Science of the Total Environme

Science of the Total Environment 407 (2009) 4189-4206



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Models for predicting disinfection byproduct (DBP) formation in drinking waters: A chronological review

Shakhawat Chowdhury^{a,*}, Pascale Champagne^a, P. James McLellan^b

^a Department of Civil Engineering, Queen's University, Kingston, ON, Canada K7L3N6

^b Department of Chemical Engineering, Queen's University, Kingston, ON, Canada K7L3N6

ARTICLE INFO

Article history: Received 2 November 2008 Received in revised form 29 March 2009 Accepted 6 April 2009 Available online 6 May 2009

Keywords: Predictive models DBP formation Model variables Natural organic matter (NOM) Model review

ABSTRACT

Disinfection for the supply of safe drinking water forms a variety of known and unknown byproducts through reactions between the disinfectants and natural organic matter. Chronic exposure to disinfection byproducts through the ingestion of drinking water, inhalation and dermal contact during regular indoor activities (e.g., showering, bathing, cooking) may pose cancer and non-cancer risks to human health. Since their discovery in drinking water in 1974, numerous studies have presented models to predict DBP formation in drinking water. To date, more than 48 scientific publications have reported 118 models to predict DBP formation in drinking waters. These models were developed through laboratory and field-scale experiments using raw, pretreated and synthetic waters. This paper aims to review DBP predictive models, analyze the model variables, assess the model advantages and limitations, and to determine their applicability to different water supply systems. The paper identifies the current challenges and future research needs to better control DBP formation. Finally, important directions for future research are recommended to protect human health and to follow the best management practices.

© 2009 Elsevier B.V. All rights reserved.

Contents

1.	Introduction	189
2.	Disinfection	191
	2.1. Disinfectants and disinfection approaches	191
	2.2. Disinfection byproducts formation and operational challenge	192
	2.3. Regulating DBP exposure concentrations	193
3.	Models and their potential applications	
	3.1. Predictive models for DBPs formation	193
	3.2. Potential application of models	197
4.	Future research needs	197
	Summary and conclusions	
Ack	nowledgement	205
Refe	erences	205

1. Introduction

The use of chlorine for drinking water disinfection has virtually eliminated most waterborne diseases resulting from drinking water ingestion (USCDC, 1997). However, chlorination forms a number of

* Corresponding author. *E-mail address*: Shakhawat@ce.queensu.ca (S. Chowdhury). disinfection byproducts (DBPs), which are of potential concern. Some of these DBPs have cancer risks as well as other acute and chronic effects to human health (King and Marrett 1996; National Cancer Institute of Canada, 1998; Wigle, 1998; Mills et al., 1998; Waller et al., 1998; King et al., 2000; Richardson et al., 2002; Villanueva et al., 2004; Xu and Weisel, 2005). To date, toxicological and epidemiological studies have characterized the effects of approximately thirty DBPs to human and animal health (Bull et al., 1985, 1990; Smith et al., 1988; Pereira, 1996; Richardson, 2005). Since their discovery in 1974, a

^{0048-9697/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.scitotenv.2009.04.006

Table 1

Components of DBPs in drinking water, their effects and regulatory limits.

				Effects		Toxicit humai		Regulatio (µg/L)	ons			
Main Group	Compounds	Acronym	Main disinfectant*	Animal	Human	RfD	SF	HC (2007)	USEPA (2006)	WHO (2004)	Aus-NZ (2004)	UK (2000)
Trihalomethanes (THMs)	Chloroform	TCM	Chlorine	Liver tumours	B-2	0.01	0.01			300		
(THINS)	Bromodichloromethane	BDCM	Chlorine	Kidney tumour	B-2	0.02	0.062	16		60		
	Bromoform	DBCM	Chlorine, ozone	Colon tumours	B-2	0.02	0.0079			100		
	Dibromochloromethane	TBM	Chlorine	Liver tumours	С	0.02	0.0084			100		
TTHMs				tumours				100	80		250	100
Haloacetic acids (HAAs)	Bromochloroacetic acid	BCAA	Chlorine	Liver tumours								
()	Bromodichloroacetic acid	BDCAA	Chlorine	Liver tumours								
	Chlorodibromoacetic acid	CDBAA	Chlorine	tumours								
	Dibromoacetic acid	DBAA	Chlorine	Liver tumours								
	Dichloroacetic acid	DCAA	Chlorine	Liver tumours	B-2	0.004	0.05			50	100	
	Monobromoacetic acid	MBAA	Chlorine	tumours								
	Monochloroacetic acid	MCAA	Chlorine								150	
	Tribromoacetic acid	TBAA	Chlorine									
	Trichloroacetic acid	TCAA	Chlorine	Liver tumours	С					100	100	
HAA5									60			
Haloacetonitriles (HANs)	Bromochloroacetonitrile	BCAN	Chlorine	Embryo death								
	Dibromoacetonitrile	DBAN	Chlorine	Skin tumours						70		
	Dichloroacetonitrile	DCAN	Chlorine	Embryo death						20		
	Trichloroacetonitrile	TCAN	Chlorine	Embryo death	C							
Haloketones (HKs)	1,1-dichloropropanone	DCP	Chlorine									
	1,1,1-	TCP	Chlorine									
	trichloropropanone											
Aldehydes	Formaldehyde		Ozone, chlorine							900	500	
	Acetaldehyde		Ozone, chlorine									
	Glyoxal		Ozone, chlorine									
	Methyl glyoxal		Ozone, chlorine									
Carboxylic acids	Formate		Ozone									
	Acetate		Ozone									
	Oxalate		Ozone									
Nitrosamines	N-		Chloramine		B-2		51					
Cyanogen halides	nitrosodimethylamine Cyanogen chloride		Chloramine							70	80	
nanues	Cyanogen bromide		Chloramine									
Chloral hydrate	cyanogen bronnue	СН	Chlorine							10	20	
Bromate			Ozone		B-2	0.004	0.7	10	10	10	20	10
Chlorate			Chlorine		5 5	5.001	5			700	20	
			dioxide							-		
Chlorite			Chlorine		D	0.03	-		1000	700	300	
			dioxide									

Primary disinfectant*: the main disinfectants for the respective DBPs are shown here. In case of alternative disinfectants, these DBPs as well as other DBPs can also be formed. If two or more disinfectants are used (for example, ozone and chlorine, chlorine and chloramine, chlorine dioxide and chlorine/chloramine, UV radiation and chlorine/chloramine, etc.), THMs, HAAs will still be formed. However, the main causing factors are shown in this column. Please note that these are not the complete list of DBPs and disinfectants. As such, number of both can be increased in future. B-2: Probable human carcinogen; C = Possible human carcinogen; HC: Health Canada; USEPA: US Environmental Protection Agency; RfD: Reference dose (mg/kg day); SF: Slope factor (mg/kg day)⁻¹; WHO: World Health Organization; UK: United kingdom; Aus–NZ: Australia–New Zealand.

number of DBPs have been investigated, including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and haloketones (HKs).

A large fraction of people living in urban areas in North America are routinely exposed to DBPs from supply waters through ingestion of drinking water, inhalation and dermal contact during regular indoor activities, such as bathing, showering, cooking as well as swimming in pools and hot tubs with chlorination or brominated disinfection systems. To protect human health, regulatory agencies around the world have imposed regulations to limit the formation of some known DBPs in drinking waters (USEPA, 2006; Health Canada, 2007; Aus–NZ, 2004; WHO, 2004; UK, 2000). Active research on DBPs formation has resulted in

the development of at least 118 predictive models, which have been presented in 48 scientific publications between 1983 and 2008 (Nikolaou et al., 1999; Sadiq and Rodriguez, 2004). In addition, many other studies have reported toxicological and epidemiological effects of DBPs to human and animal health (Mills et al., 1998; Bull et al., 1985, 1990; Cantor et al., 1998; Villanueva et al., 2004). A number of studies reported chlorine residual decay in water distribution systems (Clark and Sivaganesan, 2002; Vasconcelos et al., 1997; Rossman et al., 1994; Ginasiyo et al., 2007; Huang and McBean, 2007; Al-Jasser, 2007; Hass and Karra, 1984; Gang et al., 2003; Rossman et al., 2001). Some other studies performed risk based decision-making in the selection of appropriate disinfection approaches (Chowdhury and Husain, 2006; Chowdhury et al., 2007; Lykins et al., 1994; Reiff, 1995; Clark and Rice, 2004). Commonly used disinfectants, their byproducts, possible effects of these DBPs to human and animal health, as well as their regulatory limits are shown in Table 1. The four THM species (chloroform, bromodichloromethane, dibromochloromethane and bromoform), dichloroacetic acids, trichloroacetic acids, trichloroacetonitrile, bromate and chlorite have been reported to have carcinogenic effects to human health (Table 1). In addition, the nitrogenous DBPs, such as N-nitrosodimethylamine (NDMA) and other unknown DBPs may also pose a potential cancer risks to human health (USEPA, 2006; Mitch and Sedlak, 2002; Richardson, 2005). In Table 1, the main disinfectants for the corresponding byproducts are shown. In case of alternative disinfectants or combinations of different disinfectants, similar byproducts as well as other many unregulated byproducts may be formed (Miltner et al., 2008; Krasner et al., 2006; Richardson et al., 2008). Such as, use of ozone followed by chlorine may form bromate as well as THMs, HAAs and many other unregulated byproducts (Krasner et al., 2006). If chlorine (for primary disinfection) is followed by chloramine (for residual protection), NDMA, regulated DBPs and other DBPs may be formed. However, THMs and HAAs will be much less in these cases. The amounts of DBP formation may be characterized based on the types and combinations of disinfectants used. For example, THM and HAA formations may follow the patterns of chlorine>chlorine/chloramine>ozone/chlorine>ozone/ chloramine>chlorine dioxide/chloramine>UV radiation/chloramine, etc. However, type of byproducts may vary significantly based on the type and combination of disinfectants employed. More over, Table 1 shows a fraction of the identified DBPs to date (Krasner et al., 2006). Upon availability of the regulatory and human health related information, new byproducts can be added to this Table (Table 1).

Table 2

Basic information of disinfectants.

The protection of human health from microbiological and chemical risks, as well as making water supply systems cost-effective has been a challenge to the research community. The predictive models for DBP formation reported in the scientific literature use a range of explanatory parameters for variety of applications. As the models for DBP formation help to guide decision-making in the drinking water supply systems, the capacity and range of applicability of these models is essential and should be examined carefully. In this paper, the predictive models for DBP formation available in the scientific literatures have been reviewed. The model review examines the models following a number of criteria: the characteristics of data sources (raw water, treated water or synthetic water), model performance under a range of environmental conditions, experimental methods used in model development and estimation, types of models (mechanistic or empirical), as well as their predictive ability. An example to demonstrate the potential application of these models in guiding decision-making processes is presented. Finally, future research important to the development of improved models is identified.

2. Disinfection

2.1. Disinfectants and disinfection approaches

Chlorination as a disinfection approach for drinking water supplies was first introduced in 1902 in Middlekerke (Belgium), followed by the use of ozone as a disinfectant in Nice (France) in 1906 (MWH, 2005). The USA introduced chlorination of drinking water in Chicago and Jersey City in 1908 and Canada first started using chlorine for drinking water disinfection in Peterborough in 1916 (Chlorine Chemistry Council, 2003; Peterborough Utilities Commission, 1998). Currently, most of the water supply systems in North America use chlorine as a disinfectant (USEPA, 2006; Health Canada, 2007). In addition to chlorine, a number of other disinfectants, such as, chloramine, chlorine dioxide, ozone and ultraviolet radiation are also applied to a number of water supply systems (MOE, 2006; AWWA, 2000). The applications of various disinfectants, as well as their costs, disinfection efficiencies and stability in distribution systems are summarized in Table 2. Table 2 shows that chlorine is very effective and, in most cases, is a relatively inexpensive disinfectant. The disinfection efficiencies of disinfectants are generally

