

Disinfection by-product occurrence in selected European waters

Emma H. Goslan, Stuart W. Krasner, Cristina M. Villanueva, Glòria Carrasco Turigas, Mireille B. Toledano, Manolis Kogevas, Euripides G. Stephanou, Sylvaine Cordier, Regina Gražulevičienė, Simon A. Parsons and Mark J. Nieuwenhuijsen

ABSTRACT

In this paper we report the findings of a European survey of regulated and emerging disinfection by-products (DBPs) in drinking waters in selected regions that were part of epidemiology studies. The levels of DBPs found reflected the diverse regions from which the samples were collected, the different treatment/disinfection processes and the different source waters. In addition to a wide range of concentrations of DBPs (e.g. median trihalomethanes (THMs) of 8–85 $\mu\text{g L}^{-1}$), bromine incorporation was quite diverse (e.g. some waters were highly dominated by bromine-containing DBPs, whereas others only had chlorine-containing species). Bromine incorporation was highest in the haloacetonitriles (HANS) and was lowest in the trihalogenated haloacetic acids (THAAs). In addition, the ratios of THMs to HAAs, THMs to HANS, and THAAs to dihalogenated HAAs varied. Exposure assessment based on THMs alone was not sufficient for indicating the presence of emerging DBPs of health concern. Occurrence studies must include a more diverse group of analytes to better understand exposure to DBPs of health concern.

Key words | disinfection byproducts, haloacetic acids, haloacetonitriles, trihalomethanes

Emma H. Goslan (corresponding author)

Simon A. Parsons

Cranfield Water Science Institute, Cranfield University, Cranfield, Bedford, MK43 0AL, UK
E-mail: e.h.goslan@cranfield.ac.uk

Stuart W. Krasner

Metropolitan Water District of Southern California, La Verne, CA 91750, USA

Cristina M. Villanueva

Glòria Carrasco Turigas

Manolis Kogevas

Mark J. Nieuwenhuijsen

Centre for Research in Environmental Epidemiology (CREAL), Epidemiology, Barcelona Biomedical Research Park, Dr. Aiguader, 88, 08003 Barcelona, Spain;

CIBER Epidemiología y Salud Pública (CIBERESP), Melchor Fernandez Almagro, 3-5, 28029 Madrid, Spain;

and

Universitat Pompeu Fabra (UPF), Plaça de la Mercè, 10-12, 08002 Barcelona, Spain

Cristina M. Villanueva

Manolis Kogevas

IMIM (Hospital del Mar Medical Research Institute), Doctor Aiguader, 88, 08003 Barcelona, Spain

Manolis Kogevas

National School of Public Health, Athens, Greece

Mark J. Nieuwenhuijsen

Mireille B. Toledano

MRC-PHE Centre for Environment and Health, Department of Epidemiology and Biostatistics, School of Public Health, Faculty of Medicine, Imperial College London, St Mary's Campus, Norfolk Place, London W2 1PG, UK

Euripides G. Stephanou

Environmental Chemical Processes Laboratory, Dept of Chemistry, University of Crete, 71003 Voutes-Heraklion, Greece

Sylvaine Cordier

Inserm, U625, University of Rennes I, IFR140 Rennes, France

Regina Gražulevičienė

Department of Environmental Sciences, Vytautas Magnus University, Kaunas, Lithuania

INTRODUCTION

To date there has been considerable research and testing carried out to address the occurrence of a wide range of disinfection by-products (DBPs) of health concern in North America (Krasner *et al.* 1989, 2006; Health Canada 1995; Williams *et al.* 1997; McGuire *et al.* 2002). A few studies have looked at such DBPs in Europe (Kampioti & Stephanou 2002; Goslan *et al.* 2009; Bougeard *et al.* 2010). We know from these studies that a complex mixture of compounds is formed when disinfectants react with natural organic matter, bromide, and iodide, of which the trihalomethanes (THMs) and haloacetic acids (HAAs) are the most prevalent species. Epidemiologists have reported a number of health concerns associated with exposure to DBPs in drinking water, for example, bladder cancer (Villanueva *et al.* 2004) and some adverse reproductive health outcomes (Nieuwenhuijsen *et al.* 2009). Toxicological research has shown that certain bromine- and iodine-containing DBPs are more cytotoxic and genotoxic than their chlorine-containing analogues (Plewa & Wagner 2009). Similarly, nitrogenous DBPs, such as halonitromethanes and haloacetonitriles (HANs), have greater cytotoxicity and genotoxicity than the regulated THMs or HAAs (Plewa *et al.* 2004; Muellner *et al.* 2007; Plewa & Wagner 2009). However, most DBP occurrence studies have focused on THMs and HAAs.

Recently, the European Union (EU) funded a major research initiative (Health Impacts of Long-term Exposure to DBPs in Drinking Water (HIWATE)) to address some of the questions associated with DBPs and health concerns. The work carried out here contributed to the HIWATE project and provided additional information on the formation of THMs and HAAs, as well as that of emerging DBPs that were part of the Information Collection Rule (ICR) study in the USA (McGuire *et al.* 2002). The overall aim of the HIWATE project was to investigate potential human health risks (e.g. premature births, small for gestational age, semen quality, stillbirth, congenital anomalies) associated with exposure to low levels of disinfectants (such as chlorine) and DBPs occurring in water for human consumption and also used in the food industry (Nieuwenhuijsen *et al.* 2009). Indeed, drinking waters from this study were shown to exhibit greater cytotoxicity with greater numbers

of DBPs identified (Jeong *et al.* 2012). However, analysis of the results of the HIWATE project have shown that total and specific THMs and HAAs have limited value as predictors of other DBPs when using principal component analysis (Villanueva *et al.* 2012).

In this paper, the findings from a survey of 21 DBPs from selected cities or regions in five different European countries are reported. The DBPs measured were four THMs, nine HAAs, four HANs, two halo ketones (HKs), chloral hydrate (CH) (trichloroacetaldehyde), and chloropicrin (CP) (trichloronitromethane). The study sites were selected by the HIWATE project team to accompany epidemiology studies and to provide exposure data on DBPs. For example, Bradford (UK) was selected for study because its infant mortality rate was among the highest in the country (Born in Bradford 2011). This paper provides a snapshot of occurrence in selected locations during a single sampling event and the presentation of occurrence data in this paper is part of a larger effort to develop exposure assessment information on a range of DBPs of regulatory and health concern. One key objective of this paper was to examine how the speciation of THMs may be useful as a surrogate for exposure to other bromine-containing DBPs of health concern.

