levels of 550 $\mu\text{g/L}$, 589 $\mu\text{g/L}$ and 437 $\mu\text{g/L}$ for the upland, lowland lake and lowland river respectively (Figure 3.5). The changes equate to reductions of DBP-FP of 80%, 65% and 70% and compare to reductions in the NPOC of 88%, 27% and 34% respectively. Consequently, preferential reduction in highly reactive precursors is observed in cases of the two lowlands sources water but not in case of the upland source water. For instance, the DBP-FP reactivity levels changed from a raw water level of 132 $\mu\text{g/mg}$ to 285 $\mu\text{g/mg}$ in the treated water for the upland source. Comparative changes of 255 $\mu\text{g/mg}$ to 145 $\mu\text{g/mg}$ for the lowland river and 292 $\mu\text{g/mg}$ to 147 $\mu\text{g/mg}$ for the lowland lake samples on average so substantial reduction in the overall reactivity.

Conversion to HI revealed lower reductions of 43% in SP1 and 51% in SP2, in the lowland lake, the upland decreased in SP1 by 21%, but increased 115% in SP2, the lowland river decreased 26% in SP1 and increased slightly in SP2 by 26% compared to the raw water. Comparison across the water types showed more similarity than observed in the raw waters but continued to suggest the lowland lake exerted the greatest hazard potential. To illustrate, the HI of the lowland lake ranged between 31-123, with an average value of 80. This compared to averages of 48 and 49 for the upland and lowland river respectively.

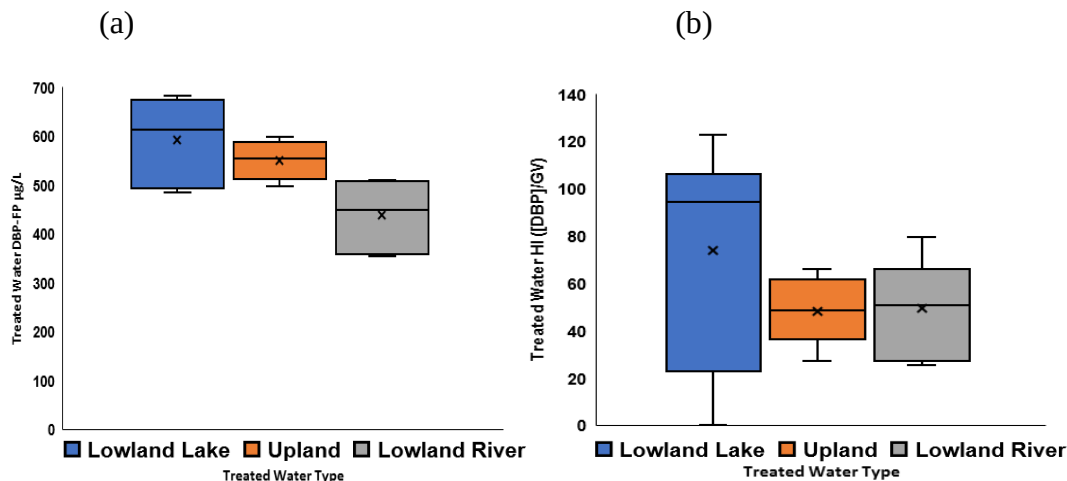


Figure 3.5 Total DBP-FP concentration(a) and the hazard Index(b) based on Guideline Values of 3 surface Treated Waters (sampled after treatment, pre chlorination)

Analysis of the DBP-FP reduction in terms of the different groups revealed significant reduction of THM across all sources with an average reduction of 81%. This is congruent with the operation of the plant being related to meeting the regulatory requirements which are based on THMs. A smaller reduction in HAA-FP was seen across all water sources with an overall average of 66% (Figure 4.6). The absolute amount varied from a high of 540 µg/L in the lowland lake to a low of 290 µg/L in the lowland river. As a consequence, HAA-FP remained the dominate DBP across all water sources, contributing 76%, 81% and 76% for the lowland lake, upland and lowland river respectively. The differences observed between THM and HAA reflect that the two groups of DBPs are known to form from different precursors and are removed through different processes (Bond *et al.*, 2011; Bond, *et al.*, 2014). Consideration of the emerging DBPs revealed a switch in the predominate species to the HAN4 whose concentration varied between 3 and 46 µg/L, contributing an average of 4.6 % to the total DBP-FP. The remaining DBPs represented average concentrations of 38 µg/L, 27 µg/L and 39 µg/L for the upland, lowland lake and lowland river water sources respectively.

The corresponding HI were dominated by the HAAs which contributed 95.7%, 96% and 98% for the upland, lowland lake and lowland river water sources respectively (Figure 6). The THMs exerted a maximum HI of 0.44, observed with the lowland lake water and contributed 0.4% across all waters. In this case the second most important group was the

HAN4 with an average HI across all waters of 1.1 and maximum of 2.4 observed in the case of the upland water.

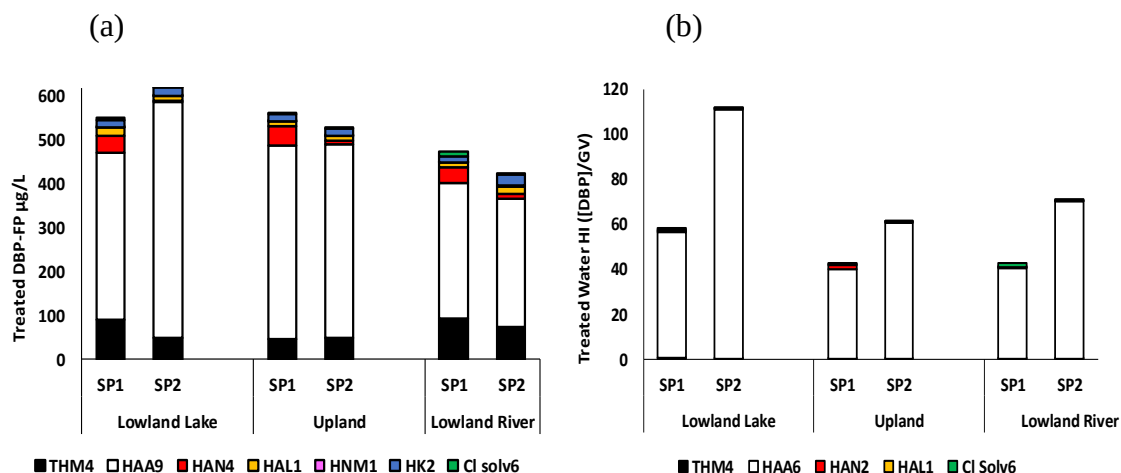


Figure 3.6 DBP-FP speciation of categories for their concentration(a) and hazard Index(b) of Treated Waters (sampled after treatment, pre chlorination)

3.4.4 Disinfection By-Products of Treated Final Waters

The total DBP formed was 140 µg/L, 85 µg/L and 72 µg/L for the lowland river, lowland lake and upland source waters respectively (Figure 3.7). Compared to the formation potential tests with the treated water, the actual DBP levels were 31%, 4% and 13% of the DBP-FP respectively. This showed the lowland river to have the highest total DBP in contrast to the raw water and the treated water FP tests where it had the lowest overall total. The reported levels converted into total HI are 13, 10 and 3 for the lowland lake, lowland river and upland source waters respectively. In terms of HI, the relative sequence has remained unchanged with an order of highest to lowest (based on average HI) of lowland lake > lowland river > upland (Figure 3.7). However, the greatest variance was observed with the lowland river with a range of 6.4-24.4 compared to 5.8 to 11.6 for the lowland lake and 1.1 to 2.4 for the upland source water.

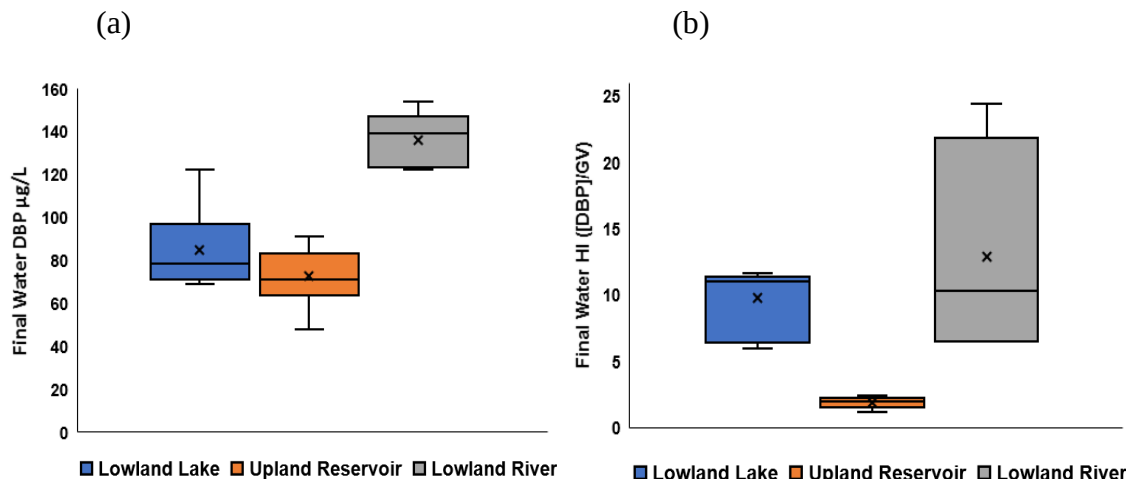


Figure 3.7 Total DBP concentration(a) and the hazard Index(b) based on Guideline Values of the final waters from 3 surface waters (sampled after treatment, post chlorination).

The relative contribution from the different DBP groups changed with the final waters compared to the FP tests **Figure 3.8**). The change is predominately observed through a reduction in the total mass of HAA formed which reduced by 93% compared to the treated water FP levels for the lowland lake water and by 94% and 79% for the upland and lowland rivers waters respectively. Consequently, HAAs contributed 46%, 36%, and 37% to the total DBP for the lowland river, lowland lake and upland source waters respectively. The corresponding contribution from THMs were 35%, 51% and 58% such that the ratio of HAA to THM was 0.73 for the lowland lake compared to 0.67 for the upland source and 1.31 for the lowland river. The THM levels were below the regulation of 100 µg/L for all samples and varied between 35 and 50 µg/L across the waters. The emerging DBPs contributed 5%, 19% and 13% to the total for the upland, lowland river and lowland lake waters respectively. However, the predominate species were different for each source water type. In the case of the lowland lake, CS6, HAN4 and HK2 contributed 4.7 µg/L, 5.7 µg/L and 1.8 µg/L respectively. In comparison, HAN4 and HNM1 were observed at the highest levels in the lowland river at average concentrations of 12.7 µg/L and 8.1 µg/L respectively. Whereas, in the case of the upland source water, HAL1 was seen to add the most additional DBP mass at 4 µg/L.

Conversion to HI reduced the impact of the emerging DBPs with the HAAs remaining the dominant contributor to the HI making up on average 90% of the total (Figure 3.8). The remaining contribution to the HI came from the CS6 and HAN4 which provided an average of 5.5% and 2.3% respectively. Interesting, although the lowland lake and upland

source had similar total DBP levels, the relative distribution of the DBP species meant that the HI of the upland source water was 80% lower than that of the lowland lake. The difference reflects the much lower levels of nitrogen and bromine found in the upland source reducing the amount of brominated and nitrogenous DBPs.

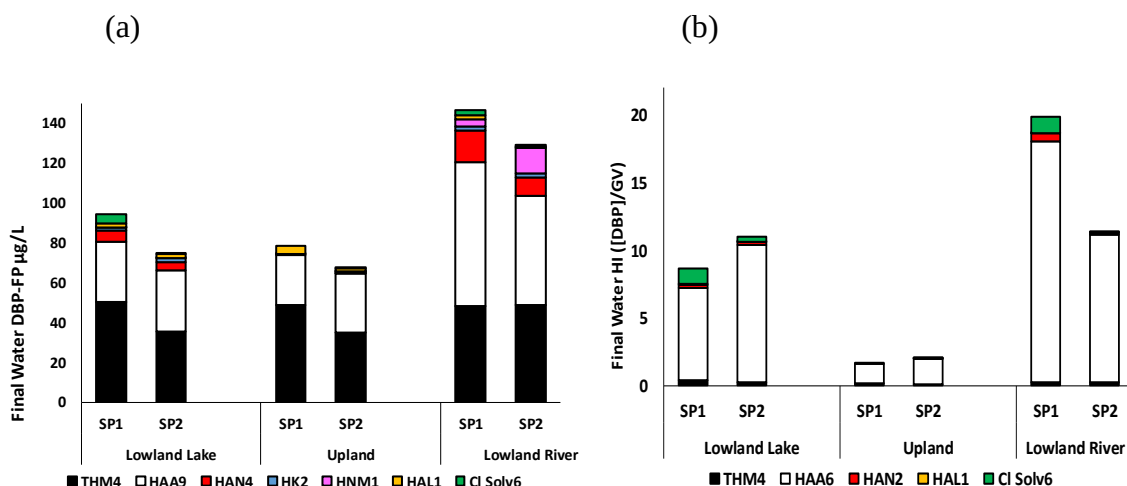


Figure 3.8 DBP speciation of categories for their concentration(a) and hazard Index(b) of Final Waters (sampled after treatment, post chlorination).

3.5 Discussion

The assessment of the traditional and emerging DBPs with respect to mass concentration and HI has revealed the predominant importance of the brominated HAAs on the overall HI. This was observed with regards to the formation potential levels of the raw and treated water and the occurrence levels of the final waters. Accordingly, the impact of considering emerging DBPs appears to be relatively minor in comparison to that of the brominated HAAs. Further, when viewed through a HI lens the significance of THMs should be queried and indicates much greater attention should be given to the HAAs and particularly the brominated HAA. In relation to emerging DBPs, the CS6 and HAN2 are the species most worth monitoring.

The HAAs with the highest potency are BCAA, BDCAA and DBAA with GV values of 1, 1 and 12 respectively. Hence changes in their concentration has a significant impact on

the total HI. In contrast, the GV of the other HAAs are all above 20 with some levels as high as 200. Comparison between the levels observed in the FP tests of the treated water compared to the occurrence samples revealed different patterns. The most apparent examples relate to the upland waters where the occurrence data indicates a dominance of DBCAA whereas the FP test indicates high levels of DBAA, MBAA, BCAA and BDCAA. Indeed, in the 2017 sample there is virtually no DBCAA observed at all. In the case of the two lowland source water types, more similarity is observed between the FP and occurrence data with regards to the species that form but the relative distributions are different. In our current investigations the change in Br- HAA species distribution from final water FP to occurrence data was different indicating the changing conditions impact the waters differently. For instance, the relative significance MBAA and BDCAA was very different with much less proportional contribution occurring in the lowland lake compared to the river in the occurrence data compared to the FP test. Importantly, this challenges the suitability of the FP test in understanding the risk associated with DBPs. The bromine substitution factor is similar in raw and treated waters, with the highest in the lowland lake with the highest bromine levels and the lowest in the upland sources, with a range of 0.01-0.05. The low bromine substitution levels may be due to competition with chlorine in excess added during the formation potential tests. In the final waters chlorinated on site at lower levels, the bromine substitution levels are higher and reflect exposure occurrence. With less chlorine, substitution of the bromine from hypobromous acid is favoured, and as such the level of bromine substitution increases to a range of 0.5-0.5. The highest substitution seen in the lowland lake with the highest bromine levels and the lowest in the upland sources with the lowest bromine levels.

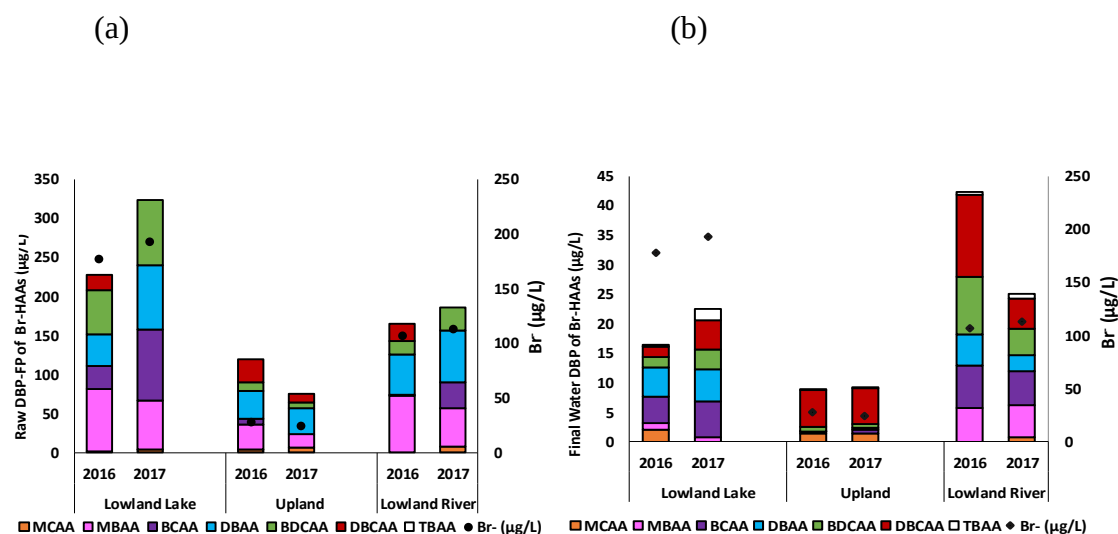


Figure 3.9: Concentration Br-HAAs in the formation potential of raw water showing DBP-FP(a) and final water chlorinated on site (b).

Consideration based on the emerging DBPs measured in the current study indicates that they are relatively minor contributors to the overall hazard index and as such can be considered as a secondary issue over that of brominated HAAs. This was particularly evident for the upland source water congruent with the low levels of nitrogen within the source water.

However, a number of the emerging DBPs were identified as the most important including HAN4 and HNM1 within the N-DBPs and CS6. Comparison across water sources and between treated water-FP and occurrence levels showed much greater variation with the FP tests. The variation was most apparent in associated with DCAN and BCAN which appear over represented in the FP test. Interestingly, in the final water occurrence samples, more contribution was observed from TCAN, BDAN and CP (Figure 3.10) again indicating the challenge associated with using a FP test when considering HI. The HNM1 DBP chloropicrin (CP), also known as nitrochloroform, was observed particularly in the lowland river occurrence samples where it was the most abundant N-DBP in the 2017 sample at a concentration of 13 µg/L. The other N-DBP of note was DBAN which made up a reasonable fraction of the occurrence sample and have a low GV value of 12 and hence contribute most to the HI with respect to the N-DBPs.

The other group of compounds that require highlighting are the chlorinated chemicals of which six were monitored in the current study: 1,2 dibromoethane (1,2 DE),

tetrachloroethylene (TTE), dibromochloropropane (DBCP), carbon tetrachloride (CT), 111 trichloroethane (TIE) and trichloroethylene (TCE). These compounds are considered artefacts released into the environment from industry before treatment and not considered to be by-products of the disinfection process. However, in the current study the levels were seen to increase during the FP tests, indicating that they could be potentially generated. For instance, measurement in the raw water prior to the FP test showed all were individually below 1 µg/L with a sum of the six compounds that ranged from <LOD-0.7 µg/L. The equivalent data in the FP test of the raw and treated water were 0.5-15 µg/L and 0.5-10 µg/L, equating to a 50% increase. In comparison, in the final water occurrence samples, the total CS6 ranged from <LOD-5 µg/L of the lowland lake, <LOD-0.5 µg/L for the upland and <LOD-3 µg/L for the lowland river (Figure 3.11). Whilst at low concentrations, the toxicity of these compounds imparts a noticeable impact onto the HI of the occurrence samples when present (Figure 3.8). In particular, DBCP and 1,2 DE were observed to contribute to the overall HI of the occurrence samples in the lowland lake and lowland river respectively.

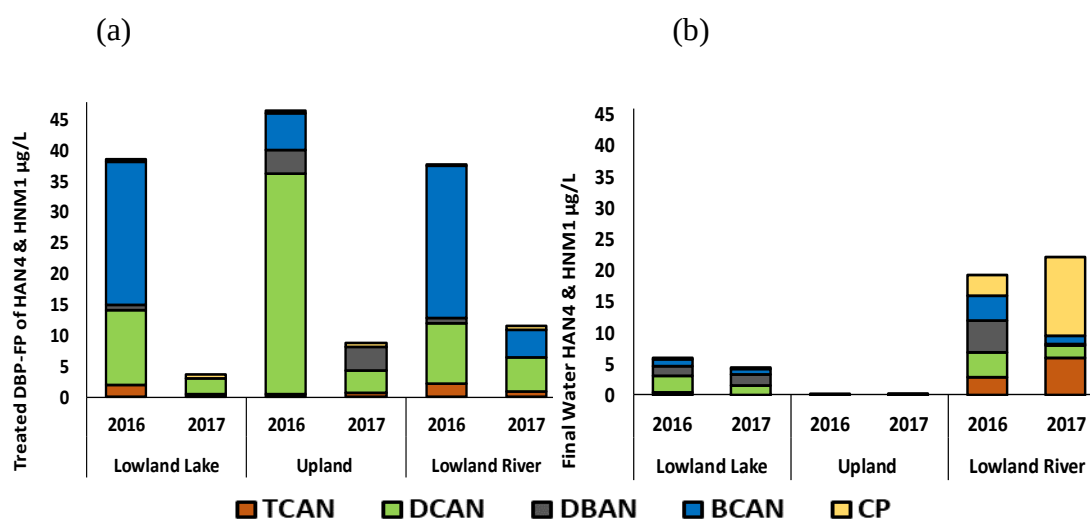


Figure 3.10: Concentration of N-DBPs in the formation potential of treated waters-FP(a), and the final water(b) chlorinated on site.