Issue		Chlorine	Chloramine	Chlorine dioxide	Ozone	Ultraviolet radiation	Reference
Application		Most common	Common	Occasional	Common	Emerging use	USEPA (2006)
Cost		Lowest	Moderate (>chlorine)	High	High	Extremely high	Clark et al. (1994)
Disinfection efficiency	Bacteria (<i>V. chloerae</i> , Coliform, <i>E. coli</i> , etc)	Excellent	Good	Excellent	Excellent	Good	MWH (2005), Sadiq and Rodriguez (2004)
2	Viruses (Polio virus, Rota virus, MS2 coliphase, etc)	Excellent	Fair	Excellent	Excellent	Fair	
	Protozoa (G. lamblia, C. parvum, E. intestinalis, etc)	Fair to poor	Poor	Good	Good	Excellent	
	Endospores	Good to	Poor	Fair	Excellent	Fair	
Organisms regrowth		Unlikely	Unlikely	Likely	More likely	More likely	MWH (2005)
Limits on free residuals		4 mg/L	4 mg/L	0.8 mg/L	-	-	USEPA (2006)
Byproducts	Regulated	4 THMs, HAAs	Traces of THMs and HAAs	Chlorite	Bromate	None	USEPA (2006)
	Unregulated	Many	Many: cyanogen halides, NDMA	Many: chlorate	Biodegradable organics	None known	Richardson (2005)
Oxidation		Strong	Weak	Selective	Strongest	None	Chlorine Chemistry Council (2003)
Odor and taste removal		Excellent	Good	Excellent	Good to poor	None	
Stability		Stable	Stable	Unstable	Unstable	Unstable	

affected by physico-chemical and biological factors. Disinfection efficiencies can be determined from the product of residual disinfectant concentration (C) and the contact time of the disinfectant in the water (*t*). Generally, the inactivation of microorganisms increases with increasing Ct value (MWH, 2005; Connell, 1997). This value, which differs as a function of disinfectant, is typically used as a design parameter for the water supply systems (Gates, 1998). The types and nature of microorganisms, as well as the treatment plant operational conditions (temperature, pH) also affect disinfection efficiencies (Sadig and Rodriguez, 2004). Chlorine is more effective against microorganisms under acidic rather than alkaline conditions. In addition, higher water temperatures typically require a lower Ct to inactivate microorganisms (Clark et al., 1994). For a specific contact time, higher chlorine doses are required for disinfection in winter compared to that of summer conditions. On the other hand, microbiological activities are higher in warmer waters than in cold waters within the water distribution systems (Arora et al., 1997). Consequently, disinfectant residuals decay rapidly when the water temperature is high, which often makes maintaining minimum residuals difficult in larger distribution systems during the summer months, especially at the extremities of the distribution systems. To maintain adequate concentrations of disinfectant residuals in the distribution systems, higher disinfectant doses are applied during the summer period. Higher temperatures and higher disinfectant residuals in the distribution systems during the summer period have also been shown to affect DBP formation (Elshorbagy et al., 2000).

The drinking water disinfection and supply systems include several physico-chemical processes (screening, coagulation, flocculation, settling and filtration) for the treatment and disinfection of drinking waters. Different treatment approaches are employed to reduce DBP precursors (NOM), turbidity and pathogens from source waters (Dempsey et al., 1984; Reckow and Singer, 1984; Edzwald, 1993; Shorney et al., 1999). A typical treatment configuration is shown in Fig. 1. Treatment systems may also include granular activated carbon (GAC) in addition to conventional filtration depending on the type of organics contained in the water (Fig. 1b). Use of GAC effectively reduces NOM and other chemicals through adsorption and catalytic degradation; consequently, reducing the formation of DBPs (Chang

et al., 2001). However, the introduction of GAC increases operational and maintenance costs by 30–50% (Chowdhury et al., 2007). Moreover, none of the currently available treatment approaches can completely remove pathogens and the precursors to DBP formation (Clark et al., 1998; Chang et al., 2001).

2.2. Disinfection byproducts formation and operational challenge

During disinfection for drinking waters, most of the chlorine demand is exhausted by reactions with NOM. Chlorine also reacts with various inorganic compounds in the water treatment plants and distribution systems (e.g., ammonia to form chloramine, Fe²⁺, Mn²⁺, S^{2-} , Br⁻, pipe materials, biofilms). The NOM and/or other inorganic substances in water react with disinfection agents such as chlorine, chloramine, chlorine dioxide and ozone to produce DBPs in drinking water during the disinfection process and in the water distribution system (Montgomery, 1993; Rathbun, 1996a,b; Chen and Weisel, 1998; Rodriguez and Sérodes, 2001). Table 1 shows that most of the THMs and HAAs are formed as a result of chlorination, while chloramine, ozone and chlorine dioxide form lower quantities of THMs, HAAs and other DBPs. However, some of the DBPs formed with chloramine, chlorine dioxide and ozone can be more toxic than those formed during chlorination. For example, N-nitrosodimethylamine (NDMA) and bromate, which are typically formed during chloramine and ozone disinfection respectively, are more toxic than THMs and HAAs (Table 1; IRIS, 2006; Richardson, 2005).

It has been shown that increases in pH can increase THM formation. As such, a reduction in pH can be employed to reduce THM formation (Stevens et al., 1976; Chowdhury and Champagne, 2008). However, a decrease in pH can lead to an increase in HAAs formation (Singer 1994; Singer et al., 1995; Nokes et al., 1999). Hence, the determination of the optimum pH range for disinfection is often necessary during the operation of water supply systems. Increase in contact time has also been noted to increase DBP formation. However, controlling contact time in water treatment plants and distribution systems is often a challenge due to variable hydraulic properties and water demands imposed in distribution systems. Temperature and seasonal variability have also been reported to affect THM formation,

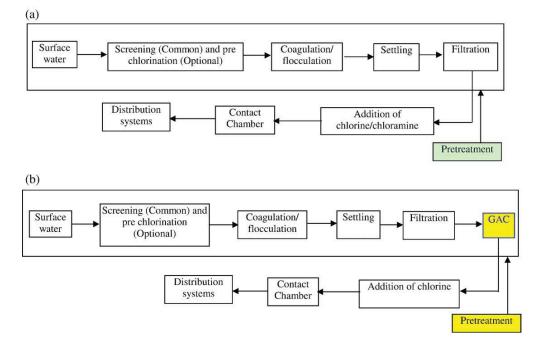


Fig. 1. Typical configuration of water treatment plant; (a). Conventional water treatment plant; (b). Addition of granular activated carbon (GAC).

where the formation of THMs during the summer months was reported to be higher than during the winter months (Golfinopoulos et al., 1998; Golfinopoulos and Arhonditsis, 2002a,b; Elshorbagy et al., 2000). Because organic/inorganic substances act as precursors for DBP formation, their removal prior to disinfection has proven to be an effective approach for reducing the DBP formation potential. Pretreatments prior to chlorination can partially remove NOM and this removal can be enhanced by using GAC, enhanced coagulation and membrane filtration, which may increase operating and maintenance costs significantly (Chowdhury et al., 2007). Formation of DBPs can also be reduced by introducing alternative disinfectants or a combination of disinfectants, including chloramine, ozone, chlorine dioxide and ultraviolet radiation followed by post chlorination to inhibit microbiological recontamination in distribution systems. However, the use of these alternative disinfectants can still lead to the formation of the more toxic DBPs as shown in Table 1 (Richardson, 2005; IRIS, 2006). Moreover, the combination of different disinfectants or disinfection processes could significantly increase capital and operating costs of the disinfection system (USEPA, 2006; Clark et al., 1994; Lykins et al., 1994).

In addition to the difficulties associated with controlling operational parameters (pH, reaction time) and environmental conditions (seasonal variability, water temperature), water quality variables such as the types and amounts of NOM, as well as the presence of bromide ions (Br⁻) contribute further challenges to the design of drinking water supply systems and the production of safe drinking water. The organic matter in the source waters contains both hydrophobic and hydrophilic fractions of NOM. The hydrophobic fractions are generally composed of the higher molecular weight NOM with activated aromatic rings, phenolic hydroxyl groups and conjugated double bonds, while the hydrophilic fractions are typically composed of the lower molecular weight NOM with aliphatic ketones and alcohols (Liang and Singer, 2003). The hydrophobic fractions of NOM exhibit higher ultraviolet absorbance (UV₂₅₄) and higher specific ultraviolet absorbance (SUVA, defined as 100UV₂₅₄/DOC) and these tend to be more reactive with chlorine than bromine, while the hydrophilic fractions of NOM exhibit lower UV₂₅₄ and lower SUVA and are generally more reactive with bromine than chlorine (Liang and Singer, 2003). Waters without Br⁻ mainly form chlorinated THMs (CHCl₃) due to reactions between hypochlorous acid (HOCl) and the hydrophobic fractions of NOM. As such, a significant fraction of the hydrophilic NOM may be left unreacted in these waters. Conversely, in waters with Br⁻, the hydrophilic fractions of NOM form brominated THMs through reactions with hypobromous acid (HOBr), while these brominated THMs may not be adequately characterized by the low SUVA or low UV₂₅₄ values. Hellur-Grossman et al. (2001) reported similar observations of hydrophilic fractions of NOM and brominated THM formation. The raw water from the Sea of Galilee (Lake Kinneret) in Israel contained TOC between 4 and 6 mg/L and very high Br⁻ ion concentrations (up to 1.9 mg/L). This water was composed mainly of hydrophilic fractions of NOM, which showed low UV₂₅₄ and low SUVA values. Therefore, the hydrophilic fractions of NOM favored brominated THMs formation in the Lake Kinneret water. The brominated THMs consisted of more than 96% of the total THMs in Lake Kinneret water (in summer, brominated THMs = 595.5 ppb and total THMs = 606 ppb; in winter, brominated THMs = 487 ppb and total THMs = 507 ppb). The UV₂₅₄ and SUVA values could not be employed to characterize the brominated THM formation for this specific source water. In addition, Br⁻ forms HOBr in chlorinated water, which is approximately 20 times more reactive with NOM than the HOCl (Uvak and Toroz, 2007); thus, favoring brominated THM formation. Increases in Br⁻ concentrations gradually shift chlorinated THM and HAA formation to bromochloro THM and HAA formation (Uyak and Toroz, 2007; Hellur-Grossman et al., 2001; Nokes et al., 1999). Further complexities arise, as the conversion of Br⁻ to brominated DBPs is not 100%. This conversion varies between 18 and 28% for THMs and

approximately 10% for HAAs formation, which also depends on the pH, water temperature and the relative distributions of hydrophobic and hydrophilic fractions of NOM (Sohn et al., 2006; Liang and Singer, 2003). The removal of hydrophilic NOM through coagulation processes is often difficult because of their low molecular weights. As such, hydrophilic NOM tends to remain in finished waters. As a result, formation of brominated THMs in finished water in the presence of bromide ions is more likely to occur.

2.3. Regulating DBP exposure concentrations

The safety of human health from drinking water contaminants (chemical and/or microbiological) has been a concern in the USA since the beginning of 19th century. In 1915, the USA imposed bacterial standards for drinking water, which became more stringent in 1925. In the early 1970s, USEPA scientists (Bellar et al., 1974) first determined that drinking water chlorination could form a group of byproducts known as trihalomethanes (THMs). In 1972, the USA passed the Clean Water Act for restoring and maintaining surface water quality. Two years later, the Safe Drinking Water Act (SDWA) was passed, which allowed the US Environmental Protection Agency to set water quality standards, which each of the States would enforce. The USEPA set the first regulatory limits for THMs in 1979. In 1996, the SDWA was amended to incorporate source water protection, operator training, funding for water system improvements and public information. In 1998, the Stage 1 Disinfectants and Disinfection Byproducts Rule (DBPR) was introduced (USEPA, 1998a,b). The Stage 1 DBPR was amended and the Stage 2 DBPR was finalized in 2006 (USEPA, 2006), which represents the current regulations on DBPs concentrations. In the Stage 2 DBPR, water supply systems must comply with maximum contaminant levels (MCLs) of 80 µg/l for total trihalomethanes (THMs) and 60 μ g/l for the sum of 5 haloacetic acids (HAA₅) as locational running annual averages (LRAAs). In Canada, Health Canada imposed regulatory limits on THMs concentrations in 1996. These regulations were reviewed periodically and the latest updated version for 2007 is currently available. The Canadian guidelines set the maximum allowable concentrations of total THMs to 100 µg/l (running annual average of quarterly samples). Regulations for HAAs are still under consideration (Health Canada, 2007). Health Canada (2007) also limits BDCM and bromate concentrations to 16 μ g/l and 10 μ g/l, respectively. In addition to the USA and Canada, the World Health Organization (WHO, 2004), Australia-New Zealand (Aus-NZ, 2004) and United Kingdom (UK, 2000) have imposed regulatory limits on exposure concentrations of a number of DBPs. The WHO regulated DBPs exposure concentrations in 1993, which was updated in 2004. Australia-New Zealand regulations were also updated in 2004. The regulatory limits on different DBPs of USEPA (2006), Health Canada (2007), WHO (2004), Aus-NZ, (2004) and UK (2000) are shown in Table 1.

3. Models and their potential applications

3.1. Predictive models for DBPs formation

Since the discovery of DBPs in drinking waters (Rook, 1974; Bellar et al., 1974), considerable research has been focused on characterization of the significant parameters involved in DBP formation. Some studies have correlated DBPs with NOM contents in raw waters (Singer and Chang, 1989; White et al., 2003). Other studies have also investigated the relationships between precursors, operational parameters and DBP formation, as well as the relationships between different species of DBPs (Singer et al., 1995; Chen and Weisel, 1998; Arora et al., 1997; Gallard and Von-Gunten, 2002; Gang et al., 2003). In the past three decades, numerous models have been developed to predict DBP formation in drinking waters. These models have investigated the effects of different water quality and operational parameters in controlling DBP formation

Table 3

Models for DBPs formation.