MATERIALS AND METHODS

Sample collection and shipping

Samples were collected from one region each in four partner countries (UK, France, Greece, and Lithuania) and in four separate regions of Spain. Samples were collected at various points throughout the distribution systems. Samples were collected in March 2010 (Rennes, France; Kaunas, Lithuania; Bradford, UK; Barcelona and the Urretza/Azpeita/Beasain area of the Basque Country, Spain), May 2010 (the Heraklion region of Crete, Greece; Avilés region in Asturias, Spain) and June 2010 (Valencia, Spain).

During sample collection, temperature, free chlorine residual, and pH were measured where possible. Sample vials contained a quenching agent and preservative in accordance with US Environmental Protection Agency

(USEPA) Methods 551.1 and 552.3 (USEPA 1995, 2003). This was sodium sulphite for THMs and CH, and ammonium chloride for HAAs, HANs, HKs, and CP. With the exception of the HAA samples, a buffer was used to lower the sample pH to 4.8–5.5 to inhibit base-catalysed degradation of the HANs, HKs and CH and to standardise the pH of all of the samples. Samples were either stored overnight in a refrigerator and shipped the following day or shipped immediately with ice packs by 24- or 48-h courier service. The temperature on arrival was noted. All samples were analysed within 1 week of collection.

DBP analysis

THM₄ (trichloro- [TCM], bromodichloro- [BDCM], dibromochloro- [DBCM], and tribromomethane [TBM]), HAN₄ (bromochloro- [BCAN], dibromo- [DBAN], dichloro- [DCAN], and trichloroacetonitrile [TCAN]), HK₂ (1,1-dichloro- [1,1-DCP] and 1,1,1-trichloropropanone [1,1,1-TCP]), CH, and CP were extracted using a modified form of USEPA Method 551.1 (USEPA 1995). This method involved salted liquid/liquid extraction with solvent extracts analysed by gas chromatography (GC) (Agilent 6890, Santa Clara, CA, USA) with micro electron capture detection (μ ECD). HAA₉ (monochloro- [MCAA], monobromo-, dichloro- [DCAA], trichloro- [TCAA], bromochloro- [BCAA], dibromo- [DBAA], bromodichloro- [BDCAA], dibromochloro- [DBCAA], and tribromoacetic acid [TBAA]) were analysed using a modified form of USEPA Method 552.3 (USEPA 1995; Tung *et al.* 2006). The samples were extracted and derivatised and the derivatised HAAs (methyl esters) were measured using GC- μ ECD (Agilent 6890). All samples were analysed in duplicate. The limit of quantification (LOQ) for each DBP was $1 \mu\text{g L}^{-1}$, with the exception of MCAA (LOQ $2 \mu\text{g L}^{-1}$).

All analytes were quantified using a ZB1-MS column (Phenomenex UK Ltd, Cheshire, UK, equivalent to DB1) and at least 50% of the samples were also run using a ZB5-MS column (Phenomenex UK Ltd, equivalent to DB5) for confirmation.

Bromine incorporation factor (BIF)

The BIF describes the molar contribution of all brominated species. All BIF values were normalised by dividing by the

number of halogens for comparison. For example, a BIF of 0 for the DHAAs corresponds to only DCAA being present, a BIF of 1 corresponds to only DBAA present and a BIF of 0.5 means that the ‘average’ species was BCAA.

For THMs, the normalised BIF can be calculated by Equation (1) (Gould *et al.* 1983; Symons *et al.* 1993):

$$\text{BIF (THMs)} = \left(\frac{1 \times [\text{BDCM}] + 2 \times [\text{DBCM}] + 3 \times [\text{TBM}]}{[\text{TCM}] + [\text{BDCM}] + [\text{DBCM}] + [\text{TBM}]} \right) \div 3 \quad (1)$$

where the THM concentrations are on a molar basis.

For HAAs, separate BIF values were calculated for the trihalogenated species (THAAs) (similar to the THMs) and the dihalogenated HAAs (DHAAs) (Krasner *et al.* 2008). The normalised BIF for DHAAs can be calculated as shown (Equation (2)):

$$\text{BIF (DHAAs)} = \left(\frac{1 \times [\text{BCAA}] + 2 \times [\text{DBAA}]}{[\text{DCAA}] + [\text{BCAA}] + [\text{DBAA}]} \right) \div 2 \quad (2)$$

Similarly, the BIF for dihaloacetonitriles (DHANs) was also calculated.

RESULTS AND DISCUSSION

The sites in Crete and Kaunas were groundwaters, whilst the other sites treated surface waters or a mixture of water types. Five of the regions were sampled when the water was cold and three when the water was warm. Water quality data and information on the water treatment processes are presented in Table 1. The THM and HAA results – segmented by cold or warm water – are presented in Figures 1(a) and 2(b) and results for the other DBPs are presented in Tables 2(a) and (b). Molar ratios are presented in Table 3.

THMs and HAAs

As expected, THM formation was lowest in the groundwater sites (Crete median $10 \mu\text{g L}^{-1}$; Kaunas median $8 \mu\text{g L}^{-1}$). The Kaunas site had historical low chlorine doses ($<1.0 \text{ mg L}^{-1}$) and residuals ($\leq 0.3 \text{ mg L}^{-1}$) which

Table 1a | Summary of treatment and disinfection processes at the water works

Water works	Source	Treatment	Disinfectant
Asturias (Spain)	Surface water	Filtration	Chlorine
Barcelona (Spain)	Surface water	Permanganate oxidation, coagulation, sedimentation, chlorine dioxide oxidation, filtration, GAC	Chlorine
Basque Country (Spain)	Surface water Groundwater	Coagulation, sedimentation, filtration Filtration	Ozone and chlorine Chlorine
Valencia (Spain)	Surface water (97%) and groundwater Groundwater	Coagulation, sedimentation, filtration No treatment	Ozone and chlorine Chlorine
Bradford (UK)	Upland surface	Coagulation, sedimentation, filtration	Chlorine
Rennes (France)	4% artificially recharged groundwater and 96% surface water	Coagulation, sedimentation, filtration (granular media), GAC	Ozone and chlorine
Kaunus (Lithuania)			
KAU1	Groundwater	Filtration	Chlorine
KAU2	Groundwater	No treatment	Chlorine
KAU3	Groundwater	No treatment	Chlorine
KAU4	Groundwater	No treatment	Chlorine
Heraklion (Greece)	Groundwater	No treatment	Chlorine

GAC – granular activated carbon.