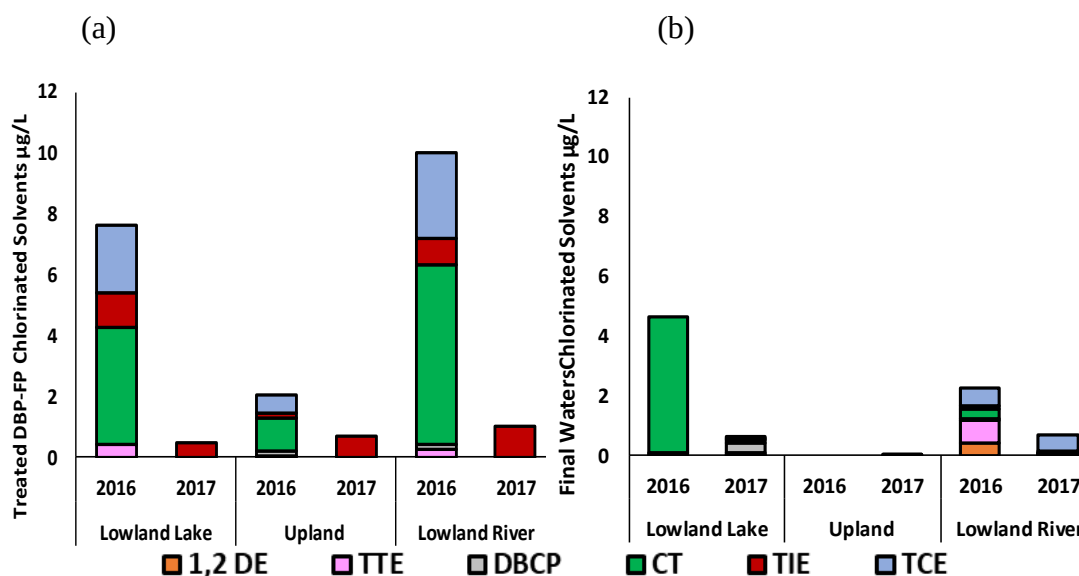


Figure 3.11: Concentration of Chlorinated chemicals in the formation potential of raw and treated waters(a), and the final water(b) chlorinated on site.

3.6 Conclusions

Different source water types will impact the total amount and distribution of the individual species of both traditional and emerging DBPs. This is particularly noted with respect to upland waters that have a lower propensity to form both emerging DBPs and brominated species of HAAs compared to lowland source waters. When viewed through a HI lens, the importance of emerging DBPs is overshadowed by the impact of brominated HAA which dominate the HI across all source waters. Accordingly, future focus should be on better monitoring and management of brominated HAAs including ways to minimise the incorporation of bromine into the chlorinated by-products. Beyond that a number of emerging DBPs made a noticeable impact including BDAN, CP (Br-N-DBPs) and DBCP and 1,2 DE (CS). There remains limited data on their formation and prevalence over the long term and this is recommended as an area of future development. Finally, when considering HI, the use of a formation potential test has been put into question as it not only generates very high absolute levels but changes the speciation of the individual DBPs.

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4 Minimisation of traditional and emerging Disinfection by-products formed in surface waters using Nanofiltration.

Minimisation of traditional and emerging Disinfection by-products formed in surface waters using Nanofiltration

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4.1 Abstract:

Membranes can be used to remove organic matter in waters with high organic carbon and high molecular weight compounds reducing traditional DBPs such as THMs. However, there is a lack of research tracking traditional and emerging DBP precursor removal across the full range of surface water types. To respond to this information gap, 2 nanofiltration membranes with different hydrophilicities were used to treat waters from three catchment types: upland, lowland lake and lowland river. DBPs with a guideline value were converted to a hazard index and removals compared in terms of HI and concentration. THM-FP and NPOC reductions of 74%, 81% were observed with the NF270 membrane and 89%, 86% with the NF90 membrane but limited removal of bromine levels was observed with both membranes, especially in the lowland lake leading to increased bromine incorporation in to DBPs, increasing the HI. Accordingly, NF treatment resulted in overall DBP-FP reductions of 70% for the NF270 membrane and 80% for the NF90 membrane corresponding to a HI increase of 20% (NF270) and a reduction of 34% (NF90).

Keywords Disinfection by-products (DBPs), Membranes, nanofiltration

4.2 Introduction

Disinfection by-products (DBPs) occur as an unintended consequence of the disinfection process used in drinking water production. In the UK, the 2010 Water Supply Regulations (Statutory Instruments, 2010) require water undertakers to ensure that disinfection by-products (DBPs) are kept as low as possible without compromising the effectiveness of the disinfection process. The regulations advise water companies to focus attention to identify and remove DBP pre-cursors and avoid conditions that encourage the formation of DBPs. The regulations set a parametric value of 100 µg/L for trihalomethanes (i.e. a group of four disinfection by-products, namely chloroform, bromoform, dibromochloromethane and bromodichloromethane) and 10 µg/l for bromate. Furthermore, regulation 4(2) states that for water to be considered wholesome it must not contain any substance which alone or in conjunction with any other substance constitutes a potential danger to human health. Hence, whilst there are no specific parametric values in the UK for other DBPs such as HAAs, these must not be present in concentrations that constitute a potential danger to human health (DWI guidance 2010, Grellier *et al.*, 2015; Nieuwenhuijsen *et al.*, 2009; Rice *et al.*, 2008). WHO have suggested a component based approach to THMs where the individual DBP is divided by their respective WHO guideline value, giving a hazard index for the mixture. According to WHO, this is an achievable, case by case hazard index taking the potency and concentration of each individual DBP in to account. This method can be used for monitoring but also to elucidate the toxicity driver with the DBP mixture (WHO, 2017).

The DBPs form due to the reaction between the disinfectant (chlorine) added and the residual organic matter (OM) in the water after treatment. Organic Matter (OM) levels and characteristics are highly variable with reported changes in relation to the DOC, the molecular weight distribution, the charge and the hydrophobicity (Huang *et al.*, 2015; Thurman *et al.*, 1985; Tian *et al.*, 2013). In addition, levels of nitrogen and bromine are also highly variable leading to a broad distribution of chlorinated, brominated and nitrogenous DBPs. For instance, lowland waters rich in algal organic matter (AOM) or

effluent organic matter (EfOM) will contain relatively high levels of organic nitrogen and so are likely to form more N-DBPs. In contrast, waters from upland catchment tend to contain limited amounts of nitrogen and bromine and so favour the formation of chlorinated by-products including THMs (Drewes *et al.*, 2002; Levchuk, *et al.*, 2018). Accordingly, much of the previous work has focussed on upland catchments in order to meet current legislative targets around the THM4 standard. However, when expanded to include HAA and emerging DBPs, lowland source waters become more important in terms of their HI (Chapter 3 & 4). Although the removal rates for DBP precursors for THM and HAA9 has been shown to be high, ranging from 77-99% with many NF membranes, as seen in table 4.1. The bromide and bromate removals remain low, leading to an increase in Br-DBPs (Siddiqui *et al.*, 2000).

Table 4.1: Bromide removal using Nanofiltration membranes

Membrane & manufacturer	TOC rejection (%)	bromide rejection (%)	TTHM rejection (%)	HAA9 rejection (%)	Chloral Hydrate rejection (%)	Bromate rejection (%)	Humic acids rejection (%)	Reference
Hydranautics, NTR 7450	70.7	3	76.6	75	*	*	*	(Chellam, 2000)
Koch Fluid Systems TFC-SR	93.6	10	96	92	*	*	*	
Dow FilmTec, NF 200B	91.4	-3.3	93.7	81.2	*	*	*	
Filmtec NF70.	93.8	40-80	98.7	97.9	87.9	*	*	(Siddiqui <i>et al.</i> , 2000)
Filmtec NF45.	92.9	40-80	99.2	97.9	89.2	*	*	
Hydranautics PVD1.	92.7	40-80	99.1	98.3	89.6	*	*	
Desal 5.	94.2	40-80	98.9	97.9	83.8	*	*	
Filmtec NF270.	*	10.1	*	*	*	15.1	*	(Lin <i>et al.</i> , 2019)
Filmtec NF90.	*	28.8	*	*	*	46.1	*	
Filmtec NF270.	*	1.3	*	*	*	5.9	70.7	(Listiarini <i>et al.</i> , 2010)
Filmtec NF90.	*	6.9	*	*	*	18.9	94.0	

*Not measured within the study

The main approach to minimising DBPs is to reduce the organic levels (precursor compounds) to as low as practical. This is achieved in the majority of surface water plants with traditional technologies such as coagulation, ion exchange, activated carbon and ozone (Bond *et al.*, 2010). In addition, at relatively small rural upland catchment sites, nanofiltration membranes are used for direct removal of the carbon (NOM) (Gough *et al.*,

2014). Nanofiltration (NF) is a high pressured membrane process with separation properties that lie in between reverse osmosis and ultrafiltration with pore sizes typically of 1 nm, which corresponds to a molecular weight cut-off (MWCO) of approximately 300-1000 Da (Mohammad *et al.*, 2015; WHO, 2011). NF is suitable for removing a wide range of pollutants from waters including NOM and so has the potential to be a useful technology for controlling DBPs (Van der Bruggen *et al.*, 2003). Reported DOC removal when treating surface waters ranges between 67–94% when using a NF with corresponding THM and HAA precursors removals of 66–92% and 66–97% indicating limited ability to preferential remove target precursors (Allgeier *et al.*, 1995). Similarly, 65-85% DOC removal was reported from a lowland lake water using the NF270 membrane on Coagulation and sedimentation treated water used as feed for bench and pilot scale tests (Park *et al.*, 2005).

The separation efficacy of NF has been linked to a number of different mechanisms such as steric hindrance (length and width of the molecule), acid charge interactions (pKa), hydrophobic interactions (log Kow), and diffusivity (Dp) (Bellona *et al.*, 2004; Bond *et al.*, 2011). Operationally, this translates to the impact of the molecular weight cut off of the membrane, its hydrophobicity and the impact of accumulated material at the membrane surface (fouling) coupled to the characteristics of the OM in the water to be treated. For instance, previous investigation into the efficacy of NF membranes for NOM removal has demonstrated that a hydrophobic NF membrane is better at removing neutral, hydrophilic surrogate compounds and a membrane with a hydrophilic surface is better at removing hydrophobic content and hence DBP precursors, especially THM precursors (Bond *et al.*, 2010, 2011). A number of groups have investigated adjusting selectivity and specificity of solute rejection by functionally the membrane with thin film composites comprised of sulfonic or carboxylic acid groups (Mohammad *et al.*, 2015; Wang, *et al.*, 2002).

Whilst NF systems are commonly used in rural upland catchment sites in Scotland and Norway (Fabris *et al.*, 2008; Sutherland *et al.*, 2015) their use for treating lowland source waters for rivers or lakes is much less well explored. Further, in most cases, the impact of using NF is viewed in relation to THM4 with a more limited data sets associated to HAA and a genuine paucity of information concerning emerging DBP. Accordingly, the

current paper re-examines the efficacy of NF membranes through the lenses of an expanded DBP list to include HAA and key emerging DBPs as well as translating that data into a hazard index to ascertain the impact NF may have on minimising the risks associated to DBPs in drinking water. To achieve this, two commercial NF membranes with varying hydrophilicities (NF 90 and NF 270) were used to treat water from three active UK sites with the source water characterized as an upland, lowland river and lowland lake. The treated waters underwent formation potential tests to monitor the resultant DBP formation levels and speciation which was used to calculate the hazard index based on World Health Organisation (WHO) guideline values (GV).

4.3 Methods and Materials

4.3.1 Analytical methods and Sampling

All standards, reagents and chemicals were purchased from Sigma Aldrich (Gillingham, UK) and Fisher UK (Loughborough, UK). Raw water before treatment was collected in large polyethylene containers and stored in the fridge from the day of sampling. Three raw All standards, reagents and chemicals were purchased from Sigma Aldrich (Gillingham, UK) and Fisher UK (Loughborough, UK). Raw water before treatment was collected in large polyethylene containers and stored in the fridge from the day of sampling. Three raw waters were sampled in the UK from a lowland lake, an upland reservoir and a lowland river to cover a wide range of precursors. Each water was sampled twice in November 2016 and May 2017 to show seasonal effects. Nanofiltration experiments were carried out in an Advantec UHP 150, 2000 mL stirred cell operated at a measure of 4 bar (Advantec, Japan). Two different membranes were used, supplied by Dow-Filmtec (Dow Chemical Company, US), the NF270 and NF90. The two membranes have similar MWCOs 200-300 Da but the NF290 is hydrophobic (contact angle 54°) and NF270 is hydrophilic (contact angle 27°). Membranes were soaked overnight in deionised water before being rinsed to remove preservation liquids. A different membrane was used for each experiment and 500 mL of permeate was collected in glass vials for the formation potential tests, and glass bottles for remaining analysis

Table 4.2: Properties of Membranes NF90 and NF270

Membrane	NF 90	NF 270	Reference
Manufacturer	Dow Chemical	Dow Chemical	
Composition on top layer	Polyamide thin-film based	Polypiperazine-based	Manufacturer
MWCO	200	200–300	Manufacturer
Contact angle	54°	27°	(Boussu <i>et al.</i> , 2006)
	Hydrophobic	hydrophilic	
Zeta potential (mM) (Charge at pH 7)	– 24.9	– 21.6	(Braeken <i>et al.</i> , 2006; Xu <i>et al.</i> , 2006)

Sodium hypochlorite was tested using a Hach Ltd., (Manchester, UK) chlorine test kit diluted with deionised water to bring the chlorine levels within the test kit range to measure the chlorine each day before use. Permeate samples in glass vials were disinfected with sodium hypochlorite at 5 times the TOC level to make sure all organic content had reacted with the chlorine. The samples were stored at 20°C ± 2°C for 7 days to ensure chlorine has reacted with the DBP precursors present. The DBPs were analysed according to EPA method 551.1 for 18 DBPs consisting of THM4, HAN4, HK2, HNM, HAL and 6 chlorinated chemicals (CS). Using EPA method 552.3, HAA9 was analysed by derivitisation and micro extraction. All DBPs were analysed using gas chromatography-electron capture detector (GC-ECD), with above the calibration range diluted with MTBE and injected again. The method used an Agilent HP 6890 Series GC System with column DB-1 and quantified using OpenLab software.

Total organic carbon (TOC), Non purgeable organic carbon (NPOC) and Total Nitrogen (TN) was performed using Shimadzu TOC-V VWP (Shimadzu, Europe). Ion concentrations were determined according to EPA method 300.1 and run on Thermo-Scientific ICS-1600. Bromine and Iodine were measured using Perkin Elmer Elan 9000 Inductively coupled plasma- mass spectroscopy (ICP-MS). All NF filtered samples were disinfected to perform a formation potential test, extracted and measured in triplicate on each instrument. Using EPA Method 551.1, the internal standard bromofluorobenzene was added to each sample. In EPA method 552.3, 1,2,3 trichloropropane was used as an internal standard and 2-bromobutanoic acid was the surrogate which was derivatised

during the methylation step. Calibration standards of 0-200 µg/L were extracted and run with each set of samples, with a low calibration point within a factor of 2 of the MRL for each sample batch. Samples were diluted with MTBE if analytes were outside calibration range to bring them within the linear range of the standard curve. With method 300.1, dichloroacetate was used as the internal standard in each calibration and sample, and a calibration from 0-5 mg/L was used, sample dilution was used if necessary. Within each sample batch, a calibration point was run after each 8-10 samples and again at the end for quality control for each instrument used. The limit of quantification (LOQ) for the DBP analysis with GC-ECD were 0.5 µg/L for all DBPs except, MCAA at 2 µg/L, IC was 50 µg/L for chloride and 0.25 mg/L for remaining ions measured. The Shimadzu TOC-V VWP had a limit of detection (LOD) of 0.5 µg/L, with automatic dilution where necessary. There was an LOD of 0.2 µg/L measuring bromine using the Perkin Elmer ICP-MS.

4.3.2 Toxicity Calculations

World Health Organisation (WHO 2004, 2011) derived guideline values (GV) based on No-observed adverse effect level (NOAEL) and tolerable daily intake (TDI) values listed in Figure 4.1), were used to calculate hazard index (HI). The *in vivo* guideline values overlap with 19 DBPs measured here, they are: THM4, HAA6, HAN2, HAL1 and CS6. THM4 contains Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform. HAA6 consists of Monochloroacetic acid, Dichloroacetic acid, Bromochloroacetic acid, Dibromoacetic acid, Trichloroacetic acid and Bromodichloroacetic acid. HAN2 is Dibromoacetonitrile and Dichloroacetonitrile with HAL1, chloral hydrate. The 6 chlorinated chemicals are; 1,2 dibromoethane, tetrachloroethylene, dibromochloropropane, carbon tetrachloride, 111 trichloroethane and trichloroethylene. The individual DBP concentration is divided by its corresponding GV value to give a hazard index ratio.

4.4 Results and Discussion

4.4.1 Raw Water Treated with nanofiltration membranes NF270 and NF90

The NPOC of the raw water was 5.21-6.25 mg/L for the lowland lake, 15.64-16.09 mg/L for the upland and 4.07-5.38 mg/L for the lowland river (Table 1). The hydrophilic membrane (NF270) reduced the NPOC to 1.23-1.39 mg/L with the lowland lake water, 1.22-2.25 mg/L for the upland source water and 0.86-1.18 for the lowland river water. This corresponded to removal levels of 76-78%, 86-92%, 78-79%. In comparison, the use of the hydrophobic membrane (NF90) enabled removal levels of 84-86% for the lowland lake, 93-94% for the upland and 78-82% for the lowland river. Overall, the NF90 delivered higher removal and enabled more consistent final water NPOCs across the three sources (Figure 4.1). Removal is known to generally reflect the MW of the organics being treated with greater resolution possible when considered in conjunction with the hydrophobicity of the organics. For instance, previous work with model compounds demonstrated removals of 24% and 92% for two compounds with MWs of 75 and 1701 g/mol, respectively (Bond *et al.*, 2010). The current data reflects this with waters from the upland catchments being more effectively removed congruent with the larger MW typically associated with the humic acid fraction that is prevalent within upland source waters. Further, the hydrophobic membrane is reported to better remove hydrophilic compounds than the hydrophilic membranes and this is reflected in the greatest difference being observed with the lowland lake which was characterised with the lowest SUVA of 1.2 compared to 3.9 and 5.4 for the lowland river and upland waters respectively.

Comparison between the two membranes also revealed significantly different IC removal from both of the lowland source waters (Figure 4.1). To illustrate, the IC in the lowland river water was reduced by 7% by the hydrophilic membrane (NF270) compared to 92% by the hydrophobic membrane (NF90). IC is made up of carbon dioxide, carbonic acid, bicarbonate anion, and carbonate, the composition of these carbon containing compounds can change seasonally, effecting treatment (Ministry of Health, 2017). The lowland lake had the highest bromine levels with had bromine reductions of up to 64% with NF90 in

SP1, corresponding to a 35% reduction in Br-HAAs. In the lowland river, reductions up to 66% were observed for NF270 and up to 66% for NF90.