Author and year	Model descriptions	R^2	Unit
I. Minear and Morrow (1983)	$THMs = -3.91 + (Br^{-})^{0.15} + 0.23\log(D) + 0.24(pH) + 10^{0.009T} + 0.26(NVTOC)$	>0.90	(µmol/L)
. Urano et al. (1983)	$THMs = 0.00082(pH - 2.8)TOC.D^{0.25}.t^{0.36}$	NR	$(\mu g/L)$
(1983) Engerholm and Amy (1983)	$CHCl_3 = k_1 k_2 (TOC)^{0.95} \left(\frac{D}{TOC}\right)^{0.28} t^z$		
Morrow and	(a) THMs = $-3.91 + (Br^{-})^{0.15} + 0.23 \log(D) + 0.24(pH) + 10^{0.0097} + 0.26(NVTOC)$		(µmol/L)
Minear (1987)	(b) THMs = $-3.94 + (Br^{-})^{0.19} + 0.35 \log(D) + 0.24(pH) + 10^{0.0097} + 0.27(NVTOC)$	NR	(1 · · / /
	(c) THMs = $-2.42 + (Br^{-})^{0.15} + 0.24 \log(D) + 0.24(pH) + 10^{-204.57} + 0.25(NVTOC)$	NR	
Amy et al. (1987)	$THMs = 0.0031(UV_{254} TOC)^{0.440}(D)^{0.409}(t)^{0.265}(T)^{1.06}(pH - 2.6)^{0.715}(Br^{-} + 1)^{0.0358}$	0.90	(µmol/L)
. Adin et al. (1991)	THMs = K_1 , K_2 .TOC. [(1/(($K_1 + K_3$)($K_2 + 0.19$))) + (1/($K_1 + K_3 - K_2 - 0.19$))×(((1/($K_1 + K_3$))) exp(-($K_1 + K_3$)(tc)) - ((1/($K_2 + 0.19$))exp(-($K_2 + 0.19$)(tc))]; $K_1 = 4.38 \times 10^{-8}$ (D); $K_2 = 11.36 \times 10^{-7}$ (D); $K_3 = 7.14 \times 10^{-13}$ (D) ²	0.90	(µg/L)
Harrington et al. (1992)	THMs = 0.00309 (TOC .UV ₂₅₄) ^{0.44} . $D^{0.409} t^{0.265} T^{1.06} (pH - 2.6)^{0.715} (Br^{-} + 1)^{0.03}$	NR	$(\mu g/L)$
Malcolm Pirnie	$\begin{aligned} CHCl_3 &= 0.078 \; (TOC \; .UV_{254})^{0.616} . D^{0.391} \; t^{0.265} \; T^{1.15} \; (pH-2.6)^{0.8} \; (Br^-+1)^{-2.23} \\ BDCM &= 0.863 \; (TOC \; .UV_{254})^{0.177} . D^{0.309} \; t^{0.271} \; T^{0.72} \; (pH-2.6)^{0.925} \; (Br^-+1)^{0.722} \end{aligned}$	NR	$(\mu g/L)$
Inc. (1992)	$DBCM = 0.505 (10C_{0}V_{254}) D^{-0.184} D^{-0.0746} t^{0.252} T^{0.57} (pH - 2.6)^{-1.35} (Br^{-1} + 1)^{2.08}$	NR	
Malcolm Pirnie	(a). THMs = $7.21(\text{TOC})^{0.004}(\text{UV}_{254})^{0.534}(D - 7.6 \times \text{NH}_3 - \text{N})^{0.224}(t)^{0.255}(\text{Br}^- + 1)^{2.01}(T)^{0.480}(\text{pH} - 2.6)^{.719}$	NR NR	(µg/L)
Inc. (1993)	(a). Thus = $7.21(10C)^{-1}(50^{-254})^{-1}(D^{-1})^{-1}$	NR	(µg/L)
	(c). $CHCl_3 = 0.997 (TOC)^{0.580} (UV_{754})^{0.580} (D)^{0.814} (t)^{0.278} (Br^- + 1)^{-4.27} (T)^{0.569} (pH - 2.6)^{0.759}$	NR	
	(d), DBCM = $22.9(TOC)^{0.253}(UV_{254})^{0.253}(D - 7.6 \times NH_2 - N)^{-0.352}(t)^{-0.292}(Br^{-1.04}(T)^{0.491}(pH - 2.6)^{0.325}(t)^{-0.325}(t)^{-0.292}(hr^{-1.04}(T)^{-0.491}(hr^{-1.04$	NR	
	(e). $CHBr_3 = 1.28(TOC)^{-0.167}(UV_{254})^{-0.167}(D - 7.6 \times NH_3 - N)^{-2.22}(t)^{0.294}(Br^{-1.48}(T)^{0.553}(pH - 2.6)^{0.198}(t)^{-0.167}(D - 7.6 \times NH_3 - N)^{-2.22}(t)^{-0.167}(D - 7.6 \times NH_3 - N)^{-0.167}(D - 7.6 \times NH_3 - N)^{-2.22}(t)^{-0.167}(D - 7.6 \times NH_3 - N)^{-0.167}(D - 7.6 \times NH_3 - N)^{-0.$	NR	
. Montgomery	(a). $CHCl_3 = 0.064(TOC)^{0.329}(UV_{254})^{0.874}(Br^- + 0.01)^{0.404}(pH)^{1.161}(D)^{0.561}(t)^{0.269}(T)^{1.018}$	0.88	$(\mu g/L)$
Watson (1993)	(b). BDCM = $0.0098(Br^{-})^{0.181}(pH)^{2.55}(D)^{0.497}(t)^{0.256}(T)^{0.519}(for D/Br^{-}<75)$	0.8	
	(c). BDCM = $1.325(\text{TOC})^{-0.725}(\text{Br}^{-})^{0.794}(D)^{0.632}(t)^{0.204}(T)^{1.441}$ (for $D/\text{Br}^{-} > 75$)	0.92	
	(d). DBCM = $14.998(TOC)^{-1.665}(Br^{-})^{1.241}(D)^{0.729}(t)^{0.261}(T)^{0.989}(for D/Br^{-}<50)$	0.82	
	(e). DBCM = $0.028(UV_{254})^{-1.175}(TOC)^{-1.078}(Br^{-})^{1.573}(pH)^{1.956}(D)^{1.072}(t)^{0.2}(T)^{0.596}$ (for $D/Br^{-}>50$) (f). CHBr ₃ = $6.533(TOC)^{-2.031}(Br^{-})^{1.388}(pH)^{1.603}(D)^{1.057}(t)^{0.136}$	083	
	(g). MCAA = $1.634(\text{TOC})^{0.753}(\text{Br}^- + 0.01)^{-0.085}(\text{pH})^{-1.124}(D)^{0.509}(t)^{0.300}$	0.86 0.82	
	(g). MCAA = $1.054(10C)$ (g) $+0.01$ (p) (f) (D) (f) (h). DCAA = $0.606(TOC)^{0.291}(UV_{254})^{0.726}(Br^- + 0.01)^{-0.568}(D)^{0.48}(t)^{0.239}(T)^{0.665}$	0.82	
	(i). TCAA = $87.182(\text{TOC})^{0.355}(\text{UV}_{254})^{0.901}(\text{Br}^- + 0.01)^{0.679}(\text{pH})^{1.732}(D)^{0.881}(t)^{0.264}$	0.98	
	(i). MBAA = $0.176(TOC)^{1.664}(UV_{254})^{-0.624}(Br^{-})^{-0.795}(pH)^{-0.927}(t)^{0.145}(T)^{0.45}$	0.80	
	(k). DBAA = $84.945(TOC)^{-0.62}(UV_{254})^{0.651}(Br^{-})^{1.073}(D)^{-0.2}(t)^{0.12}(T)^{0.657}$	0.95	
Lou and	THMs = THMo + 7.01(pH - 2.3) ^{0.11} (NVTOC) ^{1.06} (t) ^{0.764} (D) ^{0.764} (\beta)	NR	(µg/L)
Chiang (1994)	$\beta = \left\{ \int_0^\infty \left(e^{-0.0393 [\text{NVTOC}]t} \right) \frac{1}{2\sqrt{m0}} \exp\left[\frac{\left(1-\theta\right)^2}{4\theta} \right] d\theta \right\}^{0.764}$		
2. Ibarluzea	$CHCl_3 = 10.8 + 0.04(Flu) + 1.16(pH) + 0.12(T) + 1.91 (Co)$	0.82	(µg/L)
et al. (1994) 3. Ozekin (1994)	Bromate = $1.55 \times 10^{-6} (\text{DOC})^{-26} (\text{pH})^{5.82} (\text{O}_3)^{5.82} (\text{Br}^{-})^{0.73} (t_m)^{0.28}$ when $t < 20 \text{ °C}$		(µg/L)
	For higher temperature, $230ABRO_3^2 230B_T = 230ABRO_3^2 230B_{20} \circ_{C} (1.035)^{T-20}$		0.0, 7
. Siddiqui	$CHBr_3 = 2.68(DOC)^{1.28}(pH)^{-1.31}(O_3)^{0.742}(Br^{-})^{1.55}(T)^{0.956}(t_m)^{0.353}$	0.78	$(\mu g/L)$
et al. (1994)	$TOBr = 5.1(DOC)^{1.07}(pH)^{105}(O_3)^{0.766}(Br^{-})^{1.53}(T)^{01.08}$; time = 24 h	0.95	
	Bromate = $1.5 \times 10^{-3} (\text{DOC})^{-0.74} (\text{pH})^{-2.26} (\text{O}_3)^{0.64} (\text{Br}^-)^{0.61} (T_{\text{oz}})^{2.03}$	0.88	
	Bromate = $1.5(\text{DOC})^{-0.75}(\text{pH})^{-2.25}(\pi + 1)^{1.31}(\text{Br}^{-})^{0.60}$	0.64	
	Bromate = $0.26(\text{DOC})^{0.86}(\text{pH})^{3.27}(\text{DO}_3)^{0.22}(t_m + 1)^{0.25}(\text{Br}^-)^{0.67}$; (0 < t < 1 h)	0.68	
. Song et al. (1996)	Bromate = $10^{-6.11}(\text{DOC})^{-1.18}(\text{NH}_3-\text{N})^{-0.18}(\text{pH})^{5.11}(\text{O}_3)^{1.42}(\text{Br}^{-})^{0.88}(\text{IC})^{0.18}(t_m)^{0.27}$	0.93	(µg/L)
. Rathbun	$CHCl_3 = 0.442(pH)^2(D)^{0.229}(DOC)^{0.912}(Br^-)^{-0.116}$	0.97	$(\mu g/L)$
(1996a)	$BDCM = 17.5(pH)^{1.01}(D)^{0.0367}(DOC)^{0.228}(Br^{-})^{0.513}$	0.86	
	$DBCM = 26.6(pH)^{1.80}(D)^{-0.0928}(DOC)^{-0.758}(Br^{-})^{1.2}$	0.94	
P _111	$CHBr_3 = 0.29(pH)^{3.51}(D)^{-0.347}(DOC)^{-0.330}(Br^{-})^{1.84}$	0.78	(
Rathbun	THMs = 14.6 (pH - 3.8) ^{1.01} (D) ^{0.206} (UV ₂₅₄) ^{0.849} (t) ^{0.306}	0.98	(µg/L)
(1996b)	NPTOX = $42.0(13 - \text{pH})^{1.07}$ (D) ^{0.21} (Br ⁻ + 1) ^{-2.75} (UV ₂₅₄) ^{0.847} (t) ^{0.142} (a). THMs = 12.72 (TOC) ^{0.291} (t) ^{0.271} (D) ^{-0.072}	0.96	(
Chang et al.	(a). THMS = 12.72 (TOC) ^{-0.2466} (t) ^{-0.2956} (UV ₂₅₄) ^{0.9919} (D) ^{0.126}	0.94 0.97	$(\mu g/L)$
(1996)	(c). THMs = $131.75(t)^{0.2931}(UV_{254})^{1.075}(D)^{0.1064}$	0.97	(μg/L) (μg/L)
. GVillanova et al. (1997a)	$\ln(\text{CHCl}_3) = 0.348 + 0.00059(T)^3 - 0.000023(T)^4 + 0.0237(\text{pH})^2 + d + e$	0.65	(µg/L)
et al. (1997a) I. GVillanova et al. (1997b)	$\ln(\text{CHCl}_3) = 0.81Y + 0.162N + 0.00047(T)^3 - 0.0000204(T)^4 + 0.00339(\text{pH})^2 + e$	0.86	$\left(\mu g/L\right)$
. Huixian et al. (1997)**	(a). POX = $7.2t^{0.008}$ TOC $^{0.49}$ D $^{0.41}$ (pH + 8.6)exp($-468.5 / T$) (b). NPOX = $28.7t^{0.02}$ TOC $^{0.53}$ D $^{0.44}$ (20.9 - pH)exp($-632.4 / T$)	0.94 0.92	$\left(\mu g/L\right)$
2. Clark and	$THMs = A\Big(C_{A_0} - \Big(\frac{C_{A_0}(1-K)}{1-Ke^{-\omega_0}}\Big)\Big)$	K = 0.71	(µg/L)
Sivaganesan (1998)	$u = M(1 - K); K = e^{0.32} (C_{A0})^{-0.44} (\text{TOC})^{0.63} (\text{pH})^{-0.29} (T)^{0.14}; A = e^{1.49} (C_{A0})^{-0.48} (\text{TOC})^{0.18} (\text{pH})^{-0.96} (T)^{0.28} M = e^{(-2.46 - 0.19\text{TOC} - 0.14\text{pH} - 0.07T - 0.01\text{pH}, T)}$	A = 0.78	
		M = 0.42	(ug/L)
. Golfinopoulos et al. (1998)	$THMs = 13.5ln(Chla) - 14.5(pH) + 230(Br^{-}) - 140(Br^{-})^2 - 25.3(S) + 110.6(Sp) - 6.6(T.Sp) + 1.48(T.D) - 140(T.D) -$	0.98	(µg/L)