Table 1b | Characteristics of water quality of raw water and drinking water (median values) in the studied regions

Water works	Raw water		Treated water			
	TOC (mg/L)	Br (mg/L)	TOC (mg/L)	pH	Br (mg/L)	Residual chlorine (mg/L)
<i>Spain</i>						
Asturias	na	na	1.8	7.9	<LOQ	0.7
Barcelona	>5.0	0.50–1.20	1.9	na	0.16	na
Basque Country	1.6	na	1.2	7.9	<LOQ	0.6
Valencia	surface <0.1 ground na	na na	na na	7.4 7.3	0.05 na	0.5 0.1
<i>United Kingdom</i>						
Bradford	na	na	1.4	7.6	<LOQ	0.3
<i>France</i>						
Rennes	1.7	na	1.8	7.7	0.04	0.1
<i>Lithuania</i>						
Kaunus						
KAU1	3.1	na	na	7.6	0.05	0.2
KAU2	3.1	na	na	7.4	0.05	0.0
KAU3	3.1	na	na	7.4	0.05	0.0
KAU4	3.1	na	na	7.4	0.05	0.0
<i>Greece</i>						
Heraklion (Crete)	na	na	0.5	7.6	na	<0.1

na: data not available. Where median values are not available, a range has been given.

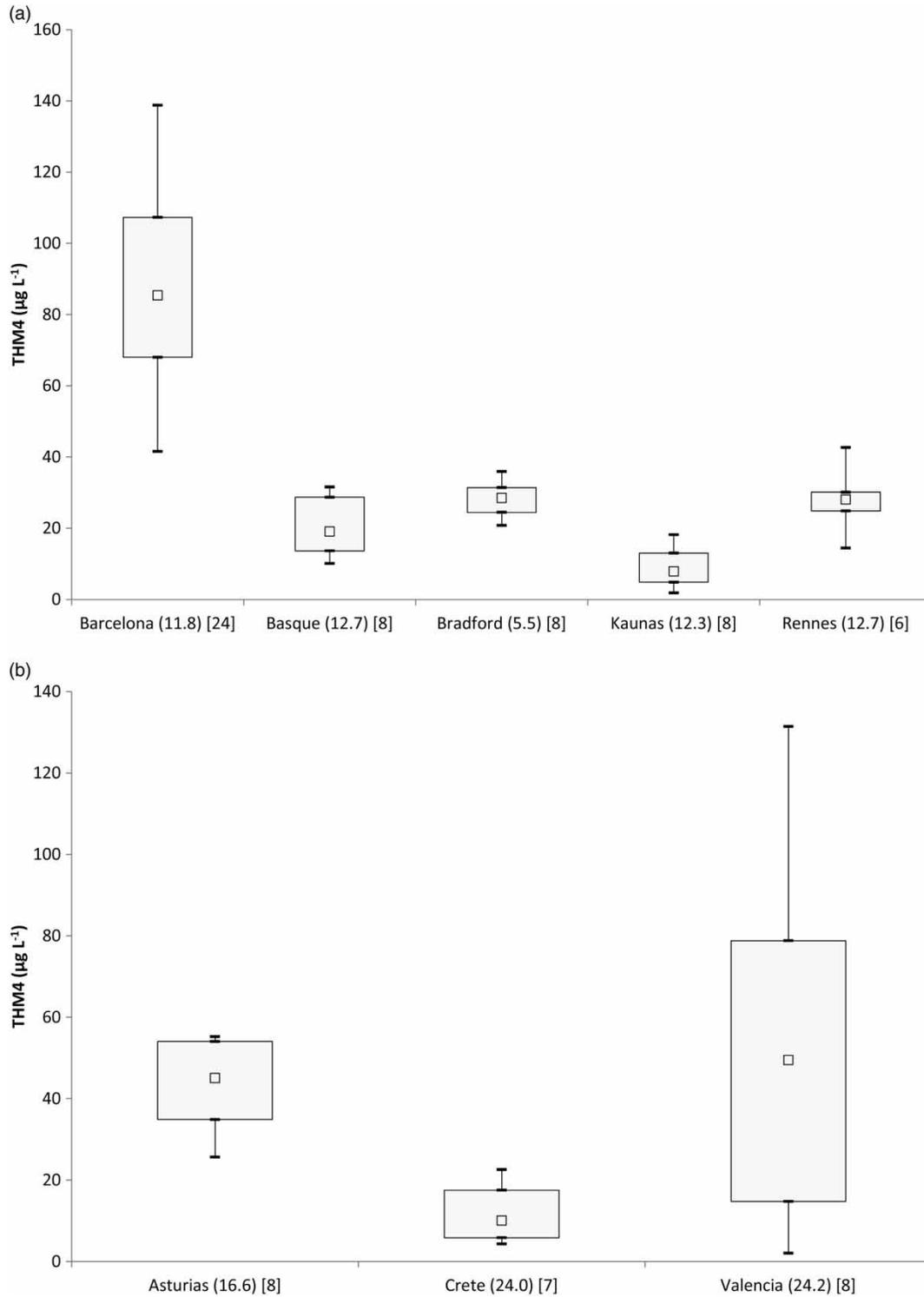


Figure 1 | (a) Occurrence of THMs in regions sampled when the water was cold, where median temperature (°C) and number of samples collected (N) for each region provided. The bottom and top of the box show the 25th and 75th percentile values, respectively, and the top and bottom of the whiskers show the maximum and minimum values, respectively. Small squares inside the boxes show the median values. (b) Occurrence of THMs in regions sampled when the water was warm.