Table 4.3: NPOC, TN, TOC, TC and IC before and after treatment with nanofiltration with 2 membranes

Sample		Sampling Point 1 (SP1)					Sampling Point 2 (SP2)				
		NPOC (mg/L)	TN (mg/L)	TOC (mg/L)	Br ⁻ (µg/L)	IC (mg/L)	NPOC (mg/L)	TN (mg/L)	TOC (mg/L)	TC (mg/L)	Br ⁻ (µg/L)
Lowland Lake	Raw	5.21	2.45	4.71	184.5	39.09	6.25	0.25	6.24	45.63	198.00
	NF270	1.23	2.07	1.44	183.00	14.85	1.39	1.33	0.88	43.98	97.80
	NF90	0.71	2.11	0.71	66.60	0.84	1.01	1.03	1.67	6.19	84.20
Upland	Raw	16.09	0.04	21.50	39.45	0.67	15.64	0.11	15.28	15.54	39.10
	NF270	1.22	0.50	1.34	21.50	0.24	2.25	0.63	6.33	6.30	28.30
	NF90	0.95	0.21	0.91	12.10	0.93	1.07	0.56	1.92	1.85	17.10
Lowland River	Raw	5.38	2.48	6.13	116.5	37.67	4.07	1.98	4.17	45.84	101.00
	NF270	0.86	2.39	1.16	111.00	33.88	1.18	3.21	1.75	42.12	31.80
	NF90	0.99	2.10	0.90	49.60	1.74	0.91	2.72	1.47	5.87	34.20

The average DBP-FP across the two sampling periods was 1677 µg/L, 2635 µg/L and 1566 µg/L for the lowland lake, upland and lowland river respectively. (Figure 4.1 and Figure 4.2). Treatment with NF resulted in a reduction in the total DBP-FP of 70% for the NF270 and 80% for the NF90 averaged across all water types. Analysis of the make-up of the total DBP by group revealed that the HAAs were the most dominant group by mass in both the raw and treated waters. For instance, the HAA9 concentration reduced from a raw water level of 1000 µg/L in the river and lake samples down to 162 µg/L and 227 µg/L respectively with the NF90 membranes. The largest reduction was observed for the upland source water where the HAA9 reduced from 1500 µg/L to 205 µg/L. Higher HAA-FP levels were observed after treatment with the NF270 membrane at 350 µg/L, 310 µg/L and 360 µg/L for the lowland lake, upland and lowland river respectively. The corresponding reductions were 85%, 86% and 77% for the NF90 membrane and 68%, 79% and 64% for the NF270 membrane. As the HAA precursors have high removal rates with each membrane across all waters, this led to the belief the HAAs are formed from hydrophobic and hydrophilic precursors.

The NF90 consistently removed more THM precursors than NF270. This was most apparent in the case of the upland water where the NF90 membrane reduced the raw water level of 760 µg/L to 28 µg/L compared to 88 µg/L using the NF270 membrane. These equate to reduction levels of 96% and 88% respectively illustrating that the NF membrane are particularly effective at removing THM precursors. The effectiveness of the NF90 towards THM-FP reduction has been reported previously when treating water from the Amadorio and Pedrera reservoirs from Alicante, Spain generating a reduction of 90% of BDCM-FP and DBCM-FP (Sentana *et al.*, 2010).

The emerging DBPs represented 15.6%, 13.8% and 16.3% of the total DBP-FP of the lowland lake, upland and lowland river respectively. The predominant groups were the HAL1 and the HNM1 with a smaller contribution from the HAN4. Average removals across all waters and membranes were 92%, 93% for the HAL1 and HNM1 respectively. The highest concentration of HAL1 was observed within the upland waters at 216 µg/L which was reduced to less than 4 µg/L and 17 µg/L by NF90 and NF 270 respectively. In contrast, a more mixed pattern was observed with HAN-FP which decreased in some cases but increased in others after treatment. This was most apparent with the case of the upland SP2 water treated with the NF270 membrane where the HAN-FP increased by 4 times compared to the raw water. Similar observations have been reported previously and has been associated to the residual hydrophilic fraction (Roccaro *et al.*, 2014). The chlorinated chemical group consists of 6 compounds with the concentration in the lowland waters changing from a raw water level of 7 µg/L to 24 µg/L in the lake and 10 µg/L in the river when using the NF270. Comparative performance with the NF90 was inconsistent with reductions ranging from 0 to 78% and an average across all waters of 35%.

Consideration of the mass concentration data in terms of HI adjusted the relative significance of the different DBPs. In relation to HI, the HAAs are even more dominant with the CS provided the majority of the remaining HI (Figure 4.1b, Figure 4.2b). Interestingly, there are four cases where the removal of organics resulted in an increase in HI most notably with the lowland water sources with the 2016 sample (SP1). The explanation relates to the speciation of the DBPs and specifically the levels of Br-HAA that form. To illustrate, in the lowland lake SP1, after the treatment with the NF270

membrane, the Br-HAA increased from 227 $\mu\text{g/L}$ to 300 $\mu\text{g/L}$, with no change to the bromine levels at 177 $\mu\text{g/L}$. In the case of the NF90, the HAA-FP decreased after treatment to 148 $\mu\text{g/L}$ but a switch in species was observed towards BCAA & BDCAA, with a concentration of 84 $\mu\text{g/L}$ (Figure 4.1a and Figure 4.2a).

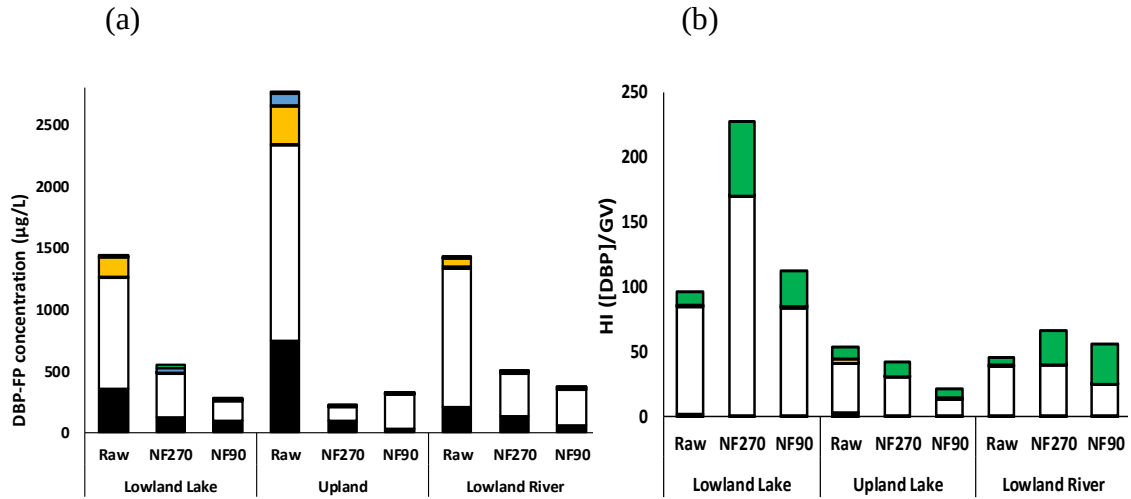


Figure 4.1: DBP categories of waters before and after nanofiltration in terms of concentration (a) and hazard index (b) from sampling point 1

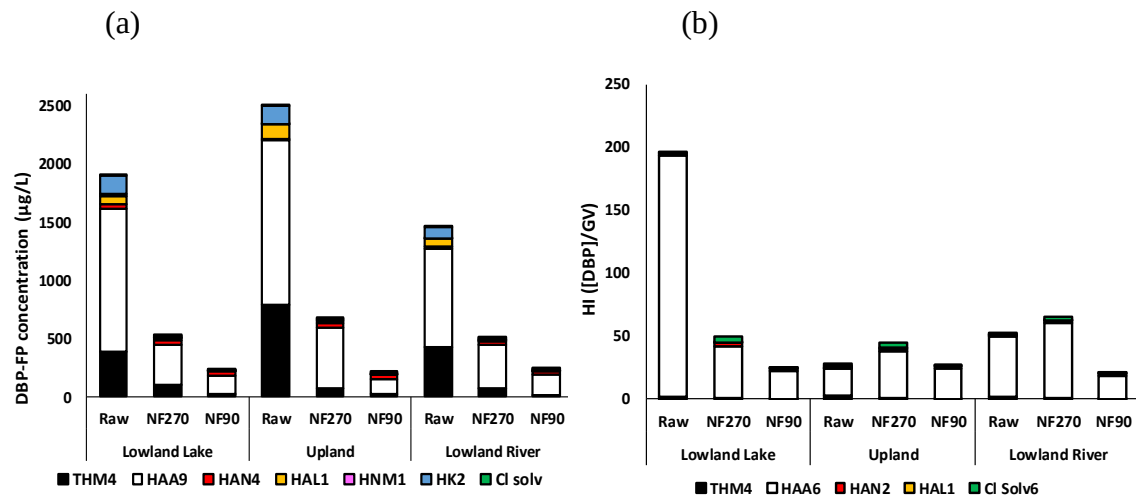


Figure 4.2: DBP categories of waters before and after nanofiltration in terms of concentration(a) and hazard index (b) from sampling point 2.

Importantly, THM contributed minimal amounts to the HI for both raw and treatment waters using either membrane. Accordingly, the use of THM as a surrogate of the whole, as regulation leans towards, appears unwise when considering HI. For instance, THM-FP was reduced to below 100 $\mu\text{g/L}$ with both membranes except the lowland lake, sampling

point 1, at 106 µg/L. However, this does not translate to a reduction in the hazard index as it is dominated mainly by the HAA group and to a lesser extent the chlorinated chemicals, HAN and HAL groups.

4.4.2 Speciation of THMs, HAAs and Chlorinated chemicals, their Concentration and Hazard Index

The dominant THM species in most cases was CF contributing 95% 99% and 94% of the total THM-FP for the lowland lake, upland and lowland river respectively (Figure 4.3a, Figure 4.4a). The upland waters generated the highest levels of chloroform with 760 µg/L in the raw waters which reduced to an average of 77 µg/L and 25 µg/L after treatment with NF270 and NF90 respectively across the two sampling periods. The residual THM levels represented 21% and 20% of the total THM-FP after treatment of the upland with NF270 and NF90 membranes, respectively. The equivalent contributions post treatment for the lowland river water were 45% and 46% of the total THM-FP. Bromine levels in the waters were significantly different with average concentrations of 109 µg/L for the river, 191 µg/L for the lake and 39 µg/L for the upland source water. The corresponding contribution made by Br-THM in the raw waters varied between 1% for the upland source to 7% for the lowland river source. Bromine was removed by 17% and 28% using NF270 and NF90 respectively, but removal of bromine varied depending on water type and season. The type of brominated compounds present can affect the speciation of the Br-DBPs formed, especially as this corresponded to a Br-DBP precursor removal of 90% using NF90 and 68% using NF270. The largest reduction is seen in the HAA group with a 51% reduction of BCAA and DBAA using both membranes. The Br-DBPs having the greatest impact on the HI are BCAA and BDCAA, the NF90 removes 66% of the BDCAA precursors compared to 41% using NF270. The Br-THMs have a low impact on the overall HI, with CF the dominant THM formed under excess of chlorine. NF treatment of the waters increased the relative levels of Br-THM, especially with the lowland source waters. For instance, in the river water, Br-THMs increased from 4 µg/L to 12 µg/L on average after NF270. However, a large difference was observed between the sampling periods with much greater levels of Br-THMs formed after treatment during SP1 where the Br-THM increased from 3.3 µg/L to 54 µg/L after NF270 and 11 µg/L after NF90. A more substantial shift towards Br-THMs was seen in the case of the lowland lake where

the levels increased from 11 µg/L to 27 µg/L and 14 µg/L with NF270 and NF90 respectively during sampling period 1.

The dominant HAAs in the raw waters were observed to be DCAA and TCAA representing a combined proportion of 74%, 95% and 8% in the lowland lake, upland and lowland river samples respectively (Figure 4.5a, Figure 4.6a). Both DCAA and TCAA were effectively reduced by NF treatment of the raw water with an average reduction of DCAA of 91% and 92% with the NF270 and NF90 respectively. Equivalent TCAA reductions were 85% and 91% across all waters. NF treatment shifted the distribution of HAAs towards the Br-HAA indicating a switch in formation pathway and enhanced incorporation of bromine congruent with the fact that NF is ineffective at removing bromide ions (Chellam, 2000). Across the trials, examples of increases in Br-HAA were seen with respect to BCAA and DBCAA and BDCAA, MBAA and DBAA without any consistency across the two sampling periods. The most important Br-HAAs are BCAA and BDCAA due to their very low GV and hence ability to have a large impact on the HI of the water even at relatively low mass concentrations. Increases of these two were observed in all waters including the upland source. To illustrate, the BCAA concentration increased from 1.4 µg/L to 22 µg/L using NF270 and from 1.4 µg/L to 15 µg/L with the NF90. However, the most notable changes were observed with the lowland lakes due to the very high bromine levels associated with the samples. In this case the BCAA concentration increased from 30 µg/L to 154 µg/L with the NF270 membrane.

As expected the HI was dominated by the BCAA and BDCAA, representing over 90% of the average HI. Comparison of the impact of the different membranes revealed that in all cases the NF90 membrane reduced both the total mass concentration of HAAs and the resultant HI. Whereas, the NF270 reduced the mass concentration but this resulted in either no change or even an increase in HI after treatment (Figure 4.3b, Figure 4.4b, Figure 4.5b, Figure 4.6b). For instance, the HI after treatment ranged from a low of 20.4 with the NF90 membrane treating the upland water from sampling period 1 to a maximum of 112 observed with the NF270 membrane treating the lowland lake during sampling period 1. THMs contributed only a minor amount to the overall HI with the levels never exceeding a value of 1.

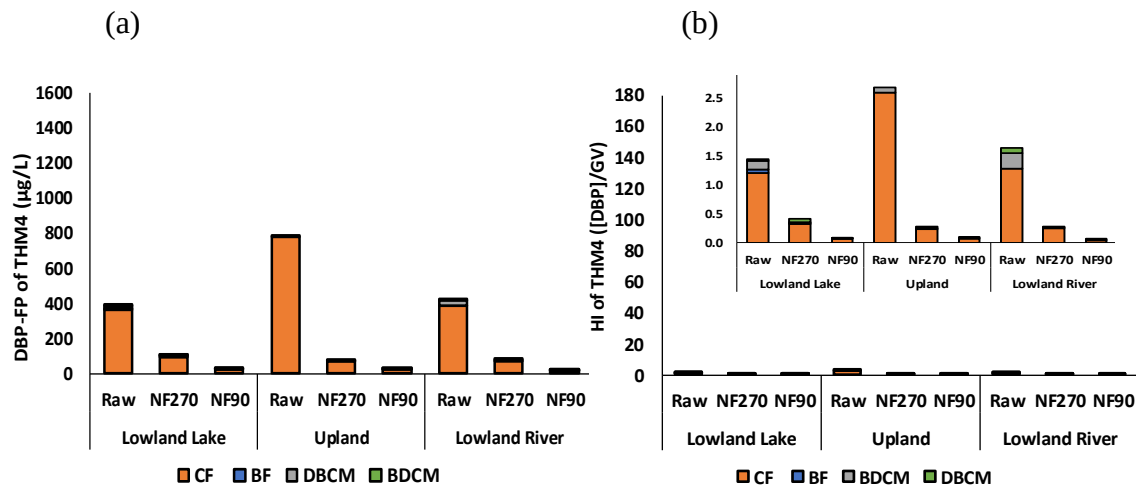


Figure 4.3: THM-FP after nanofiltration in terms of concentration (a) and hazard index (b) of 4 THMs from sampling point 1.

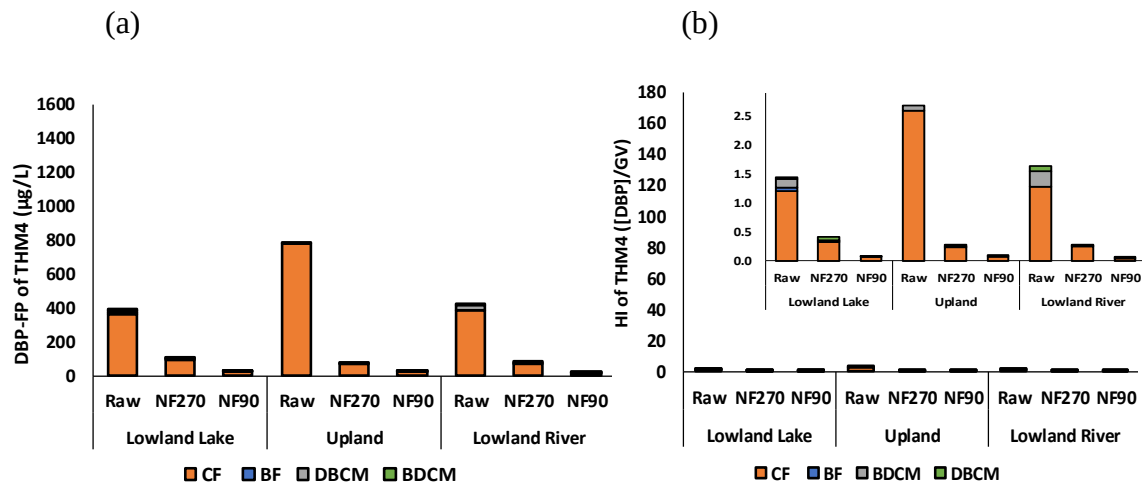


Figure 4.4: THM speciation of waters before and after nanofiltration in terms of concentration (a) and hazard index (b) from sampling point 2.

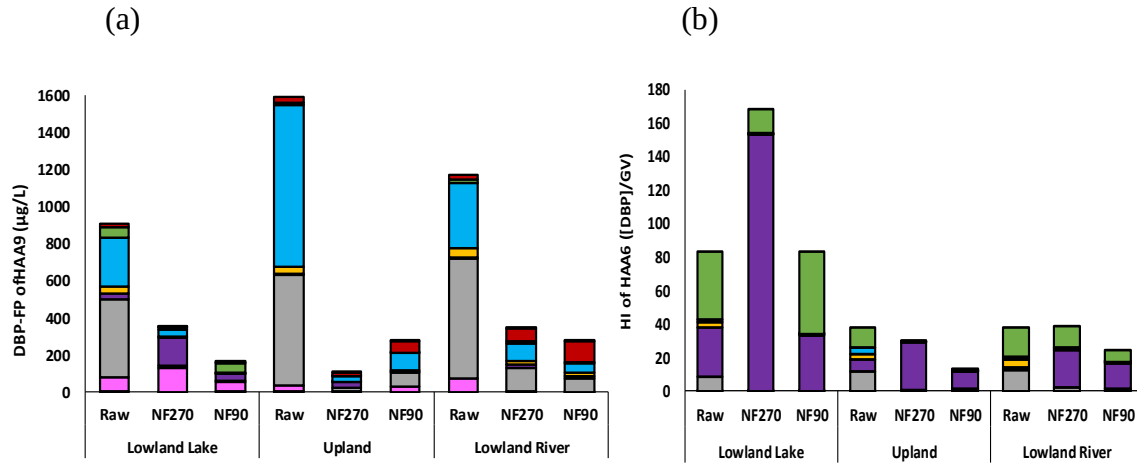


Figure 4.5: HAA-FP after nanofiltration in terms of concentration (HAA9) (a) and hazard index (b) of 6 HAAs from sampling point 1

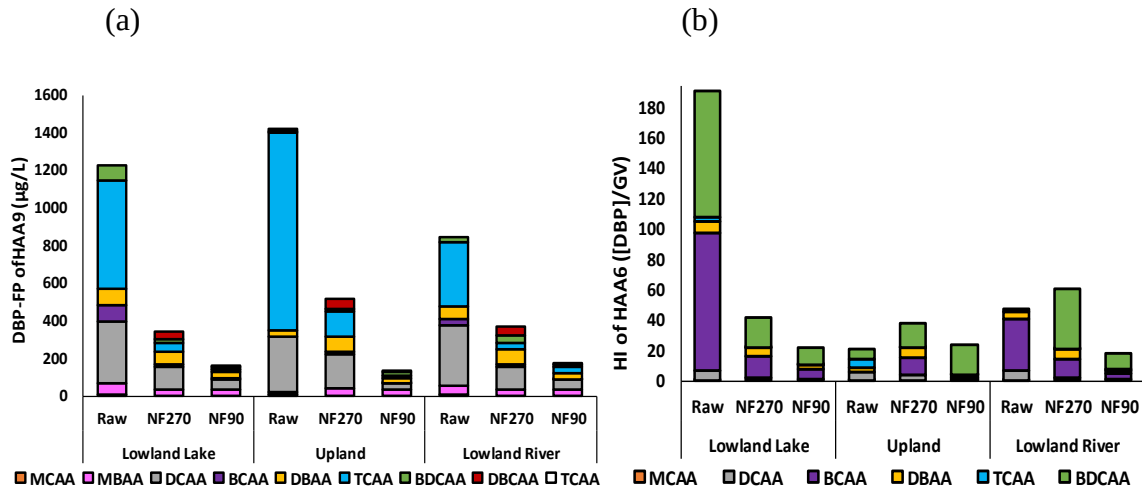


Figure 4.6: HAA-FP after nanofiltration in terms of concentration (HAA9) (a) and hazard index (b) of 6 HAAs from sampling point 2

The other major group to contribute to the overall HI are the CS. The total CS-FP for lowland lake, upland and lowland river source waters averaged 13 µg/L, 7 µg/L and 11 µg/L respectively across the two sampling periods (Figure 4.7a, Figure 4.8b). However, the total concentration and speciation of the CS changed across water sources, membranes and sampling periods indicating a high level of variability. In general, the NF 90 was more effective at reducing the total CS concentration than the NF270. To illustrate, in the case of the lowland lake sample (SP2) the total CS-FP increased from a raw water of 3 µg/L to 11 µg/L after treatment with the NF270 compared to a reduction to 1.3 µg/L after treatment with the NF90. Indeed, the use of the NF270 membrane did not greatly reduce

the CS-FP in any sample whereas a maximum reduction of 62% was observed for the NF90 with respect to the lake water source during sampling period 1, a concentration of 11 µg/L to 4 µg/L. The observed differences in concentration and speciation of the individual components after treatment indicates that some components were formed on chlorination as well as reduced (removed by the treatment). This suggests that the CS should be considered as DBPs not solely as industrial wastes.