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189-4206

4195

Author and year	Model descriptions	R^2	Unit
5. Nokes et al.	Function of various reaction coefficients of intermediate products, HOBr and HOCI	NR	(µg/L)
(1999)	() THE 0.000 DOC 1030 (10.262 (10.1149 (D)0.277 (T0.0968	0.00	((1)
6. Rodriguez et al. (2000)	(a). THMs = 0.044(DOC) ¹⁰³⁰ (t) ^{0.262} (pH) ¹¹⁴⁹ (D) ^{0.277} (T) ^{0.968} (b). THMs = 1.392(DOC) ^{1.092} (pH) ^{0.531} (T) ^{0.255}	0.90 0.34	(µg/L)
7. Milot et al. (2000)	$\frac{P = \exp[a.treatment + b.region + c.season + d.source + e]}{1 + \exp[a.temperature + b.region + c.season + d.source + e]}$		
8. Sung et al. (2000)	(a). THMs = $a(OH^{-})j(D(1 - e^{-kt}))(UV_{254})^n(algae)^p$		(µg/L)
	(b). $CHCl_3 = 2.3 \times 10^6 (OH^{-})^{0.52} (D(1 - e^{-kt}))^{0.56} (UV_{254})^{0.57} (algae)^{-0.10}$	0.93	
	(c). HAA5 = $4.8 \times 10^4 (\text{OH}^{-})^{0.35} (D(1 - e^{-\text{kt}}))^{0.43} (\text{UV}_{254})^{0.34}$ (d). TCAA = $4.7 \times 10^4 (\text{OH}^{-})^{0.41} (D(1 - e^{-\text{kt}}))^{0.70} (\text{UV}_{254})^{0.18}$	0.74 0.87	
). Westerhoff et al.	(u). $ICAN = 4.7 \times 10^{10} (D(1 - e^{-1}))^{10} (U(2 - e^{-1}))^{10} (U$	0.87 NR	(µg/L)
(2000)			(10) -)
). Elshorbagy et al. (2000)	$THMs_{t+\Delta t} = THMs_t + 0.582(CI_{t+\Delta t} - CI_t)$	NR	(µmol/L)
l. Clark et al. (2001)	THMs = $\alpha \left(C_{A_o} - \left(\frac{C_{A_o}(1-K)}{1-Ke^{-wlm}} \right) \right); \ u = M(1-K); \ K = e^{1.89} (\text{pH})^{-0.13} . (\text{Br}^- + 1)^{0.1} . (\text{Cl}_o)^{-0.75}$ $M = e^{3.96} . e^{-0.305 (\text{Br}^-)} . e^{0.0145 (\text{Cl}_o, \text{pH})} . \text{Cl}_o^{-2.32} . e^{8.46(p)} . e^{-0.231 \text{pH}}$	K = 0.95 M = 0.70	$(\mu g/L)$
	$M = e^{3.96} \cdot e^{-0.305(Br^{-})} \cdot e^{0.0145(Cl_o, pH)} \cdot Cl_o^{-2.32} \cdot e^{8.46(p)} \cdot e^{-0.231pH}$	M = 0.70	
2. Golfinopoulos and	(a). THMs = -0.26 chla + 1.57 pH + 28.74 Br - 66.72 Br ² - 43.63 S + 1.13 Sp + 2.62 T.S - 0.72 T.D	0.52	$(\mu g/L)$
Arhonditsis (2002a)	(b). CHCl ₃ = -0.32 chla + 0.68 pH + $2.51D$ + 1.93 Sp $-22.07S$ + $1.38TS$ - $0.12T.D$ (c). BDCM = -0.37 chla + 0.32 pH + 1.16 Br -29.82 Br ² + $1.88D$ + $5.17S$ - $0.37T.$ Sp $-0.12T.D$	0.51 0.62	
. Golfinopoulos and	$\frac{Vd[THMs]}{dt} = Q_{outflow}[THMs] + kVa_3 TOC^{a_1}[Halogen]^{a_2}$		(µg/L)
Arhonditsis (2002b)		0.05	
4. Korn et al. (2002)	$log(Chlorite) = -0.346 - 0.07log(pH) - 0.025log(T) - 0.597log(C + 1) - 0.136log(t + 1) - 0.0038log(NPOC.UV_{254}) + 0.293log(T).log(C + 1) + 0.393log(pH).log(C + 1) + 0.67log(NPOC.UV_{254}).log(C + 1) - 0.161log(NPOC.UV_{254}).log(t + 1) + 0.67log(NPOC.UV_{254}).log(C + 1) + 0.67log(NPOC.UV_{254}).log(NPOC.UV_{$	0.95	Mg/L
5. Gang et al. (2002)	(a). THMS = $\alpha D(1 - fe^{-kt}_r - (1 - f)e^{-kt}_s)$	NR	(µg/L)
	(b). HAAs = $\beta D(1 - fe^{-kt} - (1 - f)e^{-kt})$	NR	(+8) -7
. Serodes et al. (2003)	(a). $\log(HAAs) = 2.72 + 0.653(TOC) + 0.458(D) + 0.295(t)$	0.89	$(\mu g/L)$
	(b). $\log(HAAs) = 1.33 + 2.612(TOC) + 0.102(D) + 0.255(T) + 0.102(t)$	0.80	
	(c). HAAs = $-8.202 + 4.869(TOC) + 1.053(D) + 0.364(t)$ (d). THMs = $16.9 + 16.0(TOC) + 3.319(D) - 1.135(T) + 1.139(t)$	0.92 0.78	
	(e). $\log(\text{THMs}) = -0.101 + 0.335\text{THMo} + 3.914(\text{TOC}) + 0.117(t)$	0.89	
	(f). THMs = $21.2 + 2.447(D) + 0.499(t)$	0.56	
. Nikolaou et al. (2004)	(a). $\log THMs = 0.33 \text{pH} - 0.02 \text{pH}^2 + 0.12t - 0.004t^2$	0.53	$(\mu g/L)$
	(b). $logTHMs = -0.44pH + 7.53logpH - 1.10D + 0.2D^2$ (c). $logHAAs = 0.33pH - 0.02pH^2 + 0.48t - 0.09D$	0.58 0.28	
	(d) $\log THMs = 0.98 \log(pH) + 1.1 \log(t) - 0.01(t).(D) + 1.59 \log(D)$	0.28	
3. Al-Omari et al. (2004)	$[\text{THMs}] = 4.527 t^{0.127} D^{0.595} \text{ TOC}^{0.596} \text{ Br}^{0.103} \text{ pH}^{0.66}$	0.50	(µg/L)
9. Kolla (2004)	THMs = $0.0001D^{3.14}$ pH ^{1.56} TOC ^{0.69} $t^{0.175}$	0.77	$(\mu g/L)$
	$DCAN = 3.567D^{1.03} \text{ pH}^{-1.64} R^{0.18} t^{0.234}$	0.69	
). Lekkas and Nikolaou	$TCP = 0.785D^{3.474} \text{ pH}^{-4.659} \text{ t}^{0.147}$	0.68	(ug/L)
(2004)	(a). logTHMs = $1.546 + 0.631$ pH ² + 0.569 log(t) + 0.385 log(D) (b). logHAAs = $-0.00189 - 1.7$ pH ² + 1.5 log(pH) - 0.9 Br ⁻ + 0.875 (pH)(Br ⁻) +	0.87 0.51	(µg/L)
(2004)	$0.710\log(t) - 0.28(pH)(t) + 0.215\log(D)$	0.51	
I. Sohn et al. (2004)	(a) THMs = $10^{-1.385}$ (DOC) ^{1.098} (D) ^{0.152} (Br) ^{0.068} (T) ^{0.609} (pH) ^{1.601} (t) ^{0.263}	0.90	$(\mu g/L)$
	(b) THMs = $0.42(UV_{254})^{0.482}(D)^{0.339}(Br^{-})^{0.023}(T)^{0.617}(pH)^{1.601}(t)^{0.261}$	0.70	
	(c) THMs = $0.283(\text{DOC}^*\text{UV}_{254})^{0.421}(D)^{0.145}(\text{Br}^{-})^{0.041}(T)^{0.514}(\text{pH})^{1.606}(t)^{0.261}$ (d) THMs = $3.296(\text{DOC})^{0.801}(D)^{0.261}(\text{Br})^{0.223}(t)^{0.264}$	0.81	
	(a) THMS = $3.296(DOC)^{-0.67}(D)^{-0.67}$ (b) THMS = $75.7(UV_{254})^{0.593}(D)^{0.332}$ (Br) ^{0.0603} (t) ^{0.264}	0.87 0.90	
	$(f) THMs = 23.9(DOC^*UV_{25.4})^{0.403}(D)^{0.225}(Br^{-})^{0.141}(t)^{0.264}$	0.92	
	(g) THMs = $(THM_{mH} = 75 T = 20 \text{ °c})^* 1.156^{(pH-7.5)} 1.0263^{(T-20)}$	0.92	
	(h) $HAA6 = 9.98(DOC)^{0.935}(D)^{0.443}(Br)^{-0.031}(T)^{0.387}(pH)^{-0.055}(t)^{0.178}$	0.87	
	(i) HAA6 = 171.4(UV ₂₅₄) ^{0.584} (D) ^{0.398} (Br) ^{-0.091} (T) ^{0.396} (PH) ^{-0.645} (t) ^{0.178} (j) HAA6 = 101.2(DOC. UV ₂₅₄) ^{0.452} (D) ^{0.194} (Br) ^{-0.0698} (T) ^{0.346} (PH) ^{-0.6235} (t) ^{0.18}	0.80 0.85	
	(k) HAA6 = $5.228(\text{DOC})^{0.585}(D)^{0.665}(\text{Br})^{-0.031}(t)^{0.153}$	0.85	
	(1) $HAA6 = 63.7(UV_{254})^{0.419}(D)^{0.640} (Br)^{-0.066} (t)^{0.161}$	0.92	
	(m) HAA6 = $30.7(\text{DOC.UV}_{254})^{0.302}(D)^{0.541}(\text{Br})^{-0.012}(t)^{0.161}(t)^{0.1$	0.94	
	(n) HAA6 = (HAA6 _{@pH} = 7.5, $T_{=20C}$)*0.932 ^(pH - 7.5) 1.021 ^(T - 20) (o). TOBr = (Br ⁻) ^{1.68} .DOC ^{-0.652} .0 ₃ ⁻¹¹ .pH ^{-3.62} .TIC ^{-0.168} .(NH ₃ -N) ^{0.085} .(H ₂ O ₂) ^{-2.25}	0.85	
	(0). $IOBF = (BF^{-})^{1.53}.DOC^{-1.07}.O_{3}^{-7.6}.pH^{-1.05}.T^{1.927}$ (p). $TOBr = 0.9(BF^{-})^{1.53}.DOC^{-1.07}.O_{3}^{-7.6}.pH^{-1.05}.T^{1.927}$	0.98 0.95	
l. Uyak et al. (2005)	THMs = $0.0707(TOC + 3.2)^{1.314}(pH - 4.0)^{1.496}(D - 2.5)^{-0.197}(T + 10)^{0.724}$	0.98	(µg/L)
I. Uyak and Toroz	Log(THMs) = 1.078 + 0.398log(TOC) + 0.158log(T) + 0.702log(D)	0.83	$(\mu g/L)$
(2005) I. Tyrovola and Diamadopoulos (2005)	Bromate = $e^{-19.4} (Br^{-})^{0.8} (pH)^{7.28} (O_3)^{1.26} (t_m)^{0.89}$	0.80	$\left(\mu g/L\right)$
i. Rodrigues	$THMs = 16.0 + 1.6FA + 0.1D + 0.3T - 0.8FA \times T - 1.2FA^2 - 2.8D^2$	NR	(µg/L)
et al. (2007)	$CHCl_3 = 3.5 + 0.8FA + 0.02D + 0.07T - 0.3T^2$	NR	
	$BDCM = 4.5 + 0.7FA + 0.04D - 0.8D^2 + 0.4T^2$	NR	
	$DBCM = 4.0 + 0.4FA + 0.05D + 0.1T - 1.0D^{2} - 0.7FA^{2}$ CHBr ₃ = 4.0 - 0.2FA + 0.03D + 0.09T - 0.6 FA × T - 0.5 FA^{2} - 0.8D^{2}	NR NR	
5. Uyak and Toroz	Developed several models as a function of various reaction coefficients and the ratio between HOBr	NR	$\left(\mu g/L\right)$
(2007) 7. Hong et al. (2007)	and HOCI THMs = $10^{-1.375} t^{0.258} (D/DOC)^{0.194} \cdot pH^{1.695} T^{0.507} (Br^-)^{0.218}$	0.87	(µg/L)
	$BDCM = 10^{-3.201} t^{0.297} PH^{2.878} T^{0.414} (Br^{-})^{0.371}$	0.87	(P8/2)
	$CHCl_{3} = 10^{-0.748} t^{0.210} (D/DOC)^{0.221} PH^{1.374} T^{0.532} (Br^{-})^{-0.184}$	0.86	