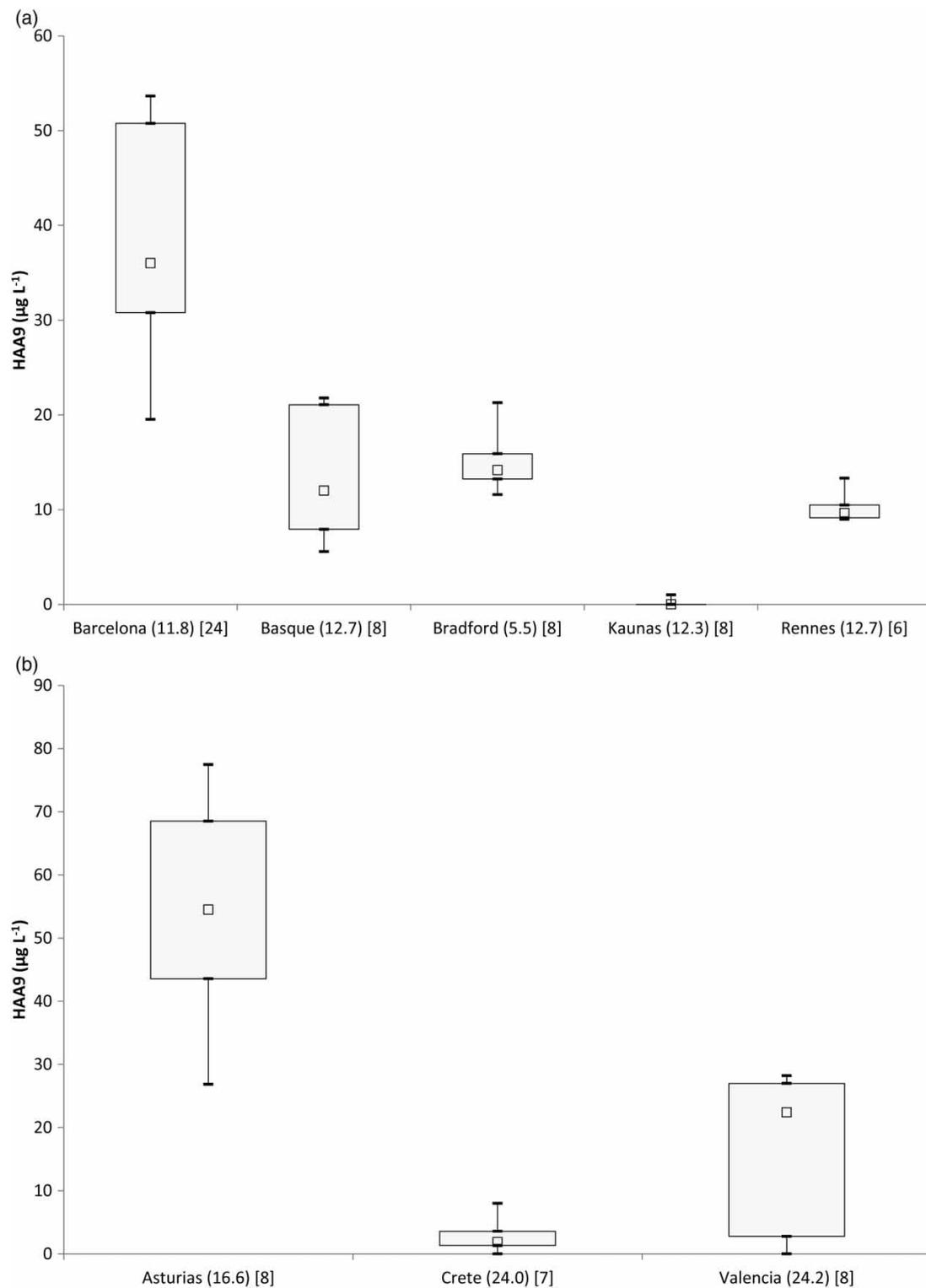


Figure 2 | (a) Occurrence of HAAs in regions sampled when the water was cold, where median temperature (°C) and number of samples collected [N] for each region provided. (b) Occurrence of HAAs in regions sampled when the water was warm.

Table 2a | Concentration and speciation of DHANS ($\mu\text{g L}^{-1}$), with number of samples (*N*) indicated

Location	DCAN Range	Median	BCAN Range	Median	DBAN Range	Median
Barcelona [24]	Nd–2.9	Nd	Nd–3.0	1.6	Nd–8.0	4.5
Basque [8]	Nd–1.6	0.8	Nd	Nd	Nd	Nd
Bradford [8]	1.2–1.9	1.6	Nd	Nd	Nd	Nd
Kaunas [8]	Nd	Nd	Nd	Nd	Nd	Nd
Rennes [6]	Nd	Nd	Nd	Nd	Nd–1.3	1.1
Asturias [8]	1.3–4.4	2.7	Nd–1.0	Nd	Nd	Nd
Crete [7]	Nd	Nd	Nd	Nd	Nd–1.2	Nd
Valencia [8]	Nd	Nd	Nd–2.1	1.4	Nd–3.6	2.5

Nd – not detected.

Table 2b | Concentration of HKS, CP, and CH ($\mu\text{g L}^{-1}$)

Location	1,1-DCP		1,1,1-TCP		CP		CH	
	Range	Med.	Range	Med.	Range	Med.	Range	Med.
Barcelona [24]	Nd	Nd	Nd–2.2	Nd	Nd–1.3	Nd	Nd–12.1	Nd
Basque [8]	Nd	Nd	Nd–1.6	1.1	Nd	Nd	Nd–4.1	2.0
Bradford [8]	Nd	Nd	1.4–2.5	1.9	Nd	Nd	1.1–2.5	1.6
Kaunas [8]	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Rennes [6]	Nd	Nd	Nd	Nd	Nd	Nd	Nd–1.6	0.5
Asturias [8]	Nd–2.7	Nd	Nd–4.2	2.5	Nd–3.8	Nd	5.1–23.2	15.3
Crete [7]	Nd–1.8	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Valencia [8]	Nd	Nd	Nd	Nd	Nd	Nd	Nd–3.3	0.5

Table 3 | Molar ratios of THMs:HAAs, THMs:HANS, and THAAs:DHAAs

Location	Ratio of THMs:HAAs (range [median])	Ratio of TBM:DBAN (range [median])	Ratio of TCM:DCAN (range [median])	Ratio of THAAs:DHAAs (range [median])
Barcelona	0.5–3.5 [1.5]	Nc ²	8,9 ^b	0.2–0.4 [0.3]
Basque	1.5–3.6 [2.0]	6–12 [7]	13–19 [17]	0.1–0.9 [0.5]
Bradford	1.6–3.0 [2.0]	Nc ²	9–19 [11]	0.4–0.8 [0.6]
Kaunas	Nc ¹	Nc ²	Nc ²	Nc ³
Rennes	1.1–4.4 [2.8]	5–6 [6]	Nc ²	0.1–0.8 [0.6]
Asturias	0.5–2.4 [0.9]	Nc ²	6–32 [10]	0.7–3.2 [0.8]
Crete	1.8–11.6 [3.0] ^a	10,13 ^b	Nc ²	0.3, 0.4 ^b
Valencia	2.0–4.9 [3.3] ^a	5–8 [6]	Nc ²	0.7–0.9 [0.9]