Irrespective of their definition, the CS have low GV and so can impart a genuine contribution to the HI even at low concentrations (Figure 4.7b, Figure 4.8b). Conversion of the mass concentration data to HI reveals that the three most impactful CS are 1,2DE, DBCP, CT. The total HI associated with the CS was higher during sampling period 1 compared to sampling period 2. To illustrate, the maximum HI associated to the CS was 4.6 during sampling period 2 and 58 during sampling period 1. In fact, the minimum HI observed during sampling period 1 was higher than the maximum observed during the second sampling period. In most cases, 1,2DE contributed the largest proportion of the HI associated with the CS. The concentration was seen to increase after treatment with both membranes during sampling period 1 and with the NF270 membrane during sampling period 2.

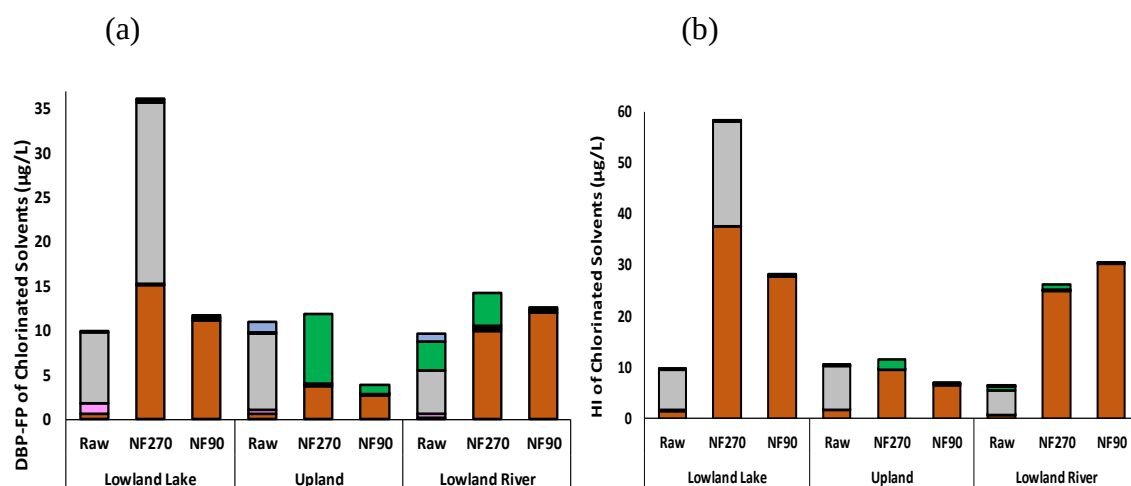


Figure 4.7 THM speciation of waters before and after nanofiltration in terms of concentration (a) and hazard index (b) from sampling point 1

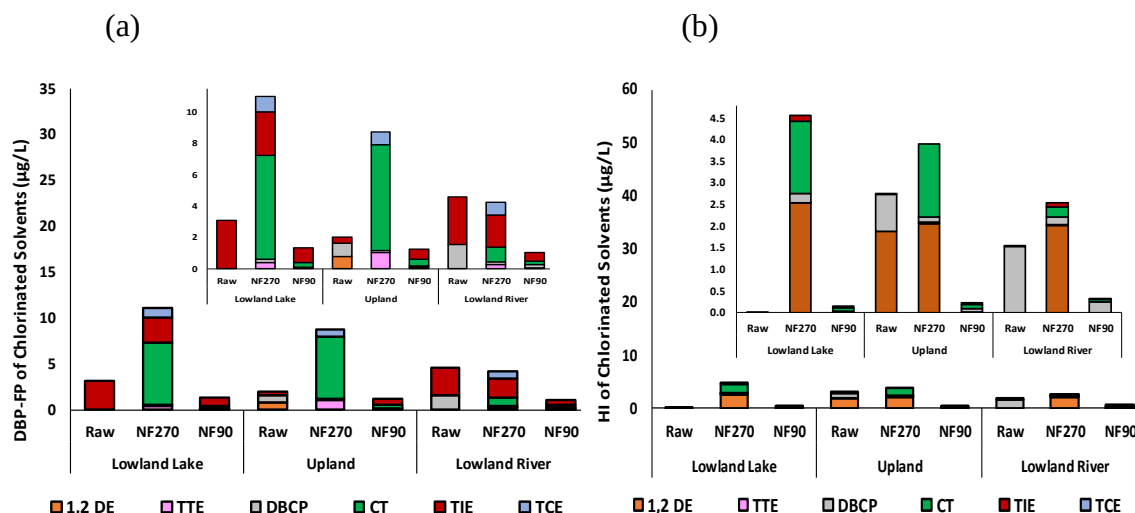


Figure 4.8: THM speciation of waters before and after nanofiltration in terms of concentration (a) and hazard index (b) from sampling point 2.

Comparison of the two membranes across all water sources and DBP groups indicates both membranes are effective at reducing chlorinated DBPs with levels of 83% for NF270 and 91% for NF90. In contrast, neither membrane was effective at reducing Br-DBPs. The NF90 membrane had no impact on the Br-DBP in the upland source water and a reduction of 48% and 32% with the lowland lake and river waters respectively. In contrast, the NF270 membrane had no effect or resulted in an increase in Br-DBP after treatment. Neither membrane is effective at rejecting bromide ions such that the ratio of [Br]:[DBP] precursor increases after treatment. This will drive the speciation towards Br-DBP, especially where the raw water already contains high levels of bromine such as the lowland water sources. It should be noted that the findings here are likely to be conservative towards the formation of Br-DBPs as they are based on formation potential tests which utilise a large excess of chlorine and this drives speciation away from Br-DBPs. Although, with poor removal of bromine, small increases of DCAA and BDCAA in the HAA group and 1,2 DE and CT in the chlorinated chemicals group had a high impact on the HI, increasing the HI at times after treatment. Further, the observations here will be reflected with other treatments that remove carbon but not bromine. Looking forward, more emphasis is required on managing not just the organic precursors but the associated halogen in the water.

4.5 Conclusions

Nanofiltration was observed to be effective at removing carbon from all source waters but was most effective against waters from upland catchment which are rich in larger MW, hydrophobic compounds. The impact of treating the water with either membrane was to effectively reduce THM-FP to levels that enable compliance against the current levels. However, the efficacy of the membranes is reduced when broadening the range of DBPs considered and assessing the risk through a hazard index rather than just mass concentration. In such cases, the relatively limited rejection of bromide ions drives a switch towards more brominated DBPs and in particular the Br-HAAs. These dominant the resultant HI and hence limit the impact of the membranes. Comparison of the two membranes revealed better performance across the whole assessment with the NF90 compared to the NF270. In fact, use of the NF270 membrane was shown to increase the HI of the water compared to that of the raw water in several cases due to the shift in DBP speciation. This indicates that hydrophobic surfaces are better suited to delivering a resilient minimisation of DBPs for both traditional and emerging groups.

4.6 References

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5 Minimisation of Disinfection by-products using Advanced Oxidation Processes UV/ H₂O₂

Minimisation of Disinfection by-products using Advanced Oxidation Processes UV/H₂O₂

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5.1 Abstract

The advanced oxidation process is a transformative process which generates a highly reactive hydroxyl radical ($\bullet\text{OH}$) to break down larger organic structures to smaller molecules. The use of H₂O₂/UV at various UV and H₂O₂ doses was explored according to their effect on traditional and emerging DBPs across 3 surface waters. At lower H₂O₂ doses across all waters increased the formation of DBPs, increasing the associated hazard index. High concentrations of H₂O₂ were needed to effectively reduce the DBP formation but was highly effective at reducing traditional as well as emerging DBPs, including the Br-DBPs and hence reducing the overall HI.

5.2 Introduction

Disinfection by-products (DBPs) are formed when natural organic matter (NOM) present in water reacts with the disinfectant used to kill harmful pathogens rendering water safe to drink. In the 1970s Rook discovered trihalomethanes (THMs) and inadvertently linked the formation of DBPs to their precursors after chlorination (Rook, 1974). Over 600 DBPs have been discovered to date and understanding their occurrence, control pathways and their associated risk has become a significant focus on recent research in this area

(Guzzella *et al.*, 2004; Plewa *et al.*, 2004, Plewa *et al.*, 2008; Wagner *et al.*, 2017; Richardson *et al.*, 2010). NOM is a highly complex mixture, its variable and unpredictable nature can make it difficult to predict the DBP formation and can have a significant effect on the quality of drinking water (Bond *et al.*, 2014; Serrano *et al.*, 2015; Williams, *et al.*, 1997). Because of this, the toxicity and exposure to DBPs can be difficult to predict (Plewa, *et al.*, 2017; WHO, 2017; Zhang *et al.*, 2017). To enable practical management of DBPs, the total THM concentration has traditionally been used as a surrogate of the whole, and a limit set at 100 µg/L in Europe to minimise the risk from all DBPs. This concept is being extended to include haloacetic acids (HAAs) with a limit of 60 µg/L as they form through a different pathway to THMs and when combined represent the majority of measured DBPs by mass within any sample (Chapter 2, Figure 2.1). However, the above approach is based on concentration rather than toxicity and when switched to incorporate toxicity, the other “emerging DBPs” become potentially more important as they have been shown to be more cytotoxic and genotoxic than their regulated counterparts (Guzzella *et al.*, 2004; Plewa *et al.*, 2017; Richardson *et al.*, 2017). Accordingly, the emerging DBPs may exert more impact on the overall toxicity of water than previously thought such that their management through water treatment needs consideration through a toxicity lens.

The type of NOM present in different source waters (upland source water, lowland rivers, lowland lakes) varies considerably with upland catchments containing organic molecules with very different characteristics than from lowland rivers. Traditional approaches to the minimisation of DBPs is through bulk carbon removal using technologies such as coagulation, ion exchange, adsorption and nanofiltration. Advanced oxidation processes (AOPs) are highly effective oxidation processes and tend to be used as an add on to conventional treatment, to target recalcitrant hazardous chemicals not removed efficiently through conventional treatment modifying their structure by transforming them into less toxic and easily biodegradable intermediates. These include trace organic micropollutants such as pesticides, pharmaceuticals, chemicals from personal care products and industrial wastes (Autin *et al.*, 2012; Khan *et al.*, 2018; Malato *et al.*, 2009; Nihemaiti *et al.*, 2018; Semitsoglou-Tsiapou *et al.*, 2016b). However, the AOP acts upon all organics and so it becomes important to understand the impact of AOPs on the DBP precursors and ultimately the resultant DBPs (Mayer *et al.*, 2015). Further, consideration is now being

given to AOPs as an alternative treatment for bulk DOC removal to reduce our reliance on coagulants (Jefferson *et al.*, 2016).

Removal with advanced oxidative processes is based on the generation of highly reactive hydroxyl radicals ($\bullet\text{OH}$) through the use of: hydrogen peroxide, photolysis, ozone or irradiation (Bond *et al.*, 2009; Glaze *et al.*, 1987; Goslan *et al.*, 2006). The main reactions of $\bullet\text{OH}$ with organic matter is thought to be through: (1) hydrogen abstraction from hydrocarbon chains (mainly in the form of amino or carboxylic acids) yielding H_2O and smaller carbon-centred reactive radicals, (2) electrophilic addition to double bonds or aromatic rings, and (3) electron transfer reactions, where $\bullet\text{OH}$ gains an electron from an organic substituent. The generated organic radicals can continue to react, extending a series of chain reactions (Legrini, *et al.*, 1993; Malato *et al.*, 2009; Matilainen *et al.*, 2010; Michael-Kordatou *et al.*, 2015). The hydroxyl radical can also react with inorganic ions naturally present in the waters causing effects in the presence of carbonate, chloride, sulphate and nitrate (Jefferson *et al.*, 2016; De Laat *et al.*, 2004; Semitsoglou-Tsiapou *et al.*, 2016a). For instance, alkalinity has been shown to inhibit UV/ TiO_2 AOP efficiency due to aggregation of particles, reducing the surface area available to react with the hydroxyl radical (Jefferson *et al.*, 2016). AOPs can also increase the formation of regulated compounds. To illustrate, at UV doses above 1500 mJ/cm^2 nitrite formation can be increased such that the concentration can exceed the EU regulatory limit of 0.1 mg/L (Semitsoglou-Tsiapou *et al.*, 2016a).

The use of hydrogen peroxide (H_2O_2) and UV radiation to produce hydroxyl radicals is one of the most well established UV-AOP system and currently the only one used in drinking water production in Europe (Khan *et al.*, 2018). The application of AOPs is expected to expand as treatment challenges become more difficult and the costs associated with delivering the required UV irradiance are decreasing due to improved efficiencies and longer lifespans of the UV lamps, most notably with respect to the development of UV-LED lighting (Khan *et al.*, 2018). Previous research into the impact of AOPs on DBP formation from surface waters found UV/ H_2O_2 was more effective than ozone based systems (O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$ $\text{H}_2\text{O}_2/\text{O}_3$) at reducing both THM-FP (77%) and HAA-FP (62%) (Lamsal *et al.*, 2011). Another study investigating AOPs on groundwater found THM-FP and HAA-FP were reduced by 43% and 68%, respectively during the

O₃/H₂O₂/UV process (Agbaba *et al.*, 2016). However, it is known that partial oxidation of organics can lead to increases in the resultant DBPs. For instance, trials with model compounds revealed dramatic increases in HAA-FP when the compounds were only partially degraded, especially evident in the case of amino acids (Bond *et al.*, 2009). The UV dose required to minimise this risk can be very high, 10,000 mJ/cm², significantly beyond levels commonly considered (Jefferson *et al.*, 2016). Existing commercial drinking water UV/H₂O₂ applications typically employ initial H₂O₂ concentrations less than 15 mg/L and UV doses of below 2000 mJ/cm² for the removal of micropollutants (WRC, 2018).

Table 5.1: List of studies using UV/H₂O₂ at pilot or full scale

Water source	H ₂ O ₂ dose (mg/L)	UV Fluence (mJ/cm ²)	References
Surface water	23	1140	(Lamsal <i>et al.</i> , 2011)
Effluent water	68-136	LP UV at 254 nm	(Audenaert <i>et al.</i> , 2013)
Surface water	0-1000	2600-26100	(Sindelar <i>et al.</i> , 2014)
Groundwater	10	600-3000	(Agbaba <i>et al.</i> , 2016)
Lowland water	5	650	(WRC, 2018)
Lowland water	20 – 40	1300-2600	(WRC, 2018)
Raw Surface water	10	200-1400	(Sarathy <i>et al.</i> , 2011)
Treated Surface water	10	200–500	(Metz <i>et al.</i> , 2011)

Previous research has focussed on traditional DBPs (THMs and HAAs) with a paucity of information available concerning emerging DBPs. Further, there is a limited dataset concerning the impacts of dose of both H₂O₂ and UV in terms of the resultant change in the DBP profile. The aim of the current study is to address these gaps through assessing the impact of dose on the resultant DBPs that form from three source water types: lowland lake, upland and lowland river. The work assesses both traditional and emerging DBPs and considers them through a hazard index perspective to understand the efficacy and risk of utilising AOPs for DBP minimisation.

5.3 Methods and Materials

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5.3.1 Analytical methods and Sampling

The standards, reagents and chemicals were purchased from Sigma Aldrich (Gillingham, UK) and Fisher UK (Loughborough, UK). 20 litres of raw water from 3 surface waters were collected in large polyethylene containers and stored in the fridge. The raw waters were sampled from the 3 sites in the winter of 2016 and 2017 the following summer. The sites covered the three main surface water source types: lowland lake, upland and lowland river.

UV/H₂O₂ experiments were all conducted in a Wedeco AG bench scale quasi-collimated beam apparatus (Herford, Germany) equipped with four 30W UVC low pressure lamps emitting monochromatic light at 254 nm. A volume of 500 mL of each raw water was placed in a large Petri dish at 25cm from the light source and stirred continuously and sampled for analysis and formation potential tests at 0, 5, 10, 15 and 20 minutes, equivalent to UV doses of 0, 2500, 5000, 7500 and 10000 mJ cm⁻². The experiments were repeated with doses of H₂O₂ of 1, 10, 20 and 40 mM.

Sodium hypochlorite was stored in the fridge and tested for chlorine each day of use with a Hach Ltd., (Manchester, UK) chlorine test kit. A formation potential test was performed where the samples were chlorinated 5 times the TOC concentration and left for 7 days to ensure chlorine had reacted with all the DBP precursors present. The DBPs were analysed using EPA Method 551.1 for THM4, HAN4, HK2, HNM, HA and chlorinated chemicals, CS6 where they were extracted with MTBE. HAA9 was analysed according to EPA method 552.3 where they were extracted under acidic conditions and derivitised. All DBPs were analysed using to an Agilent HP 6890 Series GC System with electron capture detector. The method was modified to analyse all 27 DBPs using the column DB-1 and quantified using OpenLab software. Samples above the calibration range were diluted with MTBE and re-run.

Total organic carbon (TOC), Non purgeable organic carbon (NPOC) and Total Nitrogen (TN) was performed using Shimadzu TOC-V VWP. The ions bromide, Nitrite, Nitrate and Chloride, were determined using Thermo-Scientific ICS-1600 according to EPA method 300.1. Inductively coupled plasma- mass spectroscopy (ICP-MS) was used to measure bromine and iodine with a Perkin Elmer Elan 9000 (Beaconsfield, UK). instrument. All occurrence samples were taken, extracted and derivatised where necessary in duplicate, and measured in triplicate on each instrument. Bromofluorobenzene was added to each sample for the analysis of method EPA Method 551.1 to the extraction solvent as the internal standard. 1,2,3 trichloropropane was used as an internal standard in the extraction solvent to account for any volumetric and injection differences. 2-bromobutanoic acid was as a surrogate, meaning it was derivatised during the methylation step in EPA method 552.3. 8. A set of calibration standards of 0-200 µg/L were diluted for a standard mix and extracted to run with the samples. A low calibration point within a factor of 2 of the MRL was run with each calibration. Dichloroacetate was used as the internal standard in each calibration and sample according to EPA method 300.1 with a calibration of 0-5 mg/L. The sample was diluted with ultrapure water if outside the calibration range. Quality assurance checks were performed where a calibration point was run after 8-10 samples within each sample batch and again at the end for each instrument used. The limit of quantification (LOQ) for the DBPs measured on the GC-ECD was 0.5µg/L for all except MCAA with a LOQ of 2ug/L. The IC had a LOD of 50 µg/L for chloride and 0.25 mg/Lfor remaining ions measured. The shimadzu TOC-V VWP measuring TOC, NPOC and TN had a LOD of 0.5 µg/L, with automatic dilution where necessary. The ICP-MS measuring bromine had a LOD of 0.2 µg/L.

5.3.2 Toxicity Calculations

WHO guideline values (GV) are based *in vivo* studies and used here to calculate a ratio of the hazard index (HI) of each individual DBPs with a GV (WHO 2004, 2011). However, the use of GV's restrict the inclusion of emerging DBPs (with no GV) as they have a limited DBP set to 19 DBPs. These include: THM4, HAA6, HAN2, HAL1 and 6 chlorinated chemicals (CS). THM4 consists of Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform. HAA6 consists of Monochloroacetic acid, Dichloroacetic acid, Bromochloroacetic acid, Dibromoacetic acid, Trichloroacetic acid

and Bromodichloroacetic acid. HAN2 is Dichloroacetonitrile and Dibromoacetonitrile and HAL1 is chloral hydrate. The CS6 are 1,2 dibromoethane, tetrachloroethylene, dibromochloropropane, carbon tetrachloride, 111 trichloroethane and trichloroethylene. The individual DBP concentration divided by the corresponding GV value gives a hazard index ratio, above 1 is deemed hazardous.