(continued on next page)

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189-4206

Table 3	(continued)
---------	-------------

Author and year	Model descriptions	R^2	Unit
48. Semerjian	$THMs^2 = 17.31 + 10.52D^2 + 259728.60(SUVA)^2$	0.39	(µg/L)
et al. (2008)	$THMs^2 = 42.10 + 29.23D^2 + 353375.0(UV_{254})^2$	0.33	
	$THMs^{2} = -471.11 + 0.48t^{2} + 1856.07(Br^{-})^{2} + 404.38D^{2}$	0.31	

THMs = total trihalomethanes; CHCl3 = chloroform; BDCM = bromodichloromethane; DBCM = dibromochloromethane; CHBr3 = bromoform; HAAs = haloacetic acids; MCAA = monochloroacetic acid; DCAA = dichloroacetic acid; TCAA = trichloroacetic acid; MBAA = monobromoacetic acid; DBAA = dibromoacetic acid; BCAA = bromochloroacetic acid; HAA5 = (MCAA + DCAA + TCAA + MBAA + DBAA); HAA6 = HAA5 + BCAA; POX = purgeable organic halide; NPOX = nonpurgeable organic carbon (mg/L); β = ratio between THMs formed (µg/L) and chlorine consumed (mg/L); NVTOC = nonvolatile total organic carbon (mg/L); TCC = total organic carbon (mg/L); DO = dissolved organic carbon (mg/L); UV₂₅₄ = ultraviolet absorption at 254 nm wavelength (cm⁻¹); D = chlorine dose (mg/L); T = temperature (°C); t = reaction time (hour); t_m = reaction time in minute; u = rate constant (min⁻¹); C_{A0} = initial concentration of chlorine (mg/L); K = dimensionless constant; Br⁻ = bromide ion concentrations (mg/L); NJ₃-N = ammonia nitrogen (mg/L); OBT = total organic bromine (µg/L); NPOC = nonpurgeable organic carbon; S, Sp = dummy variables for summer and spring; Chla = chlorophyll-a (mg/m³); OH⁻ = hydroxide concentration; N = dummy variable; k = rate constant; G = chlorine dioxide concentration (mg/L); D₀ = ozonation temperature (°C); f = fraction of chlorine demand for rapid reactions; k_n, k_s = rate constants for rapid and slow reactions (/h); Q_{0urflow} = outflows in the finished water reservoir; V = volume of the tank; FA = fulvic acid (mg/L); R = residual chlorine (mg/L); DCAN = dichloroacetonitrile (µg/L); TCP = 1,1,1 - trichloropropanone (µg/L).

under a variety of environmental conditions, as well as the kinetics for DBP formation. More than 48 scientific publications have reported at least 118 models that have been presented for predicting DBP formation since 1983. A number of these models have been developed through field and laboratory-scaled investigations using raw, pretreated and synthetic waters (generated using commercial humic acid or NOM collected from designated sources), while others were developed from the analysis of passively collected data obtained from a range of databases. Out of 48 existing publications, 42 have focused on models for predicting THM formation, while 8 studies examined HAA formation models, 5 reports focused on bromate formation models and 1 reported on chlorite formation model. A comprehensive chronologic summary of DBP model developed since 1983 is outlined in Table 3. In terms of the 118 models presented, the greatest area of focus was on THM formation, for which 49 models have been proposed, followed by HAAs, chloroform, bromodichloromethane, dibromochloromethane and bromate each with 14, 12, 8, 6 and 6, models respectively (Table 3). Most of these models have been developed using empirical relationships among different parameters and DBP concentrations, while a limited number of studies (6 studies) have reported DBP formation models based on kinetic relationships (Engerholm and Amy, 1983; Adin et al., 1991; Clark and Sivaganesan, 1998; Clark et al., 2001; Golfinopoulos and Arhonditsis, 2002b; Gang et al., 2002). Only 3 studies employed statistically designed experiments (e.g., factorial designs) to better determine the effects of the main factors, as well as the effects of their interactions through simultaneous variation of a limited number of parameters (Clark et al., 2001; Korn et al., 2002; Rodrigues et al., 2007). Other studies employed one-factor-at-a-time approaches by keeping the other parameters constant or used passively collected data from available databases to develop their models. However, the use of factorial designs with replications and center points of all factors for determining the significant factors and their interactions involved in DBP formation is very limited in the existing literature to date.

A number of parameters have been incorporated in the development of DBP predictive models. The parameters most frequently incorporated include total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UV₂₅₄), specific ultraviolet absorbance, defined as 100UV₂₅₄/DOC, (SUVA), pH, temperature (*T*), bromide ion concentrations (Br⁻), chlorine dose (*D*) and reaction time (*t*). The TOC, DOC, UV₂₅₄ and SUVA are often used as surrogate measures representing NOM in water. TOC indicates the total mass of organic substances (suspended and dissolved fractions), while DOC indicates the mass of the dissolved fractions and UV₂₅₄ represents the specific structure and functional groups of NOM (Edzwald et al., 1985; Croue et al., 1998; USEPA, 2001a,b). The SUVA is an indicator of NOM reactivity. A few other studies have incorporated chlorophyll-*a* and fluorescence as the surrogates for NOM in water (Golfinopoulos et al., 1998; Ibarluzea et al., 1994). A number of these models use more than one parameter from TOC, DOC, UV₂₅₄, SUVA and algae to address the effects of NOM (Amy et al., 1987; Malcolm Pirnie Inc., 1992, 1993; Sung et al., 2000; Sohn et al., 2004). In addition, a number of studies have reported using NH₃–N (Malcolm Pirnie Inc, 1993), seasonal variation (Golfinopoulos and Arhonditsis, 2002a), regional effects (Milot et al., 2000) and ratios between HOCI and HOBr (Nokes et al., 1999; Uyak and Toroz, 2007) in developing DBP formation models. As shown in Table 3, the number of water quality and operational parameters used in the reported models ranged from 2 to 8 (Garcia-Villanova et al., 1997a; Malcolm Pirnie Inc., 1993).

In general, models based on field data are more realistic as these data incorporate the responses of specific series of water treatment processes and their corresponding distribution systems (Sadiq and Rodriguez, 2004). However, some parameters affecting DBP formation are difficult to estimate in field-scale studies. For example, estimating the reaction time within distribution systems requires hydraulic simulation models, which are time consuming and not always very accurate. Moreover, field-scale models are generally site specific (Rodriguez et al., 2000). Conversely, empirical models developed through laboratory experiments have been found to be more reliable than field-scale studies because they employ controlled conditions, where effects of a particular parameter can be determined by keeping the other parameters constants or by performing factorial analyses following a statistical design of experiments. However, the DBP occurrences through reactions with residual NOM in distribution systems are not typically included in these laboratory-scale models. Table 4 briefly describes the water sources, experimental conditions, performances, advantages and limitations of the models listed in Table 3. From Table 3, it can be noted that most of the models were developed using multivariate regression techniques. Some studies developed first- and second-order kinetic models and the coefficients were estimated using multivariate regression analyses. A number of studies have reported developing DBP formation models using two parallel first-order reactions (e.g., fast and slow reactions). As can be seen from Table 3, laboratory-scale models generally considered a greater number of parameters and larger numbers of data points than models based on field-scaled studies. This may be due to the shorter time required to obtain a comprehensive data set, as well as the greater flexibility and control over experimental variables and operational conditions possible in a laboratory environment compared to a field-scale environment.

To evaluate the performance of different models, it is often required that the models be developed under similar water quality and operational conditions. It is often difficult to make precise judgments regarding the performance of reported models, as these models were generally developed using different modelling approaches, parameters and pretreatments, as well as variable water quality characteristics. A large number of models were evaluated using statistical techniques, where coefficients of determination, correlation coefficients, mean absolute errors between measured and predicted data, and distributions of residuals are often considered as indicators of model performance. However, regression models often have limitations in that these models should be used within the experimental conditions for which the models were developed (Montgomery and Runger, 2007). Despite the fact that most models presented in Table 3 are multiple regression models estimated from field or laboratory data, operating regions in the factors over which the models provide reliable predictions were seldom reported. In addition, most of the models did not consider actual water supply systems and/or external databases for model validation. Natural systems, such as water supply systems are typically associated with uncertainty from a number of sources, including model parameter selection, the distributions of model parameter values, limited data and/or lack of proper knowledge. Most of the models presented Table 3 do not include discussions on possible uncertainty associated with their respective regression coefficients and model parameter values. The model parameters may also vary temporally and spatially. As a result, it is recommended that studies also investigate the effects of simultaneous variability of different model parameters to assess possible interaction effects. This could be performed using factorial analysis for all of the model parameters using replications and center points. Only three studies in Table 3 conducted factorial analysis; however, incorporation of all of the parameters, replications and centre points were not considered in those studies. As such, interaction effects for the full set of combinations of the model parameters were generally absent in these studies.

3.2. Potential application of models

Predictive models for DBP formation have a wide range of applications in the design and management of drinking water supply systems, for regulatory agencies, in toxicological and epidemiological risk assessment studies, as well as in risk-cost trade-off analyses. These models can be employed to determine the effects of different water quality and operational parameters on DBP formation. Based on the analyses, different water quality and/or operational parameters can be adjusted to control DBP formation in drinking waters. Managers and operators of drinking water supply systems can use these models as a decision-making tool to achieve better operational control during the treatment process. This can be accomplished in different ways: (i) DBP concentrations can be controlled within regulatory limits by adjusting different parameters; (ii) operational parameters such as, pH can be controlled to prevent corrosion/scaling in water distribution systems; (iii) locations of chlorine boosting stations can be determined to ensure that free chlorine residuals are maintained for the protection of drinking water quality throughout distribution systems; and (iv) concentrations of DBPs at the extremities of distribution systems can be predicted to identify the worst case scenarios in terms of possible health risks.

Regulatory agencies can use the models to verify the status of the water supply systems. A significant number of water supply systems in the USA and Canada are more than 50 years old. These systems generally involve conventional pretreatment processes, which do not include enhanced pretreatments prior to disinfection. A number of these systems often reported relatively high concentrations of DBPs in their finished waters (USEPA, 2006; MOE, 2006). To provide a better control of DBP formation, many of these water supply systems in USA and Canada may require improvements in the near future. Upgrading these systems could reduce the risks associated with DBP exposure, however the increased cost to the municipalities may not make this option feasible. Regulatory agencies evaluate the benefits of risk reduction resulting from upgrading systems and compare these with the associated costs required for such improvements. The predictive models can be used to evaluate the required reduction in precursors (in combination with available models to determine the organic precursor removal efficiencies of different treatment processes), which allow for compliance with DBP standards, and thus estimate the needs for the upgrading of water supply systems.