^aDoes not include one sample where HAAs were not detected.^bThe ratio was only calculated for two samples in this region and both values are listed.Nc¹ – Not calculable, as HAAs were only detected in one sample at $1 \mu\text{g L}^{-1}$.Nc² – Not calculable, as DBAN or DCAN were not detected.Nc³ – Not calculable, as no THAAs were detected.

would also impact DBP levels. TBM was the predominant THM in the waters from Crete comprising 82–100% of the THMs formed (no TCM was detected), whereas TCM was the predominant species found in the waters from Kaunas. In a previous study (Kampioti & Stephanou 2002), it was reported that bromide concentrations were higher in raw waters of certain coastal cities in Greece. The highest concentrations of THMs were in Barcelona (median $85 \mu\text{g L}^{-1}$), Valencia (median $\sim 50 \mu\text{g L}^{-1}$) and Asturias (median $45 \mu\text{g L}^{-1}$). Some of the Barcelona sites were high in bromine-containing THMs. One of the rivers (Llobregat) used as a source of drinking water in Barcelona has been shown to be high in bromide ($0.5\text{--}1.2 \text{ mg L}^{-1}$) (GE Power & Water 2010). TBM was the predominant species in the waters from Valencia, whereas TCM was the predominant species in the waters from Asturias. In some of the surface water sites,

the presence of bromide impacted both the THM speciation and the class sum on a weight basis, as TBM weighs approximately twice that of TCM.

Again, the concentration of HAAs was very low in the two groundwater sites (Crete median $2 \mu\text{g L}^{-1}$; Kaunus median not detected [Nd]). In keeping with the THM data, only brominated species were detected in the waters from Crete and DCAA was the only HAA detected at Kaunus and only in one sample. As with the THMs, the highest concentrations of HAAs were in Barcelona (median $\sim 35 \mu\text{g L}^{-1}$), Valencia (median $22 \mu\text{g L}^{-1}$), and Asturias (median $55 \mu\text{g L}^{-1}$). Chlorine- and bromine-containing HAAs were formed in Barcelona and Valencia, whereas DCAA and TCAA were the dominant species in Asturias.

The molar ratio of THMs to HAAs was highest in waters from Valencia (median 3.3), Crete (median 3.0) and Rennes (median 2.8) and was lowest in waters from Asturias (median 0.9). This may have been related to the type of natural organic matter present, the way in which the water was treated and/or it may have been indirectly related to the presence of bromide. For example, the bromine-containing analogues of TCAA are not that stable (Pourmoghaddas & Dressman 1993), so they may have formed and then degraded, resulting in a higher THM:HAA ratio. Note, chlorine- and bromine-containing THMs and HAAs also formed in waters from Rennes.

The molar ratio of THAAs to DHAAs was also examined. In general, there were fewer THAAs present than DHAAs. THAAs are more associated with waters high in humic substances (Reckhow *et al.* 1990; Bond *et al.* 2011). Also, coagulation and ozonation are better at removing TCAA precursors than DCAA precursors (Reckhow & Singer 1984). Additionally, this ratio can be lower if bromine-containing THAAs form and then degrade.

Other DBPs

The highest occurrence of CH was in Asturias (median $15 \mu\text{g L}^{-1}$). Although Barcelona had a maximum concentration of CH of $12 \mu\text{g L}^{-1}$, the median level in that region was Nd. Because of the high level of bromide in this region, bromine-containing analogues of CH were probably formed. However, those species were not included in USEPA Method 551.1. Likewise Valencia, which had

high THM formation dominated by bromine-containing species, had little CH (median $0.5 \mu\text{g L}^{-1}$). Alternatively, there was more CH occurrence in the Basque Country and Bradford (medians 2.0 and $1.6 \mu\text{g L}^{-1}$, respectively) which were dominated by chlorine-containing THMs and HAAs.

DHANs were detected in most of the waters studied. In other research, the concentration of THMs was typically around ten times higher than that of the DHANs (Oliver 1983). In this study, we examined the molar ratio of TCM to DCAN and that of TBM to DBAN (Table 3) to see how the ratio of these two classes compared, with a focus on the fully chlorine-containing or the fully bromine-containing species. DBAN was the only HAN detected in waters from Crete and only in two of seven samples with TBM to DBAN molar ratios of 10 and 13. In Rennes, BDCM was the predominant THM species, whereas DBAN was the only HAN detected. Thus, there was more bromine incorporation into the DHANs than the THMs in this region, which is discussed further below. In Bradford, which was dominated by chlorine-containing THMs and HAAs, DCAN was the only HAN detected. The median molar ratio of TCM to DCAN in this region was 11. In regions in Spain dominated by chlorine-containing THMs and HAAs, DCAN was the predominant DHAN. The median TCM:DCAN ratios in Asturias and the Basque Country were 10 and 8, respectively. In regions in Spain dominated by bromine-containing THMs and HAAs, DBAN was the predominant DHAN (maximum of $8 \mu\text{g L}^{-1}$ in Barcelona). The median TBM:DBAN ratios in Barcelona and Valencia were 7 and 6, respectively. In general, the ratio of TBM:DBAN was not as high as that of TCM:DCAN. This may have been due (in part) to a higher degree of bromine incorporation into HANs than into THMs, consistent with the findings of Obolensky & Singer (2005).

The highest concentrations of other chlorine-containing DBPs (1,1,-DCP, 1,1,1-TCP, and CP) were found in Asturias, where THMs and HAAs were dominated by chlorine-containing species. Other regions dominated by chlorine-containing THMs and HAAs (Bradford and the Basque Country) also had some 1,1,1-TCP formation. In regions in this study dominated by bromine-containing THMs and HAAs, it is likely that bromine-containing HKs and

Table 4 | Normalised BIFs (range, [median])

Location	THM BIF (range [median])	THAA BIF (range [median])	DHAA BIF (range [median])
Barcelona	0.07–0.84 [0.61]	0.15–0.56 [0.43]	0.17–1.00 [0.60]
Basque	0.19–0.33 [0.28]	0.00–0.17 [0.05]	0.11–0.26 [0.21]
Bradford	0.08–0.11 [0.08]	Nc ¹	0.00–0.14 [0.07]
Kaunas	0.07–1.00 [0.63]	Nc ²	Nc ²
Rennes	0.38–0.62 [0.52]	0.18–0.67 [0.37]	0.43–0.52 [0.48]
Asturias	0.05–0.21 [0.05]	0.02–0.08 [0.02]	0.03–0.18 [0.03]
Crete	0.89–1.00 [0.96]	0.00–1.00 [0.00]	0.00–1.00 [1.00]
Valencia	0.52–0.63 [0.54]	0.31–0.37 [0.32]	0.46–1.00 [0.59]

Nc¹ – not calculable as no brominated species were detected.