5.4 Results and Discussion

5.4.1 UV/H₂O₂ optimal and sub Optimal Conditions

The NPOC levels for the raw lowland lake, upland and lowland river waters were 5.21 mg/L, 16.09 mg/L and 5.38 mg/L for SP1 and 6.25 mg/L, 15.64 mg/L and 4.07 mg/L for SP2 (Table 5.2). Averaged across all waters and UV doses, mineralisation degree of 34%, 24%, 23% and 15% were observed for H₂O₂ doses of 2 mM, 10 mM, 20 mM and 40 mM respectively indicating that the organics were transformed into organic breakdown products rather than mineralised and released as carbon dioxide (Mayer *et al.*, 2015; Sillanpää *et al.*, 2018). The maximum amount of mineralisation was observed in the upland source water at a H₂O₂ dose of 47% degree of mineralisation. The largest relative change was observed for the lowland lake source water SP2 which decreased from 6.25 mg/L to 3.1 mg/L with 20 mM H₂O₂. However, variability was observed with the impact of H₂O₂ dose where the organic levels fluctuated, offering no clear picture of a dose response profile reflecting the challenge associated with using AOPs to treat DOC rich waters. For instance, a previous trial with a lowland river water source post GAC, had a DOC of 3.5 mg/L and generated a 32% reduction at a UV dose of 10,000 mJ/cm² and a H₂O₂ dose of 8 mM (Jefferson *et al.*, 2016). In fact even a dose of 40,000 mJ/cm² only enabled a reduction of approximately 60% indicating a recalcitrant fraction that was not amenable to oxidation by •OH. The lowland lake source water had the highest and most inconsistent total bromine with levels in SP1 of 77.2 µg/L and SP2 of 198 µg/L. Equivalent data for the lowland river source water was 107 µg/L and 106 µg/L and the upland was 39.7 µg/L and 39.1 µg/L for SP1 and SP2 respectively. The bromine levels are largely unchanged throughout treatment. Overall, the AOP appeared to change the

water characteristics but maintained a high NPOC residual such that a large quantity and distribution of DBPs was expected.

Table 5.2: NPOC, UV at 254nm and SUVA for each water type with 0-40mM H₂O₂ and a UV dose of 10000mJ cm⁻²

	H ₂ O ₂ (mM)	Lake		Upland		river	
		SP1	SP2	SP1	SP2	SP1	SP2
NPOC (mg/L)	0	5.2	6.2	16.1	15.6	5.4	4.1
	2	3.7	4.0	8.5	11.6	4.2	2.4
	10	4.0	3.8	12.1	12.8	4.9	2.9
	20	4.2	3.1	13.6	13.7	4.9	2.8
	40	4.5	3.9	14.4	12.7	6.1	3.3
Br- (µg/L)	0	184.5	198.0	39.5	39.1	116.5	101.0
	2	173.6	199.4	40.5	39.9	117.4	104.3
	10	172.6	204.2	38.9	43.1	117.5	99.7
	20	169.4	176.8	37.6	39.6	119.2	98.4
	40	169.7	186.6	37.5	38.7	114.3	104.1

5.4.2 Overall Disinfection by-product concentration and associated hazard index

The sum of the 27 DBPs measured varied in the source water between the two sampling periods with an increase observed for the lake and river samples and a decrease seen for the upland source water (Figure 5.1a, b). The average DBP-FP across the two sampling periods was 1677 µg/L, 2635 µg/L and 1566 µg/L for the lowland lake, upland and lowland river respectively. These corresponded to average reactivities of 292.7 µg/mg, 166.1 µg/mg and 331.4 µg/mg indicating that the most reactive precursors resided in the upland water. The application of the AOP decreased the total DBP in most cases and this was especially evident at higher H₂O₂ doses with fluences appearing to have less impact over the range tested. Whilst there was a general decrease in DBP, in several cases the concentration increased due to the application of the AOP at low doses of H₂O₂ and occurred across the three water types. To illustrate, in the case of the lowland lake sample from SP1, the total DBP increased from an initial level of 1447 µg/L up to 1972 µg/L at 5000 mJ/cm² but then decreased when exposed to higher UV doses of 7500 mJ/cm² down to 1225 µg/L. The largest increased was observed in the case of the lowland river sample

from SP1 which increased by 99.7% from 1371 $\mu\text{g/L}$ to 2738 $\mu\text{g/L}$ when a 2 mM H_2O_2 dose was irradiated with a UV dose of 2500 mJ/cm^2 .

Comparison across the water sources revealed that the total DBP was least impacted at low H_2O_2 doses in the case of the river water. For instance, at 10000 mJ/cm^2 and 2mM H_2O_2 , the average decrease in total DBPs in the lowland lake and upland source waters was 63% and 77%, compared to an increase in the lowland river source water of 4%. Increasing the dose to 10 mM H_2O_2 had only minor impacts resulting in average decreases in DBPs of 67%, 63% and 5% for the lowland lake, upland and lowland river source waters respectively. In contrast, at H_2O_2 doses of 20 mM and 40 mM much greater reduction in the total DBP was observed even at the lowest UV doses applied of 2500 mJ/cm^2 (Figure 1). To illustrate, at a 40 mM H_2O_2 dose the average total DBP levels in the lowland lake, upland and lowland river after exposure to a UV dose of 2500 mJ/cm^2 were 145 $\mu\text{g/L}$, 57 $\mu\text{g/L}$ and 57 $\mu\text{g/L}$, a decrease of 91%, 97% and 96% respectively. Whilst in most cases the total DBP was reduced to below 40 $\mu\text{g/L}$ in a few cases more elevated levels were observed and this was particularly evident for the lowland lake source waters indicating that even under high doses of H_2O_2 and irradiance, different precursor characters will exist that exhibit a range of reactivities with chlorine.

The impact of different UV doses was observed to be relatively minor at high H_2O_2 doses. To illustrate, the average total DBP levels in the lowland lake, upland and lowland river were 265 $\mu\text{g/L}$, 75 $\mu\text{g/L}$ and 18 $\mu\text{g/L}$ at 7500 mJ/cm^2 and 136 $\mu\text{g/L}$, 103 $\mu\text{g/L}$ and 104 $\mu\text{g/L}$ at 10000 mJ/cm^2 . Accordingly, a change in UV dose from 2500 mJ/cm^2 to 10000 mJ/cm^2 decreased the total DBP by 9 $\mu\text{g/L}$ for the lowland lake source water, an increase of 46 $\mu\text{g/L}$ for the upland source waters and an increase of 47 $\mu\text{g/L}$ for the lowland lake source water. Comparison to low H_2O_2 doses (2-10 mM) reveals a more distributed picture where increasing UV dose can either decrease or increase the total DBP concentration. To illustrate, in the case of the lowland lake SP2 sample treated with 10 mM H_2O_2 , the total DBP decreased from 1906 $\mu\text{g/L}$ to 1550 $\mu\text{g/L}$, 990 $\mu\text{g/L}$, 824 $\mu\text{g/L}$ and 80 $\mu\text{g/L}$ at UV doses of 2500, 5000, 7500 and 10,000 mJ/cm^2 respectively (Figure 5.1a). Whereas, in the case of the lowland river water source sampled in SP1, the total DBP changed from 1371 $\mu\text{g/L}$ at 0 mJ/cm^2 to 1127 $\mu\text{g/L}$, 1986 $\mu\text{g/L}$, 1875 $\mu\text{g/L}$ and 1297 $\mu\text{g/L}$ at UV doses of 2500, 5000, 7500 and 10,000 mJ/cm^2 respectively. The

implication is that elevated UV doses are unnecessary when high H₂O₂ doses are applied and can cause both decrease and increase when used in conjunction with lower H₂O₂ doses. Overall, the only way to reduce total DBP is to apply sufficient H₂O₂ to ensure the required level of change.

When the mass concentration data was converted into a hazard index a different picture was observed with significantly less variation seen in terms of the upland sources compared to the variation in mass concentration. The relative HI of the three source waters were 41.7, 156 and 346 for the upland sources, lowland river sources and lowland lake sources respectively. The observed differences reflect the higher levels of bromine in the lowland river and lowland lake sources which form brominated DBPs and in particular, the formation of brominated HAAs, which due to their very low GV can have a major impact on the HI. Variation in HI was observed in relation to UV and H₂O₂ doses, with an increased HI observed even at elevated H₂O₂ doses for the lowland river source water in SP1 (Figure 5.1b). The variation was more pronounced when using lower H₂O₂ doses. For instance, at 10 mM and 5000 mJ/cm², the HI of the upland and lowland river source waters increased by 36% and 130% respectively and then decreased by 53% and 30% at a UV dose of 7500 mJ/cm² to 19.7 and 109, respectively. In comparison at 20 mM and a UV dose of 10000 mJ/cm², the reductions in the lowland lake, upland and lowland river were 96% (UV dose of 7500 mJ/cm²) and 93% (UV dose of 10000 mJ/cm²) with and with an increased H₂O₂ dose of 40 mM the reductions were similar at 94% (UV dose of 7500 mJ/cm²) and 93% (UV dose of 10000 J/cm²), respectively.

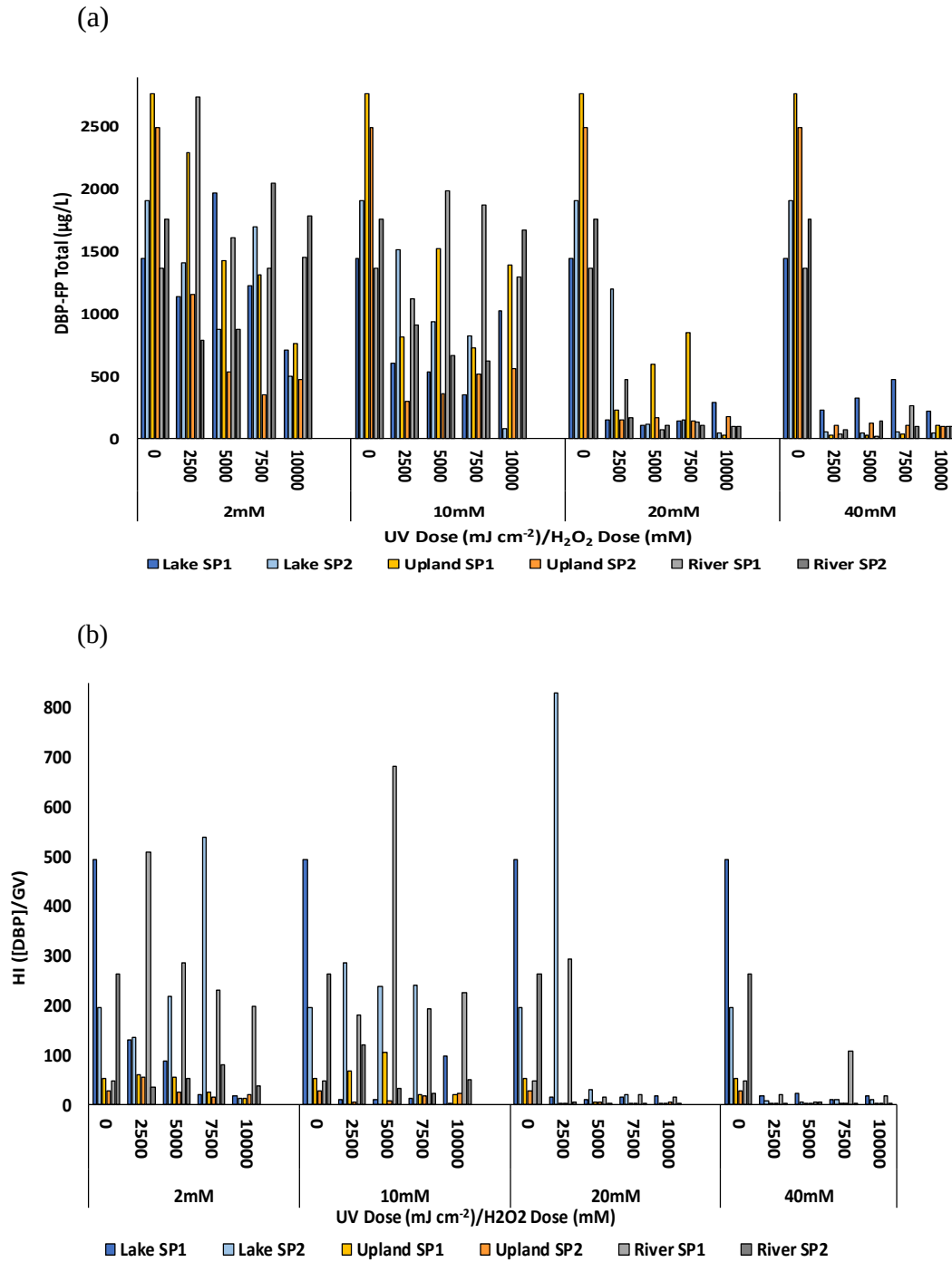


Figure 5.1: The concentration of 27 DBP-FP(a) and the corresponding HI(b) of SP1 and SP2 lake, upland and river surface water at 2 sampling points, after treatment with UV/ H_2O_2 , with 2mM, 10mM, 20mM and 40mM H_2O_2 doses at 0, 2500, 500, 7500 and 10000 mJ cm^{-2} UV dose.

5.5 Speciation of DBPs and associated HI for the Lowland Lake water

Speciation of THMs, HAAs, HANs, HAL, HNM, HKs and CS with different doses of UV/H₂O₂ doses for the lowland lake source water revealed differences between the two sampling periods. The fluctuations in total DBP was not consistent across DBP categories but showed major variation in the two main groups by mass, the THMs and HAAs (Figure 5.2). To illustrate, in the case of the water sampled in SP1 and treated with a 2 mM dose of H₂O₂ and a UV dose of 2500 mJ/cm², the total DBP reduced from 1450 µg/L to 1145 µg/L. This decrease was mainly accounted for by a reduction in HAAs which decreased from 910 µg/L (63% of the total) down to 78 µg/L. In contrast increases in mass concentration of 105%, 436%, 190%, 427% and 2000% were observed for the categories THMs, HANs, HNM, HK and CS respectively. The HAAs are then increased to 786 µg/L with a UV dose of 5000 mJ/cm² and decreased to 68 µg/L and 154 with 7500 mJ/cm² and 10000 mJ/cm². At the same dose, THM4 concentrations increased from 353 µg/L to 723 µg/L, 359 µg/L, 918 µg/L and 898 µg/L at UV doses of 2500 mJ/cm², 5000 mJ/cm², 7000 mJ/cm² and 10000 mJ/cm² respectively. The changes in THM were not reflected in any other group and this applied across the range of doses tested, for both source water sampling periods. This is important as THM4 are regulated in the UK and used as a surrogate for the total DBP concentration. The current data indicates that THM are not an effective surrogate for monitoring changes due to AOPs. However, elevated doses of H₂O₂ reduced the total THM to below 100 µg/L with an 87-99% reduction across the UV doses tested. Speciation of the THMs revealed chloroform to represent the largest fraction although relatively high levels of brominated THMs were formed congruent with the lake waters containing the highest bromine concentration at 185 µg/L. At high UV doses there is an interesting pattern related to the brominated THMs. At a 2mM H₂O₂ dose, bromoform, bromodichloromethane and dibromochloromethane were increased by 25%, 10% and 7% although the changes were much lower than observed for chloroform. Increasing the H₂O₂ dose to 10mM, all THMs are reduced but the proportional change is observed more significantly with chloroform. At elevated H₂O₂ doses this impact was no longer observed. For instance, when treating the water sampled in SP1 at a H₂O₂ dose of

20 mM and a UV dose of 10000 mJ/cm², CF, BF, BDCM and DBCM are reduced from 355 µg/L to 39 µg/L, 4 µg/L to 0.1 µg/L, 11 µg/L to 0.5 µg/L and 2 to 0.6 µg/L and at 40 mM are reduced to 3µg/L, < LOD, < LOD and 0.6 µg/L respectively.

The predominate DBP group formed from the lowland lake source water were HAAs with a concentration of 910.3 µg/L and 1227.6 µg/L in the samples from SP1 and SP2 respectively, representing 63% and 64% of the total. The impact of the AOP on HAAs was observed to differ significantly across the two sampling years (Figure 5.2 (a) & (b)). In SP1, the AOP effectively reduced HAAs although at high H₂O₂ doses the relative proportion of HAA increased in relation to the total, reflecting the decrease in THMs. The same effect was observed at high UV doses even at lower H₂O₂ doses. In contrast, the impact of the AOP on the water sampled in SP2 showed a different pattern whereby they remained high unless high H₂O₂ (40 mM) or UV (10000 mJ/cm²) doses were applied. To illustrate, at a H₂O₂ dose of 20 mM, the observed HAA concentrations were 1228 µg/L, 1147 µg/L, 65 µg/L, 79 µg/L and <LOD for UV doses of 0, 2500, 5000, 7500 and 10,000 mJ/cm² respectively. In contrast, at a H₂O₂ dose of 40 mM the same UV doses resulted in HAA concentrations of 1228µg/L, 33 µg/L, 27 µg/L, 38 µg/L and 45 µg/L, respectively. The non-brominated HAAs dominated the group congruent with the use of a formation potential test where an excess of chlorine is used and hence alters the ratio of chlorine to bromine (Bond *et al.*, 2012; Symons *et al.*, 1993). Accordingly, FP tests are expected to provide an underestimate of the contribution made by brominated species as can be seen in chapter 3. Speciation of the HAA revealed that the brominated species represented 53% of the total HAAs before treatment. Application of the AOP, decreased the Br-HAA most evidently with H₂O₂ dose. For instance, at a dose of 2 mM H₂O₂, the percentage of the HAA associated to brominated species in the SP1 sample was 88%, 15%, 12%, 14% and 7% at UV doses of 0, 2500, 5000, 7500 and 10,000 mJ/cm² respectively. In comparison at a H₂O₂ dose of 20 mM, the relative contribution of the brominated HAAs in the SP1 and SP2 samples were 88%, 1.1%, 0.6%, 1.2% and 0.9% in SP1.

The emerging DBPs combined represented a small percentage of the total DBP in the raw waters across both sampling periods reaching a maximum of 15.6% in the case of the upland water during sampling period 1, closely followed by Lake raw water, SP2 with

15.2%. The most important groups observed within the emerging DBPs where the HAN, HAL and HK in the raw waters with the addition of the CS in the treated waters Figure 5.2a, b). Both the HAL and HK decreased with the application of the AOP with near complete reduction at H₂O₂ doses of 20 and 40 mM. At lower doses, the AOP was more effective at reducing the HAL compared to the HK as 67-86% compared to 27-62%.

In contrast, the application of the AOP resulted in an increase in total HAN concentration from a raw water average level of 21 µg/L to a max of 52 µg/L with 2 mM H₂O₂, and 35 µg/L with 10 mM at a UV dose of 7500 mJ/cm² and 2500 mJ/cm². At elevated H₂O₂ doses of 40 mM, the HAN-FP is reduced to less than 0.1 µg/L with the exception of DCAN which reduced to 1.1 µg/L. Similarly, the CS were increased throughout the treatment apart from at a dose of 40 mM with sampling period 2 where the levels were reduced to below the LOD. To illustrate, CT was increased from 0.2 µg/L to 123 µg/L, 38 µg/L and 45 µg/L with 10 mM, 20 mM and 40 mM H₂O₂ dose and UV dose of 10000 mJ/cm² for sampling period 1.

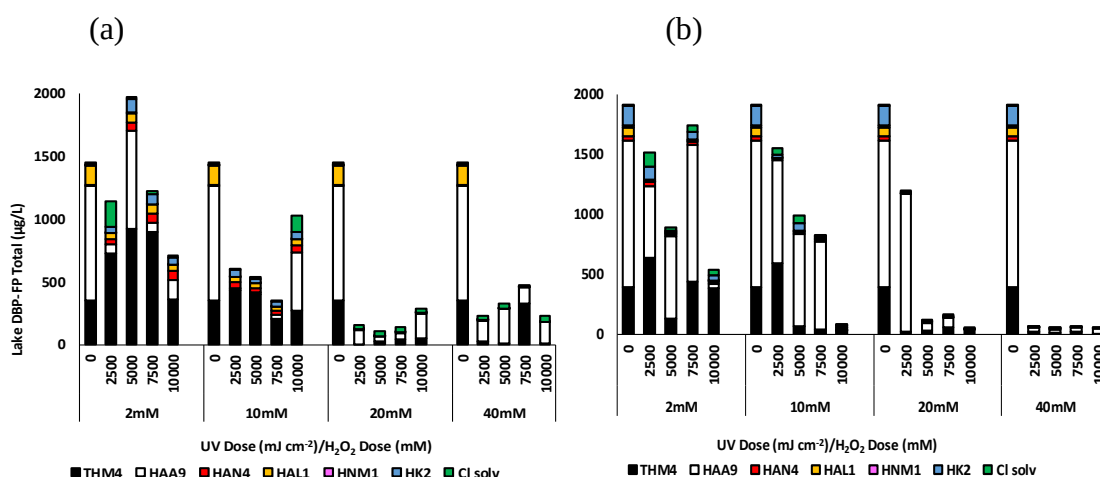


Figure 5.2: The concentration of 27 DBP-FP of SP1 (a) and SP2, (b) lake surface water after treatment with UV/H₂O₂, with 2mM, 10mM, 20mM and 40mM H₂O₂ doses at 0, 2500, 500, 7500 and 10000mJ cm⁻² UV dose, with DBP speciation.