In the recent years, there has been an increasing concern over the possible health risks associated with DBP exposure. Regulatory agencies are often guided by the risks predicted through toxicological and epidemiological studies, which are generally conducted through laboratory investigations. However, these studies are often time consuming, costly and not available for all water supply systems. As such, generation of DBP data through laboratory investigations are typically limited. DBP concentrations at a desired location can be estimated using the predictive models. These data can then be useful in estimating human exposure to DBPs through drinking water ingestion, as well as inhalation and dermal contacts. As such, human health risks can be predicted for different exposure routes. Fig. 2 presents the framework for possible use of DBP formation models in risk assessment studies. It should be noted that water quality and operational parameters can be imprecise and are often associated with uncertainty (Fig. 2). Uncertainty can be incorporated using statistical distributions as input parameter values. A hypothetical example, which incorporates uncertainty associated with DBP concentrations, is presented using the DOC based THM formation model for raw waters developed by Sohn et al. (2004) (Table 3: No. 41a). As input parameters, this model requires DOC, chlorine dose, pH, temperature, reaction time and bromide ion concentrations to predict THM concentrations. For this example, values of DOC, chlorine dose, pH, temperature, reaction time and bromide ion concentrations are assumed to be imprecise, where the minimum, most likely and maximum value are known. The parameter values are assumed to be DOC=1.9, 3.8, 8.1 mg/L; pH=5.4, 6.5, 8.7; chlorine dose (D) = 2.1, 3.5, 7.8 mg/L; water temperature (T) = 9, 15, 21 °C; bromide ion concentrations $(Br^{-1}) = 10, 60, 150 \,\mu g/L$; and reaction time (t) = 7, 12, 23 h. Using the minimum, most likely and maximum values, random data for each of the parameters have been generated following triangular distributions and the THM concentrations have subsequently been predicted using the predictive model for THM formation by Sohn et al. (2004). The frequency distributions and probability density function of the predicted THMs concentrations are shown in Fig. 3. The predicted THMs ranged between 19.5 and 246.6 µg/L with a most likely value of 78.2 μ g/L (Fig. 3). These predicted THMs concentrations can then be used to estimate the human health risks associated with THMs exposure (Fig. 2). Risk assessment approaches addressing exposure to drinking water contaminants have been presented in other studies (USEPA, 1998a,b; Jo et al., 1990; Louvar and Louvar, 1998; Chowdhury and Champagne, 2009). In addition to risk assessment studies, this model can also be used to estimate desired operational parameters, such as pH or reaction time by knowing THM concentrations. In these cases, the THM concentrations can be approximated through statistical distributions and used in the models to predict the desired pH or temperature.

4. Future research needs

Significant research has been conducted to develop predictive models for DBP formation in drinking water. The models can be used to identify factors influencing DBP formation and the decay of disinfectants in water distribution systems. The relative contributions of water quality and operational parameters to the formation of DBPs can also be determined using these models. The application of a number of these models may be limited as the models are often derived from specific data sources and/or source water quality and operational parameters. In addition to the knowledge acquired in the last three decades, there is a need for investigations that can lead to a better understanding and control DBP formation in water treatment and distribution systems; perform toxicological and epidemiological risk assessments; and, will assist in decision-making process and implementation of water treatment and supply system upgrades. Some of the existing knowledge gaps, which must be addressed in the near future, are outlined below.

○ The organic content, pH, water temperature, reaction time, bromide ion concentrations and free residual chlorine are generally

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189–4206

Table 4

Model descriptions, advantages and limitations.

No.	Model description	Advantages	Limitations
I.Minear and Morrow (1983)	This study developed multiple regression model for THMs formation through controlled chlorination in the laboratory. Raw water from the Holston River (Knoxville, Tennessee) was filtered using 0.45 µm filter paper for the experiments. The organic content was varied by adding commercially available humic acid. A series of experiments was carried out under controlled pH, temperature, bromide ion concentrations and chlorine doses at constant reaction time of 96 h. The study varied one factor by keeping the other factors constant.	The model was verified using data developed from field-sampling program. The model has strong predictive ability	Model does not consider reaction time as an explanatory variable. In waters with insignificant bromide ions, the model performance may be reduced as the formation of brominated THMs depends on the fractional characteristics of NOM in water.
2. Urano et al. (1983)	This study developed empirical model to predict THMs formation. Aqueous solution of humic acid, obtained as a reagent from coal by Wako Chemical Co. and raw water from Sagami River in Japan were used for chlorination experiments in this study. The model's applicability was tested for river and lake waters using historical data and laboratory experiments.	The model was tested using river and lake water samples as well as historical data and found to be efficient.	Reaction temperature was not considered as an explanatory variable. The R^2 value of the model is unknown.
3. Engerholm and Amy (1983)	A kinetic model for predicting chloroform formation was developed as a function of reaction time, initial total organic carbon (TOC), initial chlorine-to-TOC ratio, temperature, and pH. The laboratory chlorination experiments were conducted on synthetic water prepared by adding commercial humic acid to deionized water. This study characterized the effects of different factors by varying one-factor-at-a-time keeping the other factors constant.	The model is effective in predicting chloroform formation and provide realistic framework for predicting chloroform formation in different source waters	Temperature and pH were not included as the explanatory variables in the model. The model may not be efficient to predict THMs formation in waters with bromide ions.
4. Morrow and Minear (1987)	This study was an extended work of Minear and Morrow (1983). In this study, non-linear regression analysis was performed to develop THMs formation model using Gaussian, Dud and Marquardt methods. The effects of bromide ions on THMs formation were characterized in this study. The models were validated using twenty Tennessee raw and finished water supply systems data.	Presented different options and methodologies of modeling THMs formation. Some of the validation data showed excellent agreement with the model predictions.	Model did not consider reaction time as an explanatory variable.
5. Amy et al. (1987)	This study developed linear and non-linear regression models to predict THMs formation in drinking water using a robust database from laboratory chlorination experiments on raw waters of nine US rivers. Boundary conditions of explanatory variables were defined for the model development. Different models were developed for short-term (t <8 h) and long-term (t >24 h) THMs formation.	The models were based on robust database from several water sources with variable water quality characteristics. The R^2 value was excellent.	The study used UV_{254} and TOC in the model; however, UV_{254} and TOC are the surrogates of NOM. Thus, parameters estimation might have suffered from confounding effects. Raw water characteristics are different from the treated water characteristics, which may not represent real water supply systems in the present days.
6. Adin et al. (1991)	Authors developed a mechanistic model for THMs formation based on their formation kinetics. Humic acids were isolated from the Sea of Galilee (Lake Kinneret) water in Israel. This humic acid was used to generate water samples for chlorination experiments in laboratory scale. Model showed THMs as a function of TOC, chlorine dose and contact time.	Modeling approach allows examining the kinetics of THMs formation.	The model did not consider pH and temperature. The source had very high bromide ions concentrations (up to 1.9 mg/L), which might have effects on THMs formation, while bromide ions were not considered in the model.
7. Harrington et al. (1992)	This study developed computer program to simulate THMs formation, removal of TOC and ultraviolet absorbance by alum coagulation, and changes in alkalinity and pH. This study used the model and databases developed by Amy et al. (1987).	The model was based on very robust database from several water sources with variable water quality characteristics. The R^2 value was excellent.	The study used UV_{254} and TOC in the model. Source waters have variable water quality and chlorination characteristics
8. Malcolm Pirnie Inc. (1992)	This study developed empirical models for CHCl ₃ , BDCM and DBCM formation in drinking water from experiments with California State Project and Colorado River Aqueduct waters. The models incorporated TOC, UV ₂₅₄ , chlorine dose, pH, reaction time, temperature and bromide ion concentrations as explanatory variables.	This study developed models to predict individual THMs species. This was an advantage over the previous models that predicted total THMs	Models used UV_{254} and TOC together; however, UV_{254} and TOC are surrogates of NOM. R^2 values of the models were not reported.
9. Malcolm Pirnie Inc. (1993)	This was a follow up study of Malcolm Pirnie Inc. (1992). In this study, THMs as a whole and species wise models were developed. This study incorporated ammonia nitrogen with the other parameters in modeling THMs formation.	The effects of ammonia nitrogen (NH ₃ –N) were incorporated in the models, which was a new idea.	Models used UV_{254} and TOC together; however, UV_{254} and TOC are surrogates of NOM. R^2 values of the models were not reported.
10. Montgomery Watson (1993)	Models for four THMs species and five HAAs were developed in this study. This study combined three laboratory scale databases developed in four	Models were validated using independent database.	Combined TOC with UV ₂₅₄ in the models; Raw water characteristics and chlorination do not represent treated water characteristics and

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189–4206

Table 4 (continued)

No.	Model description	Advantages	Limitations
	different studies across USA including the works of Amy et al. (1987). Models were developed according to the ratio between chlorine dose and bromide ion concentrations in water. Good predictive abilities of these models were observed.		chlorination.
11. Lou and Chiang (1994)	Water samples from 18 locations of the Taipei River in Taiwan were collected over a period of 6 months. A predictive regression model for THMs in the distribution system was developed using THMs in the treatment plants and other factors. The model considered the effects of distribution pipes on THMs	Observed data were within 10.9% of the simulated results. Model includes water dispersion in the distribution system.	Model did not consider temperature as an explanatory variable. Measuring dispersion in a real system distribution network is extremely difficult.
12. Ibarluzea et al. (1994)	formation. Authors developed a multiple regression model for predicting chloroform formation using monthly samples (during 1 year) from the water treatment plant and the finished water of the city of San Sebastian (Spain). In addition to the normal water quality and operational parameters, they used fluorescence as an indicator of NOM instead of more common indicators mentioned in the literature such as TOC and UV ₂₅₄ .	Very simple model with relatively good results	Model does not consider reaction time as an explanatory variable. Use of fluorescence as an indicator of NOM was not justified in the previous studies or in their study
13. Ozekin (1994)	This study used ten different sources of water to develop bromate formation model through ozonation in laboratory. The initial model was developed at a constant temperature of 20 °C and a temperature adjustment model was developed as well.	Temperature adjustment had flexibility to perform water disinfection at variable temperature. This was the earliest model to predict bromate formation in water	Model validation or R^2 value was not reported.
14.Siddiqui et al. (1994)	In this work, a series of empirical models for predicting brominated byproducts were developed. The water samples were collected from three water treatment plants in USA. Data for modelling works were generated by ozonating water sample in the laboratory.	Model allowed to consider effects of temperature on bromate formation	Model showed moderate performance in predicting brominated byproducts
15. Song et al. (1996)	This study developed a multiple regression model for predicting bromate formation in drinking water. Experimental data were generated through batch reactions by varying one factor at a time approach. Isolation and fractionation of NOM was performed prior to ozonation. The model established boundary conditions to obtain the reasonable predictions of bromate formation. The model was validated using the laboratory-scaled data and with data from published literature.	The model showed very good performance in predicting bromate in natural waters. The model was validated internally by using laboratory data and externally by using data from published literature.	Variation of water temperature was not considered in the experiments. Thus, model did not allow predicting seasonal variations of bromate. The boundary conditions may impose limitations in using the model at diverse environmental conditions.
16. Rathbun (1996a)	This study developed multiple regression models for predicting CHCl ₃ , BDCM, DBCM and CHBr ₃ formation using water samples from the Mississippi, Missouri and Ohio Rivers in USA. Water samples were collected during the summer and fall of 1991 and spring from 1992 at 12 locations. The models were developed at a constant temperature	Models showed good predictability. The root mean square of the model predictions and experimental data were found good.	Raw waters do not represent characteristics and chlorination of the treated water. The models did not consider reaction time and temperature as explanatory variables.
17. Rathbun (1996b)	of 25 °C and constant reaction time of 7 days. In this work, multiple regression models for predicting THMs and NPTOX formation were developed using water samples from the three rivers as of Rathbun (1996a). However, the raw waters were filtered using prewashed 0.45 μ m low- extractable cellulose acetate membranes prior to use. A 3 × 3 orthogonal experimental design for pH and chlorine dose was followed in this study. The regression coefficients for the models were found to be comparable to the previously published literature.	Models based on a very robust database representing variable water quality of three rivers.	The models did not consider reaction temperature as explanatory variable. Interaction effects of the factors were not identified in this study
18. Chang et al. (1996)	In this work, THMs formation models were developed using raw water chlorination experiments in the laboratory following multiple regression technique. The water samples were collected from Pen-Hsing River as well as Pan- Hsing, Fong-Yuen and Chen-Chin-Hu water treatment plants in Taiwan to develop and validate THMs formation models. This study varied followed one-factor-at-a-time approach. The temperature was kept constant throughout the experiments.	The models were simple and had very good predictive ability.	One of the three models used UV ₂₅₄ and TOC, which could result in erroneous parameter estimation. The models did not consider water temperature as an explanatory variable. Raw water and treated water characteristics are different.
19. GVillanova et al. (1997a)	In this work, samples were collected from eight different locations of two conventional water treatment plants in the city of Salamanca (Spain). The samples were collected on 11 different dates to	This study developed model with reduced number of variables. The model incorporated spatial and temporal variability of sampling location and time.	This model did not consider chlorine dose, organic content, reaction time or bromide ion concentration. The model contained third and higher order polynomials of temperature which

(continued on next page)

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189–4206

Table 4 (continued)