Nc² – not calculable as no HAAs were detected.

halonitromethanes formed, which were not included in USEPA Method 551.1.

Bromine incorporation factor

In epidemiology studies, finding an association between brominated DBP species (e.g. THMs and/or HAAs) and a particular adverse health effect may be due to the presence of other brominated DBPs of higher health concern (e.g. HANs, halonitromethanes, haloacetaldehydes). This is of particular importance, as the brominated analogues of many DBPs (e.g. CP, CH) are not measured in most occurrence studies. Moreover, in cases where the brominated analogues are not determined, it may be possible to estimate the occurrence of the missing DBPs based on the BIF. Here the BIFs have been normalised (Table 4). Normalised BIFs range from 0 to 1. For THMs a value of 1 indicates that only TBM is present and a value of 0 indicates that only TCM is present. The THM BIF medians for each region ranged from 0.05 to 0.96, reflecting the diverse nature of the samples where brominated THMs can often be the dominant species. The THAA median values ranged from 0 to 0.43, indicating that there was less bromine incorporation into THAAs than THMs. A similar observation was made by Krasner *et al.* (2008), who attributed the phenomenon to the presence of the carboxylic group in the THAAs causing steric interference in the incorporation of bromine atoms. They also suggested that the brominated THAAs formed may have degraded to some extent. The DHAA BIF median values spanned a

higher range (0.03–1.00) than the THAA BIF median values and were similar to the THM BIF median values, perhaps due to their greater stability than the THAAs. In surface or groundwaters with high levels of bromide (e.g. Barcelona, Crete), median BIFs for THMs and DHAAs were high (0.6–1.0), whereas in waters dominated by chlorine-containing DBPs (e.g. Bradford, Asturias), median BIFs for these two classes of DBPs were low (0.03–0.08). Thus computation of BIF median values provides a good summary of bromine incorporation.

In the same way as Obolensky & Singer (2005), scatter-plots were constructed with all available results to investigate the six possible pairwise associations between the bromine fractions (normalised BIFs) measured for the four DBP classes (Figure 3). Dashed diagonal lines are provided as reference points only for equivalence between bromine fractions for each class pair. The number of observations (N) and Spearman's Rank correlation coefficient (S) are indicated on each plot. Correlation coefficients (S) ranged from 0.298 to 0.936. The DHAN class had the lowest correlations (0.298–0.462) with the THMs and HAAs. None of the DHAN correlations was statistically significant ($p > 0.0001$). However, most importantly was that the bromine fractions were substantially higher for the DHANs than that of the THMs or HAAs, indicating that bromine incorporation was consistently higher in the DHANs. With a much larger dataset of $N > 1000$ (Obolensky & Singer 2005, data from ICR), it was found that DHANs also had higher bromine incorporation than the other classes. The strongest correlation was observed for