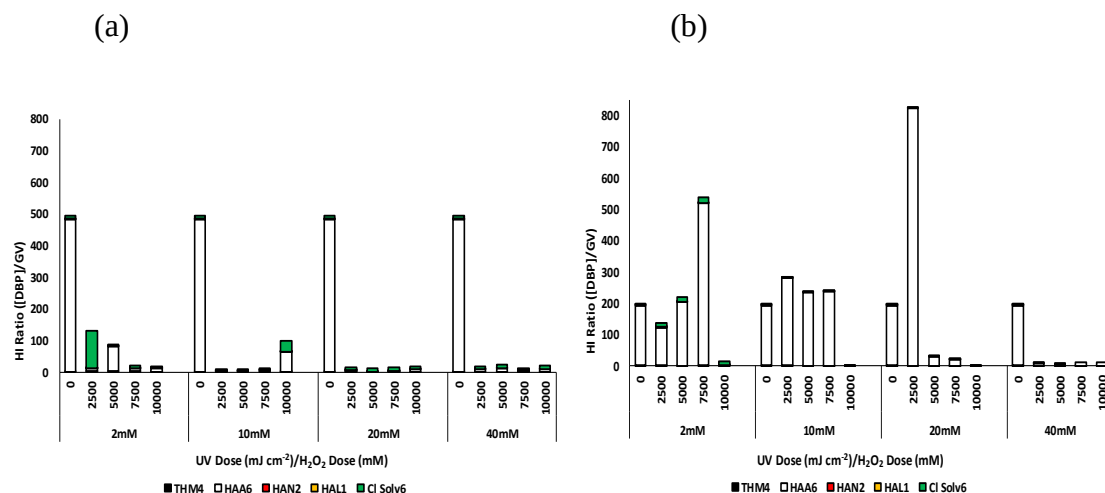


Figure 5.3: The HI of 13 DBPs with GV in SP1 (a) and SP2 (b), lake surface water after treatment with UV/H₂O₂, with 2mM, 10mM, 20mM and 40mM H₂O₂ doses at 0, 2500, 500, 7500 and 10000mJ cm⁻² UV dose, with DBP speciation.

The complexity of the picture in relation to concentration is simplified when considered in terms of HI (Figure 5.3a, b). It is important to note that an increase in concentration does not necessarily translate to an increase in the hazard index of a sample due to the differences in the toxicity of the individual species. To illustrate in the case of the SP1 at 2 mM, where the concentration of DBPs is increased after treatment, the HI has decreased by 96% at a H₂O₂ dose of 2mM and a UV dose of 10000 mJ/cm². Whereas, in SP2, the concentration is decreased after treatment, but the HI dramatically increased as observed in the cases of H₂O₂/UV doses of 2 mM/7500 mJ/cm² and 20mM/ mJ/cm². The HAAs most impacting the HI was BCAA and BDCAA contributing up to 99% of the HI at low UV/H₂O₂ doses. This compares to a maximum contribution from the other groups of 8%, 4.8%, 1.7%, and 51% for the THMs, HAN, HAL and CS respectively.

5.6 Speciation of DBPs and associated HI for the upland water

The upland source water had the highest levels of DBP-FP at 2772 µg/L and 2500 µg/L in SP1 and SP2 (Figure 5.4a, b). As the UV dose is increased the DBPs are reduced in SP1 at 2 mM and 10 mM H₂O₂ to 766 µg/L and 1403 µg/L and in SP2 to 473 µg/L and 566 µg/L. Larger reduction in DBPs are achieved through increasing H₂O₂ dose with

reduction to 31 µg/L and 109 µg/L in SP1 and 75 µg/L and 97 µg/L at doses of 20 and 40 mM H₂O₂ and a UV dose of 10000 mJ/cm². The upland water generated the highest DBP-FP and although reductions are high compared to other waters, the DBP-FP remains high and fluctuates especially at lower H₂O₂ doses.

The THM-FP in the raw waters for SP1 and SP2 are similar with concentrations of 742 µg/L and 789 µg/L, respectively. In SP1 at a UV dose of 10000 mJ/cm², the THM-FP reduced to 405 µg/L, 540 µg/L, 14 µg/L and 11 µg/L for H₂O₂ doses of 2, 10, 20 and 40 mM respectively. A greater reduction was observed in SP2 where for the same conditions the residual THM-FP was 53 µg/L, 92 µg/L, <LOD and 9.5 µg/L, respectively, indicating the importance of understanding seasonal variation in water characteristics. Within the THM category, CF contributed between 98-99% of the THM total. At a UV dose of 10000 mJ/cm², CF is reduced in SP1 from 742 µg/L to 400 µg/L, 530 µg/L, 13.7 µg/L and 11.2 µg/L and in SP2 from 778 µg/L to 52 µg/L, 90 µg/L, <LOD µg/L and 9 µg/L with H₂O₂ doses of 0, 2 mM, 10 mM, 20 mM and 40 mM, respectively.

HAA-FP in the raw waters for SP1 and SP2 are similar as with the THMs but with lower concentrations of 1592 µg/L and 1420 µg/L, respectively as can be seen in (Figure 5.4a, b). The HAA-FP concentration is mainly characterised by large concentrations of the chlorinated HAAs, DCAA and TCAA, which are reduced consistently to below 100 µg/L at 20 mM and 40 mM H₂O₂ dose. The HAA-FP decreased by 88%, 74%, 98% and 94% as a function of increased H₂O₂ dose and a high UV dose of 10000 mJ/cm². Comparison to SP2 showed poorer removal with levels at the equivalent dose of 73%, 71%, 88% and 94% respectively. Interestingly, this is the opposite pattern to the THMs where SP2 should show the greater reductions and is congruent with the two groups of DBPs being formed through different precursors/pathways. Variation was observed within the individual HAA species where the levels increased and decreased as a function of dose across the two sampling periods. For instance, MCAA concentration fluctuated throughout treatment as illustrated for SP2, where the levels increased from 6.8 µg/L to 96 µg/L, <LOD, 93 µg/L and 34 µg/L with H₂O₂ doses of 2 mM, 10 mM, 20 mM and 40 mM at 10000 mJ cm⁻² UV dose. A similar trend as seen in the other waters. The level of bromine in the water was low at between 4-35 µg/L and as such low levels of Br-HAAs formed.

The application of the AOP reduced the levels that formed to below 8 µg/L for MCAA, 3-4 µg/L for DBCAA and TBAA and less than 1 µg/L for the others.

The raw waters contained a total emerging DBP concentration of 433 µg/L and 290 µg/L for SP1 and SP2 respectively which represented between 16% and 11% of the total. The two most prominent species groups were the HAL and HKs. This remained the same after treatment in SP1, but HANs become more prominent after treatment in SP2. HNM1, HAL1 and HK2 are reduced considerably by 43-84% at 2 mM and 99.9% at higher doses. The chlorinated chemicals are low, with a total of 7 µg/L in the upland raw water, with 5 µg/L DBCP and others below 1 µg/L. Application of the AOP increased the TCE concentration to a maximum of 8 µg/L. At high doses all other CS were reduced by 99%. In contrast, the concentration of DBPs within the HAN group were observed to fluctuate with both increases and decreases compared to the raw water levels. The most apparent increases were seen for SP2 and moderate H₂O₂ doses.

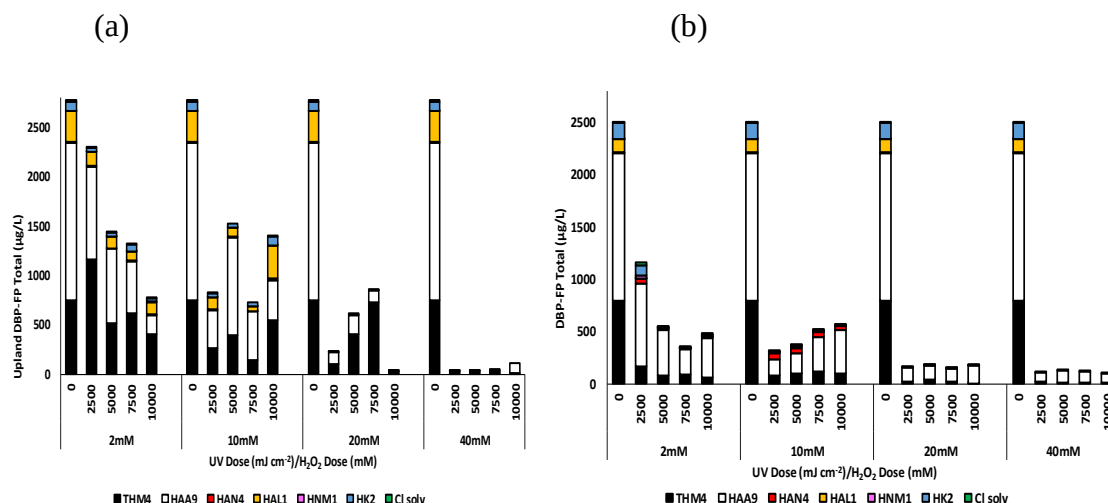


Figure 5.4:The concentration of 27 DBP-FP SP1 (a) and SP2 (b) of upland surface water after treatment with UV/H₂O₂, with 2mM, 10mM, 20mM and 40mM H₂O₂ doses at 0, 2500, 500, 7500 and 10000mJ cm⁻² UV dose, with DBP speciation.

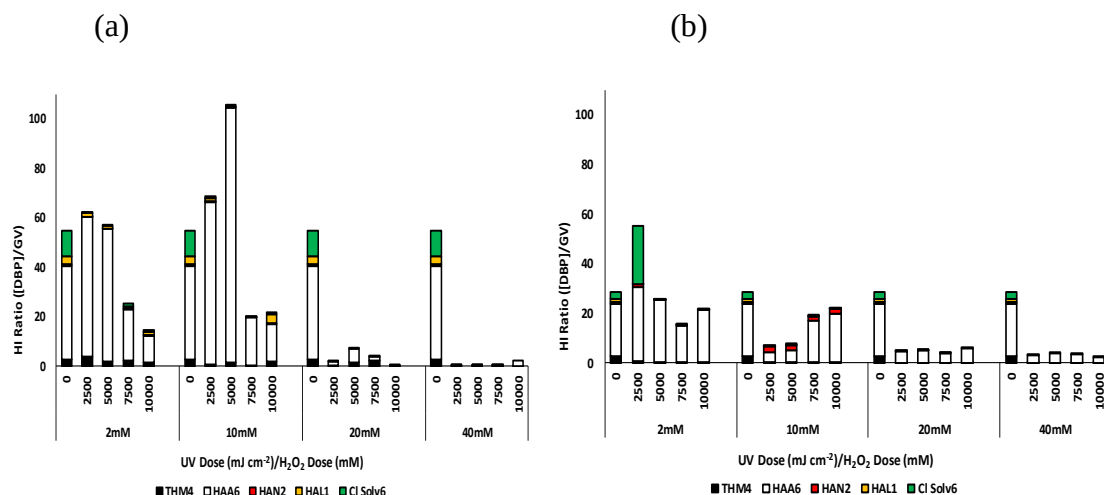


Figure 5.5: The HI of 13 DBPs with GV of SP1 (a) and SP2 (b) upland surface water after treatment with UV/H₂O₂, with 2mM, 10mM, 20mM and 40mM H₂O₂ doses at 0, 2500, 500, 7500 and 10000mJ cm⁻² UV dose, with DBP speciation.

Analysis of the data in terms of HI reveals the upland source waters to have the lowest observed range of value at between 0.4-106 (Figure 5.5a, b). In the case of SP1, the raw water had an HI of 55 which was reduced to 15, 22, 0.3 and 2 through the application of the AOP at a UV dose of 10000 mJ/cm² and H₂O₂ doses of 2 mM, 10 mM, 20 mM and 40 mM respectively. The equivalent HI values for SP2 are 28.7 for the raw water reducing to 21.8, 22.4, 6 and 2.5, indicating a less effective impact of the AOP on HI during the second sampling period.

The HAAs contributed a smaller proportion to the total HI than observed in the lowland lake case, with levels that ranged between 36 and 99%. As the upland waters had the lowest bromine levels, the Br-HAAs are lower when compared to the lake and upland waters with a HI levels of 0.2-52. The greatest impact came from BDCAA with a maximum HI of 24. UV/H₂O₂ doses of 20 mM and 40 mM H₂O₂ and 10000 mJ cm⁻² reduced the HI by 91-99% except for MCAA which increased in concentration and HI. Beyond the HAAs, the chlorinated chemicals 1,2DE and DBCP had the greatest impact on the HI adding 11 and 5 to the HI respectively at low H₂O₂ doses for SP2. In comparison, the HI from the THMs ranged between 2.6 from the raw waters to a minimum of 0.04 indicating that they impact the HI less than the CS. The HAN HI ranged from 0.01-1.3 and fluctuated at lower UV/H₂O₂ doses. At 20 mM and 40 mM, the HI was reduced to 99% with concentrations falling below the LOD.

5.7 Speciation of DBPs and associated HI for the lowland river water

The lowland river raw water had a total DBP-FP concentration of 1371 µg/L in SP1 and 1761 µg/L in SP2. Variation was observed with respect to the impact of applying the AOP in terms of the total concentration and speciation of the resultant DBPs. Increases in total DBP were observed at high and low UV doses for the 2 and 10 mM H₂O₂ concentrations (Figure 5.6a, b) More elevated H₂O₂ doses saw a more consistent reduction in total DBP. Overall the lowland river water was the more susceptible to negative consequence at low H₂O₂ doses. For instance, at a H₂O₂ dose of 2 mM the total DBP from SP2 changed from the raw water value to 795 µg/L, 881 µg/L, 2047 µg/L and 1785 µg/L for UV doses of 2500, 5000, 7500 and 10000 mJ/cm². In comparison at a H₂O₂ dose of 40 mM, the equivalent total DBPs were 78 µg/L, 142 µg/L, 96 µg/L and 104 µg/L. Similar impacts can be observed in SP2 where at low H₂O₂ doses, the total DBP can increase even at high UV doses.

A similar pattern was observed for THMs where a H₂O₂ dose of at least 20 mM was required to ensure effective reduction in the THM-FP (Figure 5.6a, Figure 5.7a). For instance, at a UV dose of 10000 mJ/cm² the THM-FP of SP1 changed from the raw water level of 408 µg/L to 495 µg/L, 380 µg/L, 50 µg/L and 4 µg/L for H₂O₂ doses of 2, 10, 20 and 40 mM respectively. CF represented the most prevalent THM which was increased by 96% and 42% at doses of 2, 10 mM and reduced by 90% and 97% at doses of 20 and 40 mM. Low H₂O₂ doses also saw an increase in BDCM from 32 µg/L in the raw water to 90 µg/L and 82 µg/L. At higher H₂O₂ doses of 20 mM and 40 mM, CF is reduced 90% to 34 µg/L (20 mM) and 97% to 9 µg/L (40 mM), remaining THMs are below 1 µg/L.

The HAA-FP concentrations in the raw waters for SP1 and SP2 differed at 832 µg/L and 1415 µg/L respectively and decreased throughout treatment with increasing UV and H₂O₂ doses. In SP1, the levels decreased by 30%, 21%, 94% and 88% through application of a UV dose of 10000 mJ/cm² and H₂O₂ doses of 2, 10, 20 and 40 mM respectively. The equivalent data for SP2 were 60%, 71%, 94.3% and 93.8% showing a much greater reduction than observed in SP1. The concentration of MCAA was increased throughout

treatment, which is consistent with all waters studied here and is increased in SP2 the most from 5.3 $\mu\text{g/L}$, to 34 $\mu\text{g/L}$ and 40.6 $\mu\text{g/L}$ at 10 mM and 40 mM H_2O_2 and 10000 mJ/cm^2 doses. In contrast, Br-HAA increased at low H_2O_2 doses but reduced with more elevated doses. For instance, BDCAA and DBCAA increased from 17 $\mu\text{g/L}$ to 153 $\mu\text{g/L}$ (2mM) and 173 $\mu\text{g/L}$ (10mM) for SP1. This compares to DBCAA which increased in SP1 from 22.4 $\mu\text{g/L}$ to 176.5 $\mu\text{g/L}$ (2mM) and 143.5 $\mu\text{g/L}$ (10mM), with 10000 mJ/cm^2 . Both reduced to below 8 $\mu\text{g/L}$ at higher UV/ H_2O_2 doses across both sampling points.

The emerging DBPs were relatively more significant in the lowland river water after treatment compared to the other two sources, with a contribution 16% and 12% in the raw waters for SP1 and SP2 but reaching a maximum of 51% during treatment (SP2, 10mM, 5000 UV dose), (Figure 5.6a, b, Figure 5.7a, b). The HAN, HNM, HAL and HK all increased with H_2O_2 doses of 2 mM and 10 mM but at higher doses were reduced by 86-99% (HAN) and 91-99% for the others. For instance, HANs increased from the raw water level of below 5 $\mu\text{g/L}$ to above 100 $\mu\text{g/L}$ for TCAN and DCAN. Similarly, CH and DCP increased to above 100 $\mu\text{g/L}$ with the 2 mM dose.

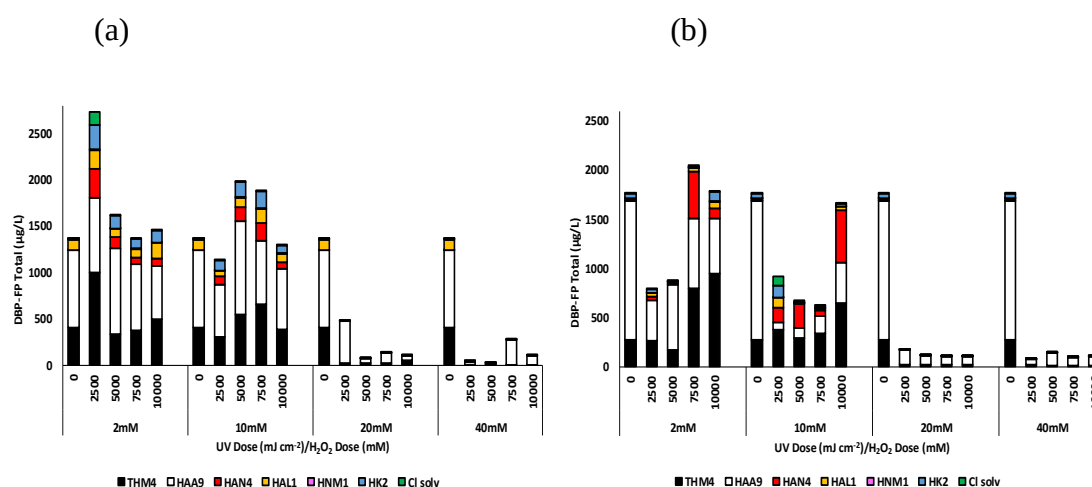


Figure 5.6: The concentration of 27 DBP-FP of SP1 (a) and SP2 (b) lowland river surface water after treatment with UV/ H_2O_2 , with 2mM, 10mM, 20mM and 40mM H_2O_2 doses at 0, 2500, 500, 7500 and 10000 mJ cm^{-2} UV dose, with DBP speciation.

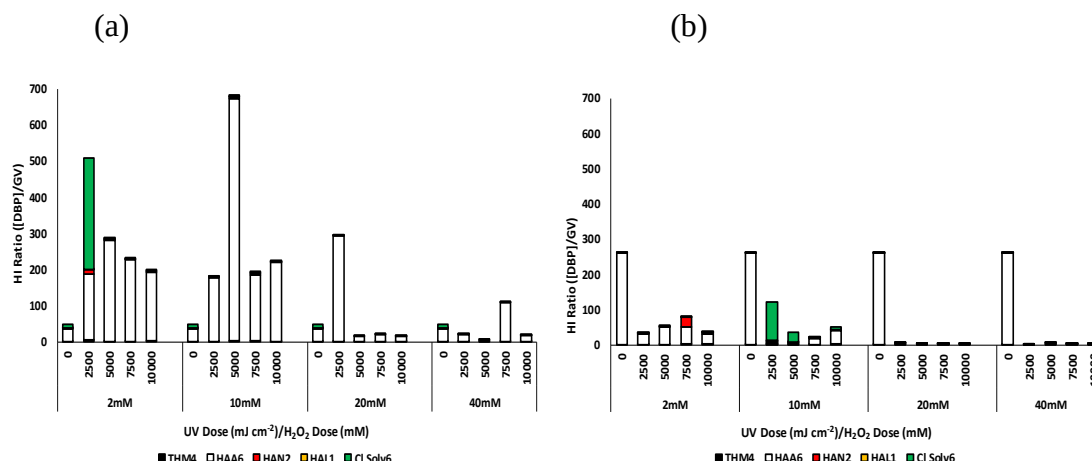


Figure 5.7: The HI of 13 DBPs with GV of SP1 (a) and SP2 (b) river surface water after treatment with UV/H₂O₂, with 2mM, 10mM, 20mM and 40mM H₂O₂ doses at 0, 2500, 500, 7500 and 10000mJ cm⁻² UV dose, with DBP speciation.