No.	Model description	Advantages	Limitations
	represent seasonal variations of chlorinated DBPs and other water quality parameters. Using these data, regression model for predicting chloroform formation was developed.		made it highly sensitive to use for the water treatment plants
20. G-Villanova et al. (1997b)	This is a continuous study of G-Villanova et al. (1997a). Water samples were collected from six locations of the distribution systems of three water supply reservoirs in the city of Salamanca (Spain). This study developed regression model for predicting chloroform formation in drinking water. This study used dummy variables to consider the locational variability within the distribution system and the effect of time of sampling in the model development.	The model incorporated spatial and temporal variability of sampling location and time. Dummy variable was used to incorporate the effects of distribution systems on chloroform formation.	This model did not consider chlorine dose, organic content, reaction time or bromide ion concentration. The model contained third and higher order polynomials of temperature which made it highly sensitive to use for the water treatment plants
21. Huixian et al. (1997)**	In this study, non-linear regression models for predicting the formation of POX and NPOX were developed using chlorination of water samples that had fulvic acid as the NOM. The fulvic acid was isolated from the Taiping Lake in China, which was used to prepare water samples and chlorination was performed in the laboratory. The effects of ammonia nitrogen on POX and NPOX formation were also investigated in this study.	This study characterized the effects of different factors including ammonia nitrogen. The models appeared with very accurate predictive abilities	Number of data is unknown. THMs, HAAs cannot be separated to check the regulatory compliance.
22. Clark and Sivaganesan (1998)	In this study, a second-order kinetic model was developed to predict THMs formation in drinking water. This study used synthetic water prepared by adding commercial humic acid to Super-Q water to perform bench-scale chlorination experiments in the laboratory. The THMs formation model was developed using a balanced equation between hypochlorous acid and substances responsible for chlorine demand. The model was validated using two field studies performed in the past (Clark et al., 1994; Vasconcelos et al., 1997).	The model allows characterizing THMs formation as a function of chlorine consumption and fundamental reaction kinetics.	The R^2 values for the model coefficients range between fair and good. It is not proved that the second-order model would give better predictions than first-order kinetics. Formation of THMs is a continuous process; thus, the assumption of balanced equation may affect the result.
23. Golfinopoulos et al. (1998)	This study developed a multiple regression model for predicting THMs formation in the finished water leaving the plant using field sampling from the Galatsi Treatment Plant of Athens. A particular feature of this model is that chlorophyll-a was introduced in the model as an indicator of NOM. This study included seasonal variability of THMs formation. Overall 82% of the predicted values were found to be within $\pm 20\%$ of the measured values.	Model represented actual water supply system and seasonal variation of THMs formation	The model did not consider reaction time as an explanatory variable. Moreover, chlorophyll-a is not a common surrogate measure for NOM in water.
24. Amy et al. (1998)	This study developed THMs formation models based on data generated from untreated river waters in USA. The model used DOC instead of both TOC and UV ₂₅₄ as indicators of NOM in their original works Amy et al., 1987).	Empirical based models were developed for haloacetic acids, chloral hydrate, and bromate.	Raw water characteristics and chlorination do not represent characteristics of treated water. Chlorination conditions of data from different source waters were different.
25. Nokes et al. (1999)	In this study, kinetic models for predicting THMs formation were developed through incorporation of HOBr and HOCI ratio and activated carbon atoms. The water samples were collected from drinking water supplies prior to their chlorination points in New Zealand. The model constants were estimated using data from experimental chlorination of 17 surface and ground waters in New Zealand.	The models analyzed the effects of bromide ions in the THMs formation kinetics	Chlorination conditions for different samples were not comparable. The models incorporated activated carbon atom to determining halogen substitution; however, the reaction kinetics for halogens substitutions are partially known. Models did not consider other factors, such as pH, temperature as explanatory variables.
26. Rodriguez et al. (2000)	This study developed THMs formation models by combining data from Amy et al. (1987), Rathbun (1996a,b) and Montgomery (1993). The models were validated using field-scale database from small water utilities in Quebec (Canada). Sensitivity analysis was also performed using field-scaled database. Field-scaled models were also developed for the raw waters in southern Quebec.	A robust database is considered to develop simple and accurate models.	The field-scaled model's predictability was poor. Many assumptions have to be made to apply the models to field-scaled data. Chlorination conditions for different databases were different. Raw waters do not represent treated water characteristics.
27. Milot et al. (2000)	This work developed models for predicting probabilities of exceeding specified values of THMs using logistic regression analysis. This study was designed to estimate the susceptibility of water utilities to human. The data for modeling were collected from several utilities in Quebec, Canada. A sensitivity analysis using this model can identify the strategy of reducing THMs formation in the distribution systems.	epidemiological study.	Models do not consider water quality and operational characteristics (chlorine dose, pH, t , T , TOC, DOC or UV ₂₅₄).
28. Sung et al. (2000)	This study developed semi-mechanistic models for THMs, HAA ₅ , CHCl ₃ and TCAA formation in drinking water using raw waters for the Massachusetts Water Resources Authority. This work incorporated	supply system, which represented seasonal variability. The models showed very good	The models did not consider temperature as an explanatory variable. The THMs and CHCl ₃ models used UV ₂₅₄ and algae together, while UV ₂₅₄ and algae represented NOM. Use of hydroxide

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189–4206

Table 4 (continued)

No.	Model description	Advantages	Limitations
	hydroxide concentration and chlorine decay kinetics in the model development The model coefficients were determined using data from October 1997 to July 1999 and the model was validated with data from August 1999 to January 2000.		concentration as a model explanatory variable was not common.
29. Westerhoff et al. (2000)	This study developed regression models to predict THMs formation and residual chlorine decay for finished water in the treatment plants. The historical data for model development were obtained from three water treatment plants in Paris from 1990 to 1996. The plants had variable water quality and operational characteristics. The model incorporated chlorine consumption and 10% of the bromide ion concentrations for THMs formation model development.	This model determined the percentages of bromide ions converted into THMs.	Model performance was not reported. The model was based on raw water data. Chlorine consumption in the plants and water distribution systems depends on pipe walls, biofilms on the pipe walls and bulk flow of water in the pipe. Conversion of bromide ions into THMs depends on temperature and pH.
30. Elshorbagy et al. (2000)	This study developed model to characterize kinetics of THMs formation using non-linear optimization in a full dynamic water distribution system. This study incorporated the bromine content factor for the model development. The model was tested and verified by applying to a portion of the Abu-Dhabi water distribution systems in the United Arab Emirates.	The model was able to predict differences in THMs formation within different nodes of the distribution systems. The model predicted bromide ions decay in the distribution systems.	Model performance was not reported. Conventional variables were not incorporated in the model development.
31. Clark et al. (2001)	This study developed kinetic models for predicting four THMs and nine HAAs formation in drinking waters. The laboratory investigations were performed using synthetic water prepared by adding commercial humic acid to Super-Q water. A two block, full factorial design was followed to perform the laboratory experiments. Two levels of chlorine doses, three levels of pH and reaction time and four levels of bromide ion concentrations were investigated in this study. The authors used a second-order rate and chlorine decay kinetics to predict DBPs formation in water distribution systems. The <i>R</i> ² values for the models were more than 0.95 except for MCAA, which was 0.53.	The models integrated mechanistic and empirical methods, which provided higher degree of flexibility for model applications.	This study conducted experimental investigations at constant organic content (TOC, DOC or UV_{254}) and temperature. The interaction effects of the factors were not characterized. It was not proved that this approach gave better results than classical regression models.
32. Golfinopoulos and Arhonditsis (2002a)	This study developed multiple regression models for THMs, CHCl ₃ and BDCM formation in finished drinking water using data from the Menidi Treatment Plant of Athens. Raw water samples were collected in duplicates from nine different points over the plant throughout June 1995–November 1998. The models incorporated the effects of seasonal variability as one of the explanatory variables. In general, these models were found to give acceptable fits over the annual cycle.	The models were developed based on the data from actual water treatment plant. Models represented seasonal variability for THMs, CHCl ₃ and BDCM occurrences.	Raw water characteristics and chlorination do not represent the treated water characteristics and chlorination. The performance of models was relatively low
33. Golfinopoulos and Arhonditsis (2002b)			The model was not validated. This model was developed based on raw water characteristics and chlorination, while water is pretreated prior to chlorination in most of the water supply systems. The conventional water quality and operational variables, such as water temperature and pH were not considered as the explanatory variables.
34. Korn et al. (2002)	This study developed chlorite formation model through bench-scale experiments using water from seven drinking water treatment plants in Canada. A two-level full factorial design was performed for the experiments instead of using conventional one- factor-at-a-time approach. This approach determined the interaction effects of the factors	This model presented the basic understanding of chlorine dioxide byproducts formation in water. Predictive capabilities of the model is high	NPOC and UV ₂₅₄ were simultaneously used; however, both characterize NOM in water.
35. Gang et al. (2002)	This research developed kinetic models to predict THMs and HAAs formation and chlorine decay kinetics through chlorination of eight Missouri surface waters (raw and alum-treated). Water samples were filtered using membrane ultra filtration prior to experiments to determine chlorine demands for different fractions of NOM.	This model used chlorine demand other than conventional chlorine dose in models. Models allowed examining the effects of molecular weights of NOM fractions on DBPs formation.	Water quality and operational variables (chlorine dose, pH, either TOC DOC or UV ₂₅₄ , temperature) were not incorporated in the models. Developed model is usable for research but may be difficult to apply to the actual water supply systems.

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189–4206

Table 4	(continued)
---------	-------------

Table 4 (continue No.	Model description	Advantages	Limitations
	Two parallel first-order reactions, based on fast and	/ availages	Linitations
	slow reaction kinetics, were incorporated in these		
36. Serodes	models. This study developed regression models for	Data from the experimental chlorination allowed	The models did not consider pH as an explanatory
et al. (2003)	predicting THMs and HAAs formation through	representing the seasonal variations of watering	variable. Models showed variable performance.
	bench-scale chlorination experiments using treated waters (prior to final chlorination) from three major	quality characteristics.	Models were not validated
	drinking water utilities in Quebec (Canada). Water		
	samples with variable conditions of water quality were collected over 6 month (May-November		
	2000) period.		
37. Nikolaou et al. (2004)	This study developed multiple regression models for predicting THMs and HAAs formation through	The models used minimum number of water quality and operational variables. These models provided	The models were based on raw water samples. Models did not consider NOM (either TOC DOC or
	chlorination of river waters (with different water	satisfactory estimations of the THMs and HAAs	UV_{254}) or reaction temperature. The R^2 values of the
	quality regarding bromide ion concentration and organic matter contents) from Lesvos island,	formation	models were very low
	Greece. The study concluded that formation of		
	THMs and HAAs in water might have some		
	stochastic character, which was difficult to describe by the conventional regression techniques.		
38. Al-Omari	This study developed a regression model to predict		Model did not incorporate temperature as an
et al. (2004)	THMs formation in drinking water for Zai water treatment plant (that supplied water to Jabal	measured and predicted THMs concentrations. Model used WaterCad software to simulate the	explanatory variable. The R^2 values of the model were not reported
	Amman water supply systems) in Jordan. The model	distribution systems using water flow	*
	was developed at 20 °C and another temperature adjustment model was proposed for higher	characteristics	
	temperature. The model was tested using data from		
	different locations throughout the Jabal Amman water supply systems. WaterCad software was used		
	to incorporate water age in the distribution pipes.		
	Results showed good agreement between measured and predicted THMs concentrations.		
39. Kolla	This study developed regression models in	In addition to THMs, DCAN and TCP were also	Models were developed using unfiltered raw water
(2004)	laboratory to predict THMs, DCAN and TCP formation in drinking water through chlorination of	modeled in this study.	samples. Reaction temperature was not incorporated in the models. The models were not
	raw water samples from five water supply systems		validated.
	in Newfoundland, Canada. The samples were collected and analyzed throughout January 2003–		
	May 2004.		
40. Lekkas and Nikolaou (2004)	This study characterized the effects of bromide ions on THMs and HAAs formation and developed	The models incorporated the effects of bromide ions on THMs and HAAs formation. Model showed	The models did not consider NOM (TOC, DOC or UV_{254}) or reaction temperature. The R^2 value for
	regression models for predicting THMs and HAAs	excellent R^2 value for THMs formation	HAAs model was low. Raw water does not represent
	formations through bench-scale experiments in the laboratory. Water samples for this study were		treated water characteristics.
	collected from Tsiknias River in Mytilene, Greece in		
	March 2000. These samples were spikes with bromide ions at different concentrations. The study		
	performed one-factor-at-a-time experiments.		
41. Sohn et al. (2004)	This study developed multiple regression models for predicting THMs, HAAs and bromate formation	Models were based on a very robust database that was developed for variable water characteristics.	The models often used DOC and UV ₂₅₄ together as the explanatory variables. Raw water characteristics
	for raw and treated waters. A total of 16 models	The models provided an option of comparing and	do not represent the treated water characteristics.
	(THMs: 7 models; HAAs: 7 models; bromate: 2 models) were developed for raw and coagulated	using different models at different environmental conditions.	Chlorination conditions for different source waters were different
	waters. The models were developed and validated	conditions.	were unterent
	using historical data assembled from Amy et al.		
	(1987, 1998) and Montgomery (1991), which were obtained from 12 raw and a subset of 8 water		
	sources subjected to alum and iron coagulation in USA. Different models were based on different		
	water quality parameters, such as, DOC, DOC^*UV_{254} ,		
	as well as raw and treated waters. Boundary		
42. Uyak	conditions for the models were established. Multiple regression model for predicting THMs	The model has excellent predictive ability. The	Raw water characteristics and chlorination do not
et al. (2005)	formation at finished water of the Kagithane water	model was directly applicable to the chlorination of	represent treated water characteristics and
	treatment plant in Istanbul City, Turkey was developed in this study. The raw water for the	raw waters.	chlorination. This model did not consider reaction time as an explanatory variable.
	treatment plant was obtained from the Alibeykoy		
	Reservoir and Terkos Lake in Istanbul. Data for THMs and other water quality and operational parameters		
	were generated through a 12-month sampling		
	program between January and December 2003. This model could be used to estimate THMs concentration		
	for different water quality and treatment processes		
43. Uyak and	with different operational conditions. This study developed regression model to predict	The model characterized effects of seasonal	The model did not characterize the effects of pipe
Toroz (2005)	THMs formation and characterized seasonal	variability on THMs formation within the water	walls and biofilms. The model did not consider pH
	variability of THMs formation within distribution	distribution systems. Model showed good	and reaction time as explanatory variables.