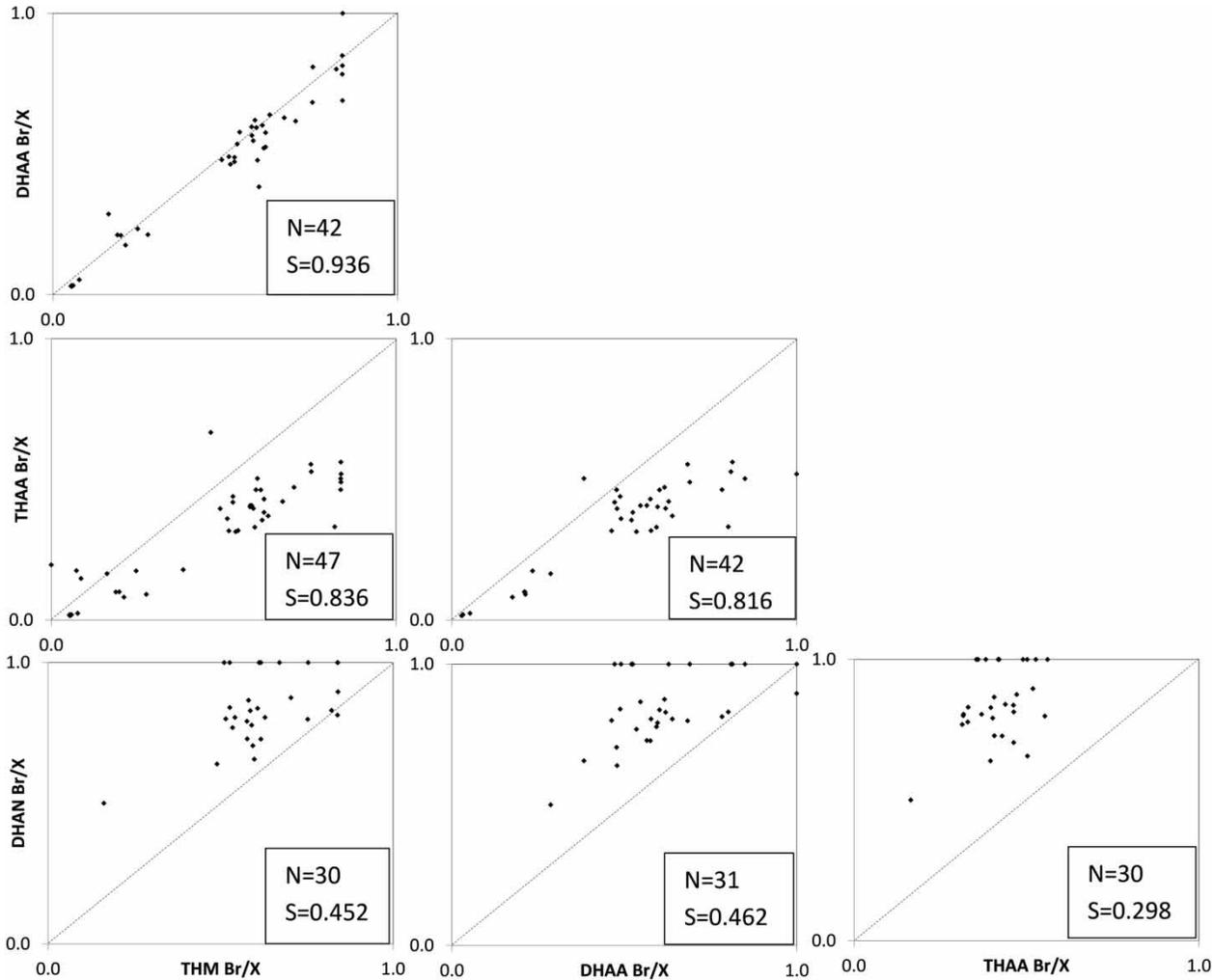


Figure 3 | Scatterplot array of bromine fraction in four DBP classes showing all data (number of observations [N] and Spearman's Rank correlation coefficient [S]). Dashed line indicates $y = x$ for reference (adapted from Obolensky & Singer 2005).

the class pair THMs/DHAAs, with an S of 0.936. Moreover, the data were (in general) clustered about the diagonal line. Thus, bromine incorporation into either class of DBPs was essentially the same. The THAA class also had strong correlations with the THMs and DHAAs ($S = 0.816\text{--}0.836$). The THM and HAA correlations were statistically significant ($p < 0.0001$). However, the data for this comparison were below the dashed lines, indicating that bromine incorporation was consistently lower in the THAAs than in the THMs or DHAAs. Thus, in an epidemiology study in which there is an association between bromine-containing THMs and an adverse health effect,

this may also be associated with bromine-containing HAAs and, in particular, bromine-containing DBPs of health concern (e.g. DHANs).

CONCLUSIONS

The levels of DBPs formed in the European waters studied was varied, which reflected the diverse regions from which the samples were collected, the different treatment/disinfection processes, and the different source waters. Levels of THMs were highest in Barcelona (Spain) and HAAs

were highest in Asturias (Spain). These regions also formed the greatest levels of DCAN (Asturias); BCAN and DBAN (Barcelona); 1,1-DCP, 1,1,1-TCP, CP, and CH (Asturias). Barcelona had the highest levels of bromine-containing THMs, HAAs, and HANs, which may pose a greater risk to health than their chlorinated analogues. Although fewer THMs and HAAs were formed in Crete (Greece) or Rennes (France), the DBPs formed were dominated by bromine-containing or bromochloro species. So it is not just the total amount of DBPs formed that is an issue, but the formation of the more toxic species that must be considered.

This study showed that there was some variability in the ratio of THMs:HAAs, THMs:HANs, and THAAs:DHAAs, where the ratios were often different for the waters dominated by bromine-containing DBPs than those containing more chlorine-containing species. So THMs by themselves may not be a good surrogate for indicating the presence of other DBPs of health or regulatory concern. However, an examination of the BIFs showed that a shift in speciation to the more bromine-containing species, which can occur in waters high in bromide or in systems with low chlorine/bromide ratios, resulted in similar shifts in a variety of measured DBPs. This suggests that individual THM species may be good surrogates for the presence of other bromine-containing DBPs of health concern. Moreover, the relative amount of bromine incorporation was highest in the DHANs and was lower in the THAAs, which agreed with results from other studies.

Future occurrence studies, especially those providing exposure assessments for epidemiology studies, should consider including methods besides USEPA Method 551.1, in order to measure bromine-containing analogues of CP and CH, which are part of emerging classes of DBPs of health concern.

ACKNOWLEDGEMENTS

The work was (partly) funded by HIWATE (www.hiwate.org). HIWATE was a three-and-a-half year Specific Targeted Research Project, funded under the EU Sixth Framework Programme for Research and Technological Development

by the Research Directorate-Biotechnology, Agriculture and Food Research Unit (Contract no. Food-CT-2006-036224). The HIWATE consortium consisted of more participants than the current author list and we would like to thank them for their input. We would also like to acknowledge the contribution of colleagues who have supported the sample collection and dispatch, including Susan Edwards, Rachel Smith, Nina Iszatt, Asta Danileviciute, Sophia Kargaki, Christine Monfort, and Vicky Patelarou. We are also very grateful to Howard S. Weinberg for his helpful advice regarding the DBP analyses.

REFERENCES

- Bond, T., Goslan, E. H., Parsons, S. A. & Jefferson, B. 2011 Treatment of disinfection by-product precursors. *Environ. Technol.* **32** (1), 1–25.
- Born in Bradford 2011 Available from: www.borninbradford.nhs.uk/research.htm (accessed 7 January 2013).
- Bougeard, C. M. M., Goslan, E. H., Jefferson, B. & Parsons, S. A. 2010 Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Res.* **44** (3), 729–740.
- GE Power & Water 2010 Trihalomethanes (THM) Precursor Reduction of Surface Water by EDR Technology. Available from: www.gewater.com/pdf/Technical%20Papers_Cust/Americas/English/TP1179EN.pdf (accessed 7 January 2013).
- Goslan, E. H., Krasner, S. W., Bower, M., Rocks, S. A., Holmes, P., Levy, L. S. & Parsons, S. A. 2009 A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland. *Water Res.* **43**, 4698–4706.
- Gould, J. P., Fitchhorn, L. E. & Urheim, E. 1983 Formation of brominated trihalomethanes: extent and kinetics. In: *Water Chlorination: Environmental Impact and Health Effects* (R. L. Jolly, ed). Vol. 4, Ann Arbor Science Publishing, Ann Arbor, MI, USA, pp. 297–310.
- Health Canada 1995 *A National Survey of Chlorinated Disinfection by-Products in Canadian Drinking Water*. Environmental Health Directorate, Health Canada, Ottawa, Ontario, Canada. Available from: www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/byproducts-sousproduits/index-eng.php (accessed 7 January 2013).
- Jeong, C. H., Wagner, E. D., Siebert, V. R., Anduri, S., Richardson, S. D., Daiber, E. J., McKague, A. B., Kogevinas, M., Villanueva, C. M., Goslan, E. H., Luo, W., Isabelle, L. M., Pankow, J. F., Grazuleviciene, R., Cordier, S., Edwards, S. C., Righi, E., Nieuwenhuijsen, M. J. & Plewa, M. J. 2012 Occurrence and toxicity of disinfection byproducts in European drinking waters in relation with the HIWATE