The hazard index is again dominated by HAAs and to a lesser extent the chlorinated chemicals and HANs. The HI for lowland raw river water SP1 was 50 compared to 263 for SP2. application of the AOP reduced the HI in SP2 consistently whereas in SP1 the AOP increased the HI for all UV doses at low H₂O₂ concentrations but only in specific cases at elevated H₂O₂ concentrations. The HAA represents an average of 90% of the total HI with three occasions where the contribution reduced to below 60%. In these cases, the CS contributed up to 60% of the total HI. All other DBPs contributed relatively minor amounts to the overall HI. BDCAA has the highest impact on the HI with a range of 2-316, followed by BCAA with a range of between 0.75-65. BDCAA increased at lower UV/H₂O₂ doses from 67.5 in the raw waters to a max of 134 with 2mM and 317 with 10mM but reduced 94% to 4 with 20 and 40 mM 10000 mJ/cm². Similar patterns were observed with HANs and CS showing that delivery of a low HI water required substantial doses to H₂O₂ to ensure effective treatment and minimisation of DBPs.

5.8 Conclusions

The advanced oxidation process H₂O₂/UV has been shown to be effective at managing DBP from raw waters as long as very high H₂O₂ doses are used. Operation at lower doses

poses a significant risk which could result in an increase in either DBP mass concentration and/or hazard index. Comparison across the three water source types revealed that the greatest risk was associated to the lowland river water. Importantly, across all waters the impact of the AOP was different in regard to THM and HAAs such that monitoring of both groups is recommended as a minimum if exploring the potential of AOPs for DBP control. The other main observation was that at elevated H₂O₂ doses, the brominated DBP were effectively reduced resulting in stable low HIs.

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6 Discussion: Implications for the Treatment of Drinking Water

Discussion: Implications for the Treatment of Drinking Water

6.1 How does consideration of hazard index change our perception concerning disinfection by-products

It is clear through this thesis the DBPs deemed important in terms of concentration does not necessarily translate to the individual DBPs significantly linked to increasing the hazard index. The regulation focuses on concentration of a small group of DBPs as a total, a group of 4 THMs to a total of 100 µg/L and in the US, a group of 5 HAAs to a total of 60 µg/L. The regulation does not consider the individual DBP speciation and their associated hazard of exposure. Using the guideline values derived by WHO focuses on the individual counterparts within groups as the individual DBPs formed can vary according to source water, treatment conditions and seasonality. This can be seen from chapter 4 where waters from different sources were used to perform a DBP potential test to elucidate DBP precursors present in each water source. The amount and speciation of DBPs can be highly variable depending on the type of NOM present in each water. The upland waters generated the highest levels of DBPs overall and the regulated THMs, therefore, considered hazardous according to the regulation. Using the WHO guideline values, the THMs, especially chloroform which in some instances can be the highest individual DBP in terms of concentration, can become insignificant with a GV of 300 µg/L. The brominated THMs carry more weight in comparison, with bromodichloromethane guideline value set at 120 µg/L, bromoform and dibromochloromethane at 100 µg/L. In waters with higher levels of bromine, not removed by treatment, higher levels of brominated THMs will be formed, sometimes higher than the chlorinated THM chloroform. In a lowland lake water source sampled after chlorination from chapter 3 which had bromine levels above 100 µg/L, although, THMs remained low, the Br-THMs represented 63% and 72% of the total THM. The probability of forming Br-THMs and Br-DBPs becomes higher with high levels of bromine in the

waters, this becomes important when looking at the hazard outside the regulated THM4 and even the HAA5.

THM regulation has no doubt achieved a higher quality of drinking water, in advancing treatment technologies to remove NOM and precursors to THMs, and in doing so removing precursors to other DBPs with similar removing properties. But the issue is not whether THMs regulation focus has been beneficial but rather if they should be used as a surrogate for the formation and control of other DBPs and with more research on emerging DBPs, this focus may be misplaced and outdated. The use of a small, measurable surrogate in the drinking water industry is practical, measuring all DBPs would be unfeasible, but this thesis has shown neither THMs or HAAs to be a good representative for all the DBPs formed over various water sources, not to mention their basis as indicators of exposure to the full range of DBPs. Bulk water parameters also give limited predictions for the DBPs formed and the HI, with total bromine correlating to the total HI with an r^2 value of 0.37, as seen in chapter 2.

As previously mentioned in the introduction, the hazard index is the addition of the hazard quotients and sums the exposure in relation to reference values; in this case the guideline values are derived from WHO. They are transparent, quick, easy to apply and suitable as an initial screening tool but they do have limitations. In some cases the reference values are not directly comparable, incorporating varying scientific judgements, review periods, methods and policy (WHO, 2017). In regards to DBPs, the list of 19 with GVs is limited when compared to the long exposure list. They are based on robust *in vivo* scientific studies, but these are expensive, take time and are often based on exposure to a single chemical, not taking antagonistic and synergistic effects in to account, if present (Hudrey, 2015). The GV list is limited and it is difficult to apply for new and data-poor chemicals where no GV has been derived. Development of the guideline values for individual chemicals may be needed to refine the risk assessment (WHO, 2017).

We are exposed to a huge range of DBPs, a mixture which is only partially defined, making the hazard of exposure difficult to assess. In measuring 27 individual DBPs in this PhD, it gives a better understanding of the formation of a wide range of DBPs with different water sources and conditions, contributing to the understanding of exposure in terms of hazard index. Turning the concentration in to a hazard index using the guideline

values not only gives the hazard of exposure but takes into account the potency of the individual DBPs, not concentration of a group. The potency as opposed to the concentration is important to consider, as one or two individual DBPs can be more potent than others with more toxicological significance. These are the DBPs where focus should turn and become a priority for water companies and regulators. The DBPs of priority should take not only concentration into account but potency, those DBPs with a low guideline value, with a high chance of occurrence. The DBPs with the lowest GV are brominated DBPs from the HAA group, Bromochloroacetic acid, Bromodichloroacetic acid, both with a provisional guideline value of 1 µg/L and an occurrence of 0.5 µg/L-12 µg/L. The chlorinated chemicals with low guideline values are also bromine containing, consisting of 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane they have a GV of 0.4 µg/L and 1 µg/L but with lower occurrence probability of <2 µg/L in final waters from chapter 3. However, looking at the formation potential of the raw waters from chapter 4, there is a probability of these forming in waters containing higher bromine. The contribution of these 4 brominated DBPs accounts for 57% -94% of the total hazard index in final waters from chapter 3 but account for between 0.8%-16.3% of the total DBP concentration.

6.2 What is the significance of the emerging disinfection by-products

Understanding DBP formation, occurrence and control has been a major focus of recent research but emphasis has been based on the regulated DBPs, THM4 and HAA5. These represent the DBPs abundantly formed, with established methods of analysis, they have not been significantly linked to toxicity of exposure (Krasner *et al.*, 2006) but there has been a small but consistent risk to bladder cancer in people exposed to DBPs over an extended period of time (Hrudey *et al.*, 2015; Hrudey & Fawell, 2015). As THMs have not shown toxicological significance, exposure to emerging DBPs must be responsible. Current regulation with its concentration focus has driven a shift towards alternative disinfections which in turn can produce higher concentrations of emerging by-products, some of which have shown higher toxicity in *in vitro* bioassays than their chlorinated

counterparts. Little is known about these emerging DBPs and their toxicological effect, if any (Richardson *et al.*, 2017).

As previously noted, the most significant DBPs contributing to the hazard index are not those significantly linked to concentration. The major contributors to HI are brominated DBPs, specifically the HAAs, Bromochloroacetic acid and Bromodichloroacetic acid. These are not part of the HAA5 regulated in the US, listed in table chapter 2 (Table 2.1) and can therefore be considered emerging DBPs. The emerging DBPs explored in this thesis are brominated and nitrogenated, as well as chlorinated containing DBPs consisting of 4 HAAs outside HAA5 regulation, HAN4, HNM1, HK2, HAL1 and chlorinated chemicals. Chlorinated chemicals consist of 6 individual chlorinated compounds, previously considered artefacts released into the environment from industry before treatment. They are currently not considered to be by-products of the disinfection process but their measurement in the raw waters from chapter 4, all below 1 µg/L individually, are increased within the FP tests. As their formation is increased during FP, they could potentially be formed through disinfection and therefore are considered emerging DBPs. All 6 have an associated GV, or provisional GV and have shown throughout the thesis to have a high impact the HI, only second to the HAAs on occasion, the highest contributions from the brominated solvents. There are 12 Br-DBPs studied here, spanning across 4 DBP categories, nine having a corresponding GV which is lower than the chlorinated counterparts (WHO, 2018). In the lowland lake raw water source, the contribution of Br-DBPs to the total DBP concentration was 56.5% in SP1 (Figure 3.2), this translating to 99% contribution in the HI, becoming even more significant. In waters with high bromine content, upon disinfection with chlorine can rapidly oxidise to hypobromous acid, reacting quickly, increasing bromine substitution in to the DBPs, forming higher amounts of Br-DBPs and increasing the HI for those with GV. The emerging nitrogenated DBPs, consisting of 5 DBPs, HAN4 and HNM1, two of HANs have a corresponding GV, DCAN and DBAN which is nitrogenated and brominated, with a low guideline value of 12 µg/L and can be formed abundantly in waters with high nitrogen and bromine.

The regulations do not reflect the guideline values available and the current state of knowledge around this area but with insufficient toxicological data it is difficult to know which specific DBPs to emphasise for regulation and monitoring at the treatment works.

Therefore, measuring a wide range of emerging DBPs, without guideline values and robust *in vivo* toxicological studies on all available DBPs, a full priority list is not currently possible. However, the emerging DBPs with GVs should be considered for priority, especially those with high toxicological significance that regularly occur at concentrations above their GV. In the case of water treatment monitoring, measuring DBPs with no GV or limited toxicological data may not be warranted as there is limited knowledge whether they are toxicologically significant. However, because health effects associated with DBPs cannot be explained based on currently regulated DBPs, further toxicological research on emerging DBPs is needed.

6.3 What is the significance of water source and advanced water treatments in minimising the hazard index associated with disinfection by-products

A significant finding throughout this research is the impact of the source water on the DBPs formed and their impact on the associated HI is important. The amount and type of organic matter and characteristics are highly variable within source waters with reported changes in relation to the DOC, the molecular weight distribution, the charge and the hydrophobicity (Huang *et al.*, 2015; Thurman *et al.*, 1985; Tian *et al.*, 2013). Inorganic precursors, especially halide and nitrogen containing ions, for example bromine, which is difficult to remove during conventional treatment, in higher concentrations converting the DBP speciation towards brominated DBPs as the halide incorporation increases. This can be seen in the lowland waters which may be rich in algal organic matter (AOM) or effluent organic matter (EfOM) will contain relatively high levels of organic nitrogen and so are likely to form more N-DBPs (Goslan *et al.*, 2017). In contrast, waters from upland catchment tend to contain limited amounts of nitrogen and bromine and so favour the formation of chlorinated by-products including THMs (Drewes *et al.*, 2002; Levchuk, *et al.*, 2018). The water sources studied here were lowland lake, upland and lowland river, consisting of a range of raw water characteristics as can be seen in Table 3.1. The upland sources characteristically have high organic carbon with an average of 16 mg/L in raw

waters. They form high concentrations of THMs and DBPs, this is true for the upland sources studied in this thesis, forming the highest THM, HAA and overall DBP levels (Chapter 3,4,5). They also form high THM-FP, HAA-FP and DBP-FP with an average of 747 µg/L, 1592 µg/L and 2533 µg/L, respectively throughout. High organic carbon and DBP-FP results are also mirrored in the study of DOC and THM precursor removal of upland water, where the DOC was 11.7mg/L and THM-FP concentrations of 1384 µg/L were found (Gough *et al.*, 2014). As the upland sources also typically contain lower bromine levels and increased competition with the chlorine halogen during formation potential tests give low Br-THM-FP of the raw waters percentage of less than 1% can also be seen in chapter 3 compared to 4.8% of the total THM-FP (Gough *et al.*, 2014).

When comparing the hazard index, the upland sources were the lowest due to the low bromine and nitrogen levels leading to reduced formation of Br-HAAs and other Br/N-DBPs. The highest levels of DBPs were consistently chlorinated DBPs, having a lower GV and hence a lower contribution to the HI. In contrast, the lowland lake and river raw waters have similarly low organic carbon, with high levels of bromine, the lake consistently high over sampling points at 190 µg/L, corresponding to the highest levels of Br-DBP-FP and hence, the highest HI. The molar ratio of Br^-/Cl_2 and their reactive species HOBr/HOCl can have an impact on the DBPs formed and their speciation, especially as HOBr reacts with NOM faster than HOCl (Cowman and Singer, 1996). Because of this, as Br^-/Cl_2 molar ratio increases the concentrations of the Br-DBPs BDCAA and DBCAA increase (Chang *et al.*, 2001). This increase can also be seen in the lowland lake, with the highest bromine levels, leading to high Br-DBPs, specifically the Br-HAAs impacting the HI throughout.

Treatment of the raw waters focuses heavily on the removal of the regulated THM precursors and because of this are significantly removed in the WTW. In focussing on THM removal, the HAAs which are known to have different precursors (Bond *et al.*, 2012) and show no correlation in their formation (Chapter 3). This selectivity and focus could be misleading in terms of toxicity and hazard of exposure to emerging DBPs. Much of the previous work has also focussed on upland catchments in order to meet current legislative targets around the THM4 standard (Ritson *et al.*, 2014; Gough *et al.*, 2015).

However, when expanded to include HAA9 and emerging DBPs, lowland source waters become more important in terms of their HI (Chapter 3 & 4).

Comparison of the advanced treatments, nanofiltration and advanced oxidative processes reveals that the DBP-FP is much reduced using AOPs at high H₂O₂ doses, but at lower doses the DBPs can increase up to 200% the original raw water concentration, causing the HI in the river water to increase by over 13 times. This increase in DBP-FP formation can also be seen in the literature with THM-FP and HAA-FP increasing up to 110% and HAN was increased as high as 260% (Wang *et al.*, 2015). The increase seen is due to partial oxidation of organics within the waters leading to an increase in the DBP formation. This increase is also be seen in trials using model compounds revealing dramatic increases in HAA-FP when the compounds were only partially degraded (Bond *et al.*, 2009). The water source and type of DBP precursors available influences the efficiency of the DBP reduction. The upland water originally had the highest DBP formation but are reduced by AOP at lower doses compared to the lake and river water, the HI is also reduced after AOP treatment. The nanofiltration membranes did not reduce the DBPs to the extent of AOPs at high UV/H₂O₂ doses. AOPs reduced the TOC up to 95% for the upland waters but the lowest reduction of 5% was seen in the lowland lake water. DBP-FP was reduced to a maximum of 97% but at high UV/H₂O₂ doses, at lower doses, 76% DBP-FP reduction was observed but DBP formation was also increased. The THM-FP and HAA-FP were reduced by up to 99% and 96%, respectively, at high UV/H₂O₂ doses. Previous research into the impact of AOPs on DBP formation from surface waters found THM-FP and HAA-FP were reduced by 77% and 62%, respectively (Lamsal *et al.*, 2011). Another study investigating AOPs on groundwater found THM-FP and HAA-FP were reduced by 43% and 68%, respectively (Agbaba *et al.*, 2016).

Using different membranes, the DBPs were reduced up to 78.6% in upland waters, the reduction heavily depends on each water type and sampling time. The reduction with membranes was more stable throughout, with reductions of DBP-FP from 65%-89% possible. These high precursor removal rates are mirrored in other studies with rejection rates of THM and HAA9 between 77-99% and 75-98% respectively, depending on the nanofiltration membrane used (Chellam, 2000; Siddiqui *et al.*, 2000). TOC removals of

65-94% were seen across the waters within the current study, similar TOC removals of 70-94% observed across two studies using a range of 7 nanofiltration membranes (Chellam, 2000; Siddiqui *et al.*, 2000). The bromide and bromate removal rates remain low within literature and the current study, which can lead to an increase in Br-DBPs (Siddiqui *et al.*, 2000). The AOPs had little effect on the bulk water parameters, NPOC, TN and bromine but reductions of 77-89% NPOC and bromine reductions of up to 56% can be achieved in upland source waters. The upland had the lowest bromine, but in comparison a reduction range of 5%-20% in the lake and river source water was achieved, (Chapters 5&6, Table 4.2, Table 5.2). Using UV/H₂O₂, a reduction of NOM as UV₂₅₄ and DOC were 94% and 78%, respectively, with DOC removal increasing with UV doses increased (Goslan *et al.*, 2006).

6.4 What is the best way forward to minimise the hazard index associated with disinfection by-products

The evaluation of current regulations and guidelines and the development of new ones requires the involvement of interdisciplinary teams that include chemists, toxicologists, epidemiologists, statisticians, engineers and regulators. The utility of regulations or guidelines must be judged in terms of the relative occurrence of identified DBPs and the toxic potency for relevant human health effects at concentrations (drinking water exposure levels) that are relevant (Hrudey & Fawell, 2015). According to the *in vivo* guideline values hazard index, the THMs are less potent, and although are widely regulated are not the main drivers of toxicity (WHO, 2017b). THMs are regulated in many countries and HAA5 are regulated in the US. The HAA5 does not contain the brominated species which according to the hazard index from the guideline values are more potent. As drinking water treatment selectively removes the regulated THMs, it should be re-optimised for efficient removal of HAA precursors, especially Br-HAAs as they are paramount to reducing the HI. Removal or reduction of bromine would also have a positive effect on the HI but this is difficult to do with current treatment practises, ion

exchange may remove bromide ion. Bromine incorporation into DBPs may be controlled during disinfection by controlling the pH during the process.

THM analysis follows an established EPA method 551.1 which includes HAN4, HK2, HNM1, HAL1 and CS6 within the same method. Their extraction and analysis are under the same conditions as the THMs, with the addition of an analytical standard for each of the DBPs. The standards are available in a standard mix from many chemical companies, including Sigma Aldrich, UK. The analysis of these emerging DBPs is possible using a GC-ECD and a GC-MS, the same for the regulated THM4. Time would need to be taken to set up the method to include each DBP in the analysis, to ensure no peak overlapping and the introduction of internal standards as an extra quality control check (EPA, 1995). Each DBP is then included in the quantitative method for individual quantitation. The HAA analysis began with EPA method 552.1 (EPA, 1992), which includes the analysis of 6 HAAs, MCAA, DCAA, TCAA MBAA, BCAA and DBAA, this includes the HAA5 regulated in the US plus the analysis of MBAA which is not regulated. The only Br-HAA regulated is DBAA. The HAA group includes 9 HAAs which are analysed in subsequent methods 552.2 and 552.3 and includes all 9 HAAs, the sample preparation, extraction and derivitisation for DBP group is the same (EPA, 2003; Pawlecki *et al.*, 1997). Mixed standards are available for the nine HAA for simultaneous analysis. The analysis of 4 HAAs specified in Chapter 3 are closely linked to the HI associated with the DBP total, these include Br-HAAs not included in the HAA5 regulation.

6.5 References

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7 Conclusions and Further Work

7.1 Conclusions

- Emerging DBPs do not have substantial impact on the total DBP load, in terms of concentration, but when converted to HI, using the WHO guideline values, or the LC50 values, they can become important. The significance of the regulated THM4 (and HAA5 in the US) becomes lessened in terms of hazard, and the Br-HAAs and HANs becoming significant, in terms of potency and important for future regulation. Specifically, Br-HAAs, when looking at toxicity through a WHO GV lens and the HAN group when using the LC50 data to generate HI.
- THM4 and HAA5 (US regulated) represent a large proportion of the DBP concentration and can look to give a good representation of the overall concentration, but they do not correlate with the unregulated, emerging DBPs. This is significant as the unregulated DBPs, Br-HAAs and HANs have a higher impact on the associated hazard, and these should be considered for future monitoring.
- The speciation of the individual DBPs within each category becomes important to consider when translating the concentration to hazard, especially in waters with high bromine and nitrogen levels. The importance of this is that the mass of DBPs formed does not mirror the associated overall hazard from each water site. This is most evident with waters rich in organic nitrogen precursors and/or high levels of bromine due to the formation of increased levels of Br-DBPs and Br-N-DBPs.
- Using an extended DBP list to include the emerging DBPs (those with GV values), places lowland waters in a higher risk category than previously considered. Taking potency as well as concentration of the individual DBPs into account gives a vastly different picture compared to concentration alone, and different again to looking at the concentration of THM4, where regulation is currently focussed.

Lowland waters, especially those with high nitrogen (EfOM or algal blooms) and bromine should be studied in further detail, especially as bromine can be difficult to remove through conventional treatment.