- epidemiology study. *Environ. Sci. Technol.* **46** (21), 12120–12128.
- Kampioti, A. A. & Stephanou, E. G. 2002 [The impact of bromide on the formation of neutral and acidic disinfection by-products \(DBPs\) in Mediterranean chlorinated drinking water](#). *Water Res.* **36** (10), 2596–2606.
- Krasner, S. W., McGuire, M. J., Jacangelo, J. G., Patania, N. L., Reagan, K. M. & Aieta, E. M. 1989 The occurrence of disinfection by-products in US drinking water. *J. Am. Water Works Assoc.* **81** (8), 41–53.
- Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Scilimenti, M. J., Onstad, G. D. & Thruston Jr., A. D. 2006 [Occurrence of a new generation of disinfection byproducts](#). *Environ. Sci. Technol.* **40**, 7175–7185.
- Krasner, S. W., Lee, C. F. T., Chinn, R., Hartono, S., Weinberg, H., Richardson, S. D., Pressman, J. G., Speth, T. F., Miltner, R. J. & Simmons, J. E. 2008 Bromine incorporation in regulated and emerging DBPs and the relative predominance of mono-, di-, and trihalogenated DBPs. In: *Proceedings of the American Water Works Association Water Quality Technology Conference*. American Water Works Association, Denver, CO, USA.
- McGuire, M. J., McLain, J. L. & Obolensky, A. 2002 *Information Collection Rule Data Analysis*. American Water Works Association Research Foundation and American Water Works Association, Denver, CO, USA.
- Muellner, M. G., Wagner, E. D., McCalla, K., Richardson, S. D., Woo, Y. T. & Plewa, M. J. 2007 [Haloacetonitriles vs. regulated haloacetic acids: are nitrogen-containing DBPs more toxic?](#) *Environ. Sci. Technol.* **41** (2), 645–651.
- Nieuwenhuijsen, M. J., Smith, R., Golfinopoulos, S., Best, N., Bennett, J., Aggazzotti, G., Righi, E., Fantuzzi, G., Bucchini, L., Cordier, S., Villanueva, C. M., Moreno, V., La Vecchia, C., Bosetti, C., Vartiainen, T., Rautiu, R., Toledano, M., Iszatt, N., Grazuleviciene, R. & Kogevinas, M. 2009 [Health impacts of long-term exposure to disinfection by-products in drinking water in Europe: HIWATE](#). *J. Water Health* **7** (2), 185–207.
- Obolensky, A. & Singer, P. C. 2005 [Halogen substitution patterns among disinfection byproducts in the Information Collection Rule database](#). *Environ. Sci. Technol.* **39** (8), 2719–2730.
- Oliver, B. G. 1983 [Dihaloacetonitriles in drinking water: algae and fulvic acid as precursors](#). *Environ. Sci. Technol.* **17** (2), 80–83.
- Plewa, M. J. & Wagner, E. D. 2009 *Quantitative Comparative Mammalian Cell Cytotoxicity and Genotoxicity of Selected Classes of Drinking Water Disinfection By-Products*. American Water Works Association Research Foundation, Denver, CO, USA.
- Plewa, M. J., Wagner, E. D., Jazwierska, P., Richardson, S. D., Chen, P. H. & McKague, A. B. 2004 [Halonitromethane drinking water disinfection byproducts: chemical characterization and mammalian cell cytotoxicity and genotoxicity](#). *Environ. Sci. Technol.* **38** (1), 62–68.
- Pourmoghaddas, H. & Dressman, R. C. 1993 Determination of nine haloacetic acids in finished drinking water. In: *Proceedings of the American Water Works Association Water Quality Technology Conference*. American Water Works Association, Denver, CO, USA.
- Reckhow, D. A. & Singer, P. C. 1984 The removal of organic halide precursors by preozonation and alum coagulation. *J. Am. Water Works Assoc.* **76** (4), 151–157.
- Reckhow, D. A., Singer, P. C. & Malcolm, R. L. 1990 [Chlorination of humic materials: Byproduct formation and chemical interpretations](#). *Environ. Sci. Technol.* **24** (11), 1655–1664.
- Symons, J. M., Krasner, S. W., Simms, L. A. & Scilimenti, M. 1993 Measurement of THM and precursor concentrations revisited: the effect of bromide ion. *J. Am. Water Works Assoc.* **85** (1), 51–62.
- Tung, H.-H., Unz, R. F. & Xie, Y. F. 2006 HAA removal by GAC adsorption. *J. Am. Water Works Assoc.* **98** (6), 107–112.
- USEPA 1995 *Method 551.1: Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-liquid Extraction and Gas Chromatography with Electron-capture Detection*. Revision 1.0, National Exposure Research Laboratory, USEPA Office of Research and Development, Cincinnati, OH, USA.
- USEPA 2003 *Method 552.3: Determination of Haloacetic acids and Dalapon in Drinking Water by Liquid-liquid Microextraction, Derivatization and Gas Chromatography with Electron Capture Detection*. Revision 1.0, Technical Support Center, USEPA Office of Ground Water and Drinking Water, Cincinnati, OH, USA.
- Villanueva, C. M., Cantor, K. P., Cordier, S., Jaakkola, J. J., King, W. D., Lynch, C. F., Porru, S. & Kogevinas, M. 2004 [Disinfection byproducts and bladder cancer: A pooled analysis](#). *Epidemiology* **15** (3), 357–367.
- Villanueva, C. M., Castaño-Vinyals, G., Moreno, V., Carrasco-Turigas, G., Aragonés, N., Boldo, E., Ardanaz, E., Toledo, E., Altzibar, J. M., Zaldua, I., Azpiroz, L., Goñi, F., Tardón, A., Molina, A. J., Martín, V., López-Rojo, C., Jiménez-Moleón, J. J., Capelo, R., Gómez-Acebo, I., Peiró, R., Ripoll, M., Gracia-Lavedan, E., Nieuwenhuijsen, M. J., Rantakokko, P., Goslan, E. H., Pollán, M. & Kogevinas, M. 2012 [Concentrations and correlations of disinfection by-products in municipal drinking water from an exposure assessment perspective](#). *Environ. Res.* **114**, 1–11.
- Williams, D. T., LeBel, G. L. & Benoit, F. M. 1997 [Disinfection by-products in Canadian drinking water](#). *Chemosphere* **34** (2), 299–316.