- Bromine is usually found in the form of bromide in waters which can be removed using ion exchange mechanisms and activated carbon treatment technologies, or a combination of these with nanofiltration. These types of treatments can be optimised for bromine removal depending on the remainder NOM present. Removing or regulating bromide may reduce Br-DBPs forming but as we can see from chapter 2, 10-20 µg/L bromine can have varying impact on the HI. The variation of waters and DBP precursors present can have an impact on the concentration and speciation of Br-DBPs formed.
- Upland source waters are known to form high levels of THMs and have accordingly been under scrutiny to meet the THM4 regulation. However, looking outside the regulated THMs, they form the lowest emerging DBPs, in particular Br- and N- DBPs, due to their low levels of bromine and total nitrogen. As a consequence of this, the upland waters have the lowest associated HI when compared to the lowland sources.
- AOPs reduced the DBPs and HI more efficiently than nanofiltration but only when high H₂O₂ levels are used. The AOPs at lower H₂O₂ doses increased the DBPs formed and the associated HI, especially in the lowland lake waters. The correct H₂O₂ and UV dose when using AOPs becomes increasingly important, and higher doses may be needed when the source water is known to be highly variable.
- Nanofiltration reduced the DBP precursors considerably, becoming important in waters with high seasonal variability. When considering the emerging DBPs, bromine was inefficiently removed, leading to high Br-DBPs and increased HI in lowland waters. Comparing this to AOPs, at high H₂O₂ and UV doses, Br-DBPs were more effectively reduced, leading to lower HIs.

7.2 Further Work

Further work on the minimisation of DBPs and their precursors should involve conventional as well as advanced treatments, tested with a wider range of source waters, including ground waters. Investigation of various treatments and conditions include, coagulation, ion exchange, activated carbon and ozone to name a few, elucidating their impact on the DBPs formed with an emphasis on those contributing to the hazard index. Treatments can be further tested in the lab under various optimal and sub-optimal conditions and also on site after each treatment to show the removal of precursors throughout. Further studies involving AOX would be useful to determine treatment efficiency and removal of the total concentration of the inorganic and organic halogens, chlorine, bromine and iodine within NOM but would be limited for DBP production predictions. Further speciation tests using IC or ICP-MS would give a better understanding of the speciation of brominated and iodinated DBPs which may form. The speciation would also give a better indication of the HI as brominated and iodinated DBPs are known to be more genotoxic and cytotoxic than their chlorinated counterparts.

There is a lack of knowledge on the exposure to mixtures of DBPs formed during disinfection of drinking water, with the mixture itself only partially defined. Measuring a vast array of regulated and emerging DBPs throughout this thesis, seeks to define the DBP mixture from different water sources, under various conditions, to elucidate the hazard of exposure to a more defined mixture, but further research in the area is needed. There is a lack of toxicity data for emerging DBPs, more *in vivo* and *in vitro* studies are needed to expand the WHO guideline values to enable a comprehensive assessment of the hazard as a whole mixture, not just on individual compounds. Defining the mixture is a key step in this. Analytical methods outside the used of gas chromatography to liquid chromatography with mass spectrometry would be advantageous, giving the opportunity to seek and quantify DBPs outside the scope of volatility (Wang *et al.*, 2016). Ionisation techniques outside electron ionisation would be highly beneficial when measuring emerging DBPs. Softer ionisation techniques for example, chemical ionisation and atmospheric pressure chemical ionisation, teamed with tandem mass spectrometry are far

more selective to non-volatile, polar compounds, allowing background minimisation for higher selectivity (Ding & Chu, 2017; Richardson, 2004). A mass spectrometry scan capability would also be useful for a broad compound scan, to show DBP precursor removal efficiency and selectivity to compare different treatments under various conditions. Recent developments in the use of ion chromatography coupled with tandem mass spectrometry, is also a quick method for the determination of low levels of HAAs and ionic acids currently unexplored at low concentrations (Kanda *et al.*, 2008).

The importance of Br-DBPs and N-DBPs removal has become apparent throughout this thesis. Further research is needed to track the removal of nitrogen and bromine, and the reactive species which favour the formation of Br- and N- DBPs, as removal can reduce the hazard of the mixture. Pollutants in source waters can also contribute to the formation of DBPs and their removal throughout drinking water treatment is important. The type of pollutants present can vary widely and depend heavily on the water source, polyorganic pollutants, both natural and anthropogenic can occur from pharmaceuticals, personal care products and agricultural sources (Ding *et al.*, 2018). Tracking their concentration through treatment, while monitoring the impact on DBPs formed is important, with a focus on those contributing to hazard and under regulation. These pollutants and some heavy metal compounds may have a synergistic effect under certain conditions on the formation of DBPs considered more toxic. However, interactions within the drinking water are difficult to predict, particularly for long term effects and at environmentally low levels of exposure (Richardson *et al.*, 2008). More research in this area is needed to help define the criteria for potential synergistic effects in the formation of DBPs considered more hazardous (Altenburger *et al.*, 2015; WHO, 2017).

7.3 References

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APPENDICES

Appendix A

A.1 DBPs Measured throughout this thesis and the analytical method

Table 7.11 DBPs Measured throughout this thesis and the analytical method

No.	Category	Sub category	Analytical method
1	Halonitromethanes (HNM)	trichloronitromethane (TCNM)	GC-ECD
2	Haloketones (HK2)	1,1-dichloropropanone (1,1-DCP) 1,1,1-trichloropropanone (1,1,1-TCP)	
3	Haloacetonitriles (HAN4)	Bromochloroacetonitrile (BCAN) Dibromoacetonitrile (DBAN) Dichloroacetonitrile (DCAN) Trichloroacetonitrile (TCAN)	
4	Trihalomethanes (THM 4)	trichloromethane (CF) bromodichloromethane (BDCM) dibromochloromethane (DBCM) tribromomethane (BF)	
5	Haloaldehyde (HAL1)	Trichloroacetaldehyde, Chloral Hydrate (CH)	GC-ECD
6	Haloacetic acids (HAA9)	Bromochloroacetic acid (BCAA) Bromodichloroacetic acid (BDCAA) Chlorodibromoacetic acid (CDBAA) Dibromoacetic acid (DBAA) Dichloroacetic acid (DCAA) Monobromoacetic acid (MBAA) Monochloroacetic acid (MCAA) Tribromoacetic acid (TBAA) Trichloroacetic acid (TCAA)	EPA method 552.3 Derivatisation GC-ECD
7	Chlorinated Chemicals	Carbon tetrachloride(CT) 1,1,1 trichloroethane(1,1,1 TCE) Trichloroethylene(TCE) 1,2-Dibromoethane(1,2 DBE) Tetrachloroethylene(TETCE) Dibromochloropropane (1,2 DBCP)	GC-ECD
	Chlorate Chlorite Nitrite Bromate		EPA method 7.1 IC

A.2 WHO GV values derived and followed for HI

Derived from WHO and by Prof. John Fawell

Table A1 GV values derived and followed for HI

DBP group	Compound	Guideline value (µg/L)	How was it derived	Ref.
Trihalomethanes (THMs)	Trichloromethane (CF)	300	A TDI of 15 µg/kg body weight was derived from the lower 95% confidence limit for 5% incidence of hepatic cysts, generated by physiologically based pharmacokinetic modelling, in dogs that ingested chloroform in toothpaste for 7.5 years, using an uncertainty factor of 25 (10 for intraspecies differences in toxicokinetics and toxicodynamics and 2.5 for differences in interspecies toxicodynamics). The guideline value allocation to water is 75% of TDI, assuming weight of 60 kg adult and consumption of 2 litres/day.	Assessment date: 2004 Principal references: IPCS (2000) Disinfectants and disinfectant by-products IPCS (2004) Chloroform WHO (2005) Trihalomethanes in drinking-water
	Tribromomethane (BF)	100	A TDI of 17.9 µg/kg body weight, based on the absence of histopathological lesions in the liver in a well-conducted and well documented 90-day study in rats, using an uncertainty factor of 1000 (100 for intraspecies and interspecies variation and 10 for possible carcinogenicity	Assessment date: 2004 Principal references: IPCS (2000) Disinfectants and disinfectant by-products

			and short duration of exposure). The guideline value allocation to water is 20% of TDI, assuming weight of 60 kg adult and consumption of 2 litres/day.	WHO (2005) Trihalomethanes in drinking-water
	Dibromochloromethane (DBCM)	100	A TDI of 21.4 µg/kg body weight, based on the absence of histopathological effects in the liver in a well-conducted and well-documented 90-day study in rats, using an uncertainty factor of 1000 (100 for intraspecies and interspecies variation and 10 for the short duration of the study); an additional uncertainty factor for potential carcinogenicity was not applied because of the questions regarding mouse liver tumours from corn oil vehicles and inconclusive evidence of genotoxicity. The guideline value allocation to water is 20% of TDI, assuming weight of 60 kg adult and consumption of 2 litres/day.	Assessment date: 2004 Principal references: IPCS (2000) Disinfectants and disinfectant by-products WHO (2005) Trihalomethanes in drinking-water
	Bromodichloromethane (BDCM)	120	The WHO guideline value was 60 µg/L based on a risk extrapolation from a positive carcinogenicity study in which animals were dosed by gavage in corn oil. A later study in which animals were dosed in drinking water showed no indication of carcinogenicity. <i>[As BDCM was negative for carcinogenicity in a recent NTP bioassay in which it was dosed in drinking -water, exceedances of the guideline value</i>	Assessment date: 2004 Principal references: IPCS (2000) Disinfectants and disinfectant by-products USNTP (1987). Toxicology and carcinogenesis studies of bromodichloromethane in F344/N rats and B6C3F1 mice (gavage studies)

			are not likely to result in an increased risk of cancer.(WHO, 2017)] The WHO guideline is under review since the use of the risk extrapolation would be inappropriate. The no observed effect level in the 2-year study in rats was 6 mg/L, with the application of an uncertainty factor of 300 to account for extrapolation from rats to man, the variation within the human population and gaps in the database this would give a potential TDI of 20 µg/kg body weight.	WHO (2005) Trihalomethanes in drinking-water
Haloacetic acids (HAAs)	Dibromoacetic acid (DBAA)	12	IPCS (2000) established a TDI of 20 µg/kg of body weight per day for dibromoacetic acid, based on a 79-day male reproductive toxicity study (Linder <i>et al.</i>, 1995, 1997) showing altered spermiation at daily gavage doses of 10 mg/kg of body weight per day and higher, with a NOAEL of 2 mg/kg of body weight per day. A total uncertainty factor of 100 was used (10 each for inter- and intraspecies differences). NTP published a 2 year carcinogenicity study in rats and mice administered high doses of dibromoacetic acid in drinking water. Mesotheliomas were observed in the top dose in male rats along with mononuclear cell leukaemia in female rats and in the top and middle doses in males. Liver tumours were observed in mice at the higher doses. The no effect level in rats was 2 mg/kg bodyweight per	WHO (2004a), WHO (2017) NTP (2007) STUDIES OF DIBROMOACETIC ACID (CAS NO. 631-64-1) IN F344/N RATS AND B6C3F1 MICE (DRINKING WATER STUDIES) NATIONAL TOXICOLOGY PROGRAM NTP TR 537 NIH Publication No. 07-4475

			day. Using this as a point of departure with an uncertainty factor of 1000 to reflect inter and intraspecies differences and variation and potential carcinogenicity. This gives a drinking water value of 12 µg/L assuming an allocation of 20% of the TDI to drinking water and is an order of magnitude lower than the value developed by IPCS based on reproductive toxicity.	
	Bromochloroacetic acid (BCAA)	1	In a 2 year study in rats and mice in which BCA was dosed in drinking water (NTP TR549 2009) there were clear signs of carcinogenicity. Based on a linearised multistage model the drinking water goal developed by the California regulator was 0.7 µg/L (rounded to 1.0). This is not a standard which is 60 µg/L for 5 named HAAs.	NTP (2009) Toxicology and Carcinogenesis Studies of Bromochloroacetic Acid in F344/N Rats and B6C3F1 Mice (Drinking Water Studies) , WHO (2017)
	Bromodichloroacetic acid (BDCAA)	1	A two year study in which bromodichloroacetic acid was administered to rats and mice in drinking water (NTP TR583 2015) demonstrated carcinogenicity in all dose levels. Based on a risk extrapolation using the linearised multistage model, a drinking water goal of 0.95 µg was determined (rounded to 1.0).	NTP (2015) Toxicology Studies of Bromodichloroacetic Acid in F344/N Rats and B6C3F1/N Mice and Toxicology and Carcinogenesis Studies of Bromodichloroacetic Acid in F344/NTac Rats and B6C3F1/N Mice (Drinking Water Studies) , WHO (2017)

	Monochloroacetic acid (MCAA)	20	A TDI of 3.5 µg/kg body weight, based on a LOAEL of 3.5 mg/kg body weight per day from a study in which increased absolute and relative spleen weights were observed in male rats exposed to MCAA in drinking water for 2 years, using an uncertainty factor of 1000 (100 for interspecies and intraspecies variation and 10 for use of a minimal LOAEL instead of a NOAEL and database deficiencies, including the lack of a multigeneration reproductive toxicity study) The allocation to water is 20% of TDI, assuming weight of 60 kg adult and consumption of 2 litres/day. No evidence of carcinogenicity of monochloroacetate was found in 2-year gavage bioassays with rats and mice. Monochloroacetate has given mixed results in a limited number of mutagenicity assays and has been negative for clastogenicity in genotoxicity studies. IARC has not classified the carcinogenicity of monochloroacetic acid.	Assessment date: 2003 Principal reference: WHO (2004) Monochloroacetic acid in drinking-water
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	Dichloroacetic acid (DCAA)	50	Because the evidence for the carcinogenicity of dichloroacetate is insufficient, a TDI of 7.6 µg/kg of body weight was calculated based on a study in which no effects were seen on the livers of mice exposed to dichloroacetate at 7.6 mg/kg of body weight per day for 75 weeks (DeAngelo <i>et al.</i>, 1991) and incorporating an uncertainty factor of 1000 (100 for intra- and interspecies variation and 10 for possible carcinogenicity). The guideline value is designated as provisional on the basis of technical achievability. Basis of guideline value derivation: Linear multistage model applied to combined data for carcinomas and adenomas in male mice exposed to doses up to 429 mg/kg body weight per day for up to 2 years. The concentration associated with a 10⁻⁵ upper-bound excess lifetime cancer risk is 40 µg/l. In some circumstances, however, it may not be possible to adequately disinfect potable water and maintain DCA levels below 40 µg/l, so the provisional guideline value of 50 µg/l is retained.	Assessment date: 2004 Principal reference: WHO (2005) Dichloroacetic acid in drinking-water
	Trichloroacetic acid (TCAA)	200	A TDI of 32.5 µg/kg of body weight is based on a NOAEL of 32.5 mg/kg of body weight per day from a	Assessment date: 2003

			study in which decreased body weight, increased liver serum enzyme activity and liver histopathology were seen in rats exposed to trichloroacetate in drinking-water for 2 years (DeAngelo <i>et al.</i> , 1997), and incorporating an uncertainty factor of 1000 (100 for intra- and interspecies variation and 10 for database deficiencies, including the absence of a multigeneration reproductive study, the lack of a developmental study in a second species and the absence of full histopathological data in a second species). The guideline value allocation to water is 20% of TDI, assuming weight of 60 kg adult and consumption of 2 litres/day.	Principal reference WHO (2003) Trichloroacetic acid in drinking-water
HANs	Dichloroacetonitrile	20	A TDI value of 2.7 µg/kg of body weight is based on a LOAEL of 8 mg/kg body weight per day for increased relative liver weight in male and female rats in a 90-day study, using an uncertainty factor of 3000 (taking into consideration intraspecies and interspecies variation, the short duration of the study, the use of a minimal LOAEL and database deficiencies). The guideline value for dichloroacetonitrile is provisional owing to limitations of the toxicological database.	Assessment date: 2003 Principal references: IPCS (2000) Disinfectants and disinfectant by-products WHO (2004) Halogenated acetonitriles in drinking-water
	Dibromoacetonitrile	12	Dibromoacetonitrile: 11 µg/kg body weight, based on a NOAEL of 11.3 mg/kg body weight per day for decreased	Assessment date: 2003 Principal references: IPCS

			body weight in male rats in a 90-day drinking-water study and an uncertainty factor of 1000 (accounting for interspecies and intraspecies variation, subchronic to chronic extrapolation and database insufficiencies) The WHO guideline value is 70 µg/l from the assessment carried out in 2003. However, more recent data is available. In a two year carcinogenicity study in rats and mice in which DBAN was dosed in drinking water the NOAEL was 2 mg/kg bodyweight per day (NTP 2010). Applying an uncertainty factor of 1000 (10 for interspecies extrapolation, 10 for intraspecies variation and 10 for a cancer endpoint) the TDI is 2 µg/kg bodyweight. This translates into a drinking water guideline value of 12 µg/L assuming an allocation of 20% of the TDI to drinking water.	(2000) Disinfectants and disinfectant by-products WHO (2004) Halogenated acetonitriles in drinking-water NTP (2010)
HAL	Trichloroacetaldehyde/ Chloral Hydrate (CH)	100	A health-based value of 0.1 mg/l (rounded figure) can be calculated on the basis of a TDI of 0.0045 mg/kg body weight derived based on an increased incidence of liver histopathology observed in mice in a 2-year drinking-water study, allocating 80% of the TDI to drinking-water (because most exposure to chloral hydrate is from drinking-water) and assuming a 60 kg adult consuming 2	Assessment date: 2004 Principal references: IPCS (2000) Chloral hydrate IPCS (2000) Disinfectants and disinfectant by-products WHO (2005) Chloral hydrate in drinking-water

			litres of water per day. However, because chloral hydrate usually occurs in drinking-water at concentrations well below those of health concern, it is not considered necessary to derive a guideline value.	
Chlorinated chemicals	Carbon tetrachloride	4	TDI and guideline value based on a NOAEL of 1 mg/kg body weight per day for hepatotoxic effects in a 12-week oral gavage study in rats, adjusting for daily dosing and applying an uncertainty factor of 500 (100 for interspecies and intraspecies variation, 10 for the duration of the study and a modifying factor of 0.5 because it was a bolus study)	(IPCS, 1999), IARC (1999)
	1,2-Dibromo-3-chloropropane	1	The guideline value of 1 µg/l should be protective for the reproductive toxicity of DBCP. Recent epidemiological evidence suggests an increase in cancer mortality in individuals exposed to high levels of DBCP. It was found to be genotoxic in a majority of <i>in vitro</i> and <i>in vivo</i> assays. The guideline values associated with these excess lifetime cancer risks are therefore 10, 1, and 0.1 µg/litre, respectively. An adequate margin of safety exists at these concentrations for the reproductive toxicity of DBCP.	WHO (2003) 1,2-Dibromo-3-chloropropane in drinking-water
	1,2-Dibromoethane	0.4	Lower end of the range (and thus more conservative estimate) of lifetime low-dose cancer risks calculated by linearized multistage modelling of the incidences of haemangiosarcomas and tumours in the stomach, liver, lung and adrenal cortex (adjusted for the observed high	IPCS (1995) Report of the 1994 meeting of the Core Assessment Group IPCS (1996) 1,2-Dibromoethane WHO (2003) 1,2-

			early mortality, where appropriate, and corrected for the expected rate of increase in tumour formation in rodents in a standard bioassay of 104 weeks) of rats and mice exposed by gavage.	Dibromoethane in drinking-water
	Tetrachloroethene/tetrachloroethylene	40	TDI and guideline value based on hepatotoxic effects observed in a 6-week gavage study in male mice and a 90-day drinking-water study in male and female rats, and taking into consideration carcinogenic potential (but not the short length of the study, in view of the database and considerations regarding the application of the dose via drinking-water in one of the two critical studies). It reportedly produces liver tumours in mice, with some evidence of mononuclear cell leukaemia in rats and kidney tumours in male rats. However, overall evidence indicates that this compound is not genotoxic.	WHO (2003) Tetrachloroethene in drinking-water
	Trichloroethene	20	TDI and provisional guideline are based on a developmental toxicity study in rats with a BMDL10 (the lower 95% confidence limit corresponding to a 10% increase in extra risk of fetal heart malformations over background) of 0.146 mg/kg body weight per day and using an uncertainty factor of 100 for intraspecies and interspecies variation. The guideline value is protective for both cancer and non-cancer endpoints. The genotoxicity data are not fully conclusive, but there appears to be	WHO (2005) Trichloroethene in drinking-water

			evidence to show that TCE has a weak, likely indirect, genotoxic effect at high doses. Therefore, the mutagenic potential for this compound cannot be disregarded.	
	1,1,1-Trichloroethane	2000	A health-based value can be calculated based on changes in the kidney that were consistent with hyaline droplet nephropathy observed in a 13-week oral study in male rats, and taking into account the short duration of the study. However, because 1,1,1- trichloroethane occurs at concentrations well below those of health concern, it is not considered necessary to derive a formal guideline value.	WHO (2003) 1,1,1-Trichloroethane in drinking-water