DWR-706

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189-4206

Table 4 (continued)

No.	Model description	Advantages	Limitations
	systems of the Buyukcekmece water treatment plant in Istanbul City (Turkey). The investigation was based on a 30-week sampling program, undertaken during the spring, summer and fall of the year 2003. THMs and other water quality and operational parameters were monitored at points along the distribution system between the treatment plant and the system's extremity. The study found that the THMs formation in the distribution systems were 1.2–1.8 times higher than the THMs formation in the finished water at the treatment plants during summer period, while these were much less during spring and fall.	predictability	
44. Tyrovola and Diamadopoulos (2005)	This study developed a multiple regression model for predicting bromate formation in drinking water during ozonation of groundwater containing elevated bromide ion concentrations. The groundwater samples from aquifers in coastal areas (Northwestern area of Crete, Greece) were ozonated in a semi-batch reactor under typical ozonation conditions. This study characterized effects of different parameters, such as ozone dose, reaction time, pH and bromide ion concentrations on bromate formation. The model simulated the effect of water quality characteristics and treatment processes on bromate formation.	The model was capable of estimating the concentration of bromate concentration in ozonated groundwater, which contain low concentrations of ammonia and dissolved organic carbon. The model had very good predictive ability. Model was developed by considering the seasonal variability	The model did not consider NOM (TOC, DOC or UV_{254}) and temperature as explanatory variables.
45. Rodrigues et al. (2007)	This study developed THMs formation models through laboratory experiments using synthetic water, which was prepared by using hydrophobic fraction of fulvic acid. The fulvic acid was collected from Caldeirao dam in Guarda, Portugal and the hydrophobic fractions were isolated using XAD-8 resin. This study performed fractional factorial design with center points followed by response surface analysis through Box–Behnken design. The models incorporated interactions of different	This study followed statistical design approach to characterize the effects of different factors. In this study, interaction effects of different factors were assessed statistically.	This study did not identify pH and reaction time as significant factors. This study did not consider any replication to consider experimental errors.
46. Uyak and Toroz (2007)	factors. This study developed four THMs and three HAAs (DBAA, DCAA, BCAA) formation models using chlorination of Buyukcekmece lake water, Istanbul, Turkey. The raw water was filtered using 0.45 µm filter paper prior to chlorination. Bromide ions were spiked to six different levels ranging from 0.05 to 4.0 mg/L for the experiments. This study incorporated the ratio between HOBr to HOCl in the model development. The experiments follow one- factor-at-a-time approach.	This study characterized the effects of the ratio between HOBr to HOCl in the formation of THMs and HAAs species.	The models did not consider the organic contents (TOC, DOC or UV ₂₅₄), pH, temperature or reaction time. The models were not validated and R^2 values were not reported.
47. Hong et al. (2007)	This study developed multiple regression models for THMs, BDCM and CHCl ₃ formation in drinking water under different chlorination conditions using samples from Dongjiang River in Hong Kong. This study identified the effects of bromide ions on THMs formation. This study followed an orthogonal design, which allows the variation of only one parameter at a time while other parameters maintain a designated "baseline" condition.	This study characterized the effects of bromide ions on different species of THMs formation. This study included variable water characteristics	Raw water characteristics and chlorination do not represent treated water characteristics and chlorination.
48. Semerjian et al. (2008)	The study developed predictive models for THMs formation in Lebanon based on field-scale investigations as well as laboratory-controlled experimentations. Predictive models showed variable <i>R</i> ² values. The laboratory-scale simulated distribution system trihalomethane (SDSTHM) tests were conducted on selected public drinking water sources; namely the Kfar Helda WTP and Zheyma in Lebanon to predict as well as evaluate THMs formations under controlled laboratory conditions. Seasonal variability of THMs formation was considered n this study.	This study developed models for both laboratory and field-scale, which provided flexibility in the model selection	Models did not consider pH and temperature as the explanatory variables. The R^2 values of the models were very low.

changed continuously in water treatment plants and distribution systems. A limited number of studies have determined the interaction effects from the simultaneous variability of some of these factors (Rodrigues et al., 2007; Clark et al., 2001; Korn et al., 2002). Korn et al. (2002) developed a chlorite formation model using a two-level full factorial design for six factors (chlorine dioxide, pH, temperature, reaction time, UV_{254} and NPOC). However, the authors did not incorporate THMs or HAAs in their study. Rodrigues et al. (2007) used fractional factorial experimental designs to investigate THM formation, using five factors (fulvic acid,

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189-4206

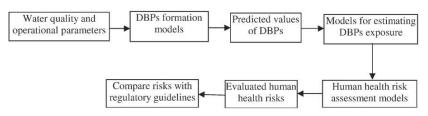


Fig. 2. Use of models in risk assessment studies.

pH, reaction time, chlorine dose and temperature). They did not find pH and reaction time to be statistically significant to THM formation. However, Rodrigues et al. (2007) did not include replicates in their experimental design, which could be employed to provide a better estimate of the noise variance for use in assessing statistical significance, which might have an impact on their conclusions. Clark et al. (2001) performed a three-level full factorial design for three factors (pH, reaction time and bromide ion concentration) keeping total organic carbon (TOC) and temperature constant. As such, they did not characterize the effects of TOC and temperature throughout their study. Other studies did not generally consider interaction effects from the simultaneous variability of different factors on DBP formation. To fill this critical gap, it may be beneficial to perform full factorial experimental designs with replications and center points including all significant variables in THM formation (e.g., DOC, chlorine dose, pH, water temperature and reaction time) in the assessment and formulation of predictive model.

- The presence of bromide ions has been demonstrated to have a critical effect on the formation of different DBP species including bromodichloromethane, dibromochloromethane, bromate, bromoform, etc. (Uyak and Toroz, 2007; Hellur-Grossman et al., 2001; Nokes et al., 1999; Liang and Singer, 2003). The hydrophobic and hydrophilic fractions of NOM typically follow different reaction pathways with bromide ions to form DBPs. In general, brominated DBPs are increased and chlorinated DBPs are decreased in the presence of bromide ions. In recent years, regulatory agencies (e.g., Health Canada, 2007) have imposed limitations on bromodichloromethane concentrations in drinking water to address its possible chronic and sub-chronic effects on human health. As such, in addition to total THMs, research should be focused on the prediction of brominated species formation in water, which could also be modeled independently.
- The majority of DBP predictive models have been developed based on multiple regression techniques by varying one factor at a time while keeping other factors constant. Future research could incorporate alternative experimental techniques, such as modeling based on fundamental reaction kinetics, as well as robust modelling approaches, such as fuzzy rule-based modeling (Chowdhury and Husain, 2006), adaptive neuro fuzzy inference system (ANFIS) modeling and artificial neural networks (Milot et al., 2002). The use of hybrid modelling methodologies could also be investigated, e.g., the use of different approaches to establish DBP kinetic coefficients, followed by the use of these coefficients relating them to water quality and operational parameters, thereby reducing uncertainty in their prediction.
- A number of models reported in the literature are intended for the prediction of total THMs and HAAs. Despite the fact that other DBPs (e.g., *N*-nitrosodimethylamine, chlorite and chlorate) have also been identified as having potential chronic effects on human health, predictive models for these compounds are very limited. Models to predict other DBPs are also required to perform comprehensive investigations on human health effects and compliance to regulatory limits. The availability of these models would also permit the evaluation of benefit–cost ratios of specific water supply systems,

leading to consideration of alternatives for possible control of water quality and operational parameters, as well as water supply system upgrades should these be necessary.

- Water supply systems require compliance with regulations regarding the potential presence of pathogenic microorganisms and chemical species with effects on human health, which often creates a need for trade-off studies. To ensure the safety of the water supply from pathogenic microorganisms, water distribution systems must provide adequate disinfection and a free residual disinfectant. An initiative to predict free chlorine residuals and DBP formation simultaneously would assist in such trade-off studies. The kinetic models developed by Clark et al. (2001) could be considered as the initial efforts in this direction.
- Large-scale databases of DBP concentrations considering data from 15 to 30 years are generally limited as the recognition of the health effects of these species and their monitoring are relatively new. Development of systematic databases for DBP concentrations would accelerate future research to estimate possible effects from DBP exposure from an epidemiological perspective. These types of studies are essential in regulating and establishing limits for DBP formation in drinking water to protect human health.

5. Summary and conclusions

This study performed a review on the available models to predict DBP formation in drinking waters. Forty eight (48) studies addressing 118 models for predicting DBP formation were included in this review. A number of challenges have been identified, which relate to water supply systems in controlling DBP formation under varying water quality and operational characteristics, as well as the need to maintain the microbiological safety throughout the water distribution systems. Based on the literature reviewed, different modelling approaches have been used to relate water quality and operational parameters with DBP concentrations in water. Most of the reported models have used DOC (or

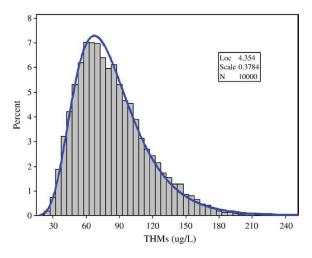


Fig. 3. Predicted THMs concentrations using Sohn et al. (2004) model.

TOC), disinfectant dose, pH, temperature, and reaction time as the explanatory parameters. The majority of the studies reported empirical approaches following multiple linear and non-linear regression techniques in the development of their respective models, while a limited number of investigations incorporated kinetics into their modelling approaches. The number of the models based on laboratory-scaled studies was the highest, while a number of other studies proposed models based on actual water distribution systems. DBP predictive models can be useful for operational purposes during water treatment, water quality management for the evaluation of water treatment facilities, exposure assessments in epidemiological studies, human health risk assessments, and estimating the benefits and impacts of DBP regulations. However, research is necessary to develop models that are more representative of real water supply systems by incorporating simultaneous variations of multiple parameters. In addition, evaluation of models is also required. Simultaneous predictions of DBP formation and free chlorine residuals could assist in the analysis of trade-off studies involving risks associated with pathogenic microorganisms and chemical exposures, as well as costs associated with the upgrading of water supply systems.

Acknowledgement

The first author acknowledges support in the form of a Canada Graduate Scholarship (CGS) from the Natural Sciences and Engineering Research Council of Canada (NSERC).

References

- Adin A, Katzhendler J, Alkaslassy D, Rav-Acha C. Trihalomethane formation in chlorinated drinking water: a kinetic model. Water Res 1991;25(7):797–805.
- Al-Jasser AO. Chlorine decay in drinking water transmission and distribution systems: pipe service age effects. Water Res 2007;41:387–96.
- Al-Omari A, Fayyad M, Qader AA. Modeling trihalomethane formation for Jabal Amman water supply in Jordan. Environ Model Assess 2004;9:245–52.
- Amy GL, Chadik PA, Chowdhury ZK. Developing models for predicting trihalomethane formation potential kinetics. J Am Water Works Assoc 1987;79(7):89–97.
- Amy GL, Siddiqui M, Ozekin K, Zhu HW, Wang C. Empirical based models for predicting chlorination and ozonation byproducts: haloacetic acids, chloral hydrate, and bromate. USEPA 1998 EPA report CX 819579.
- Arora H, LeChevallier MW, Dixon KL. DBP occurrence survey. J Am Water Works Assoc 1997;89(6):60–8.
- Aus–NZ. Australian drinking water guidelines 6. Australian National Health and Medical Research Council; 2004.
- AWWA (American Water Works Association). Disinfection Systems survey committee report, water quality division. J Am Water Works Assoc 2000;9:24–43.
- Bellar TA, Lichtenberg JJ, Kroner RC. The occurrence of organohalides in chlorinated drinking waters. J Am Water Works Assoc 1974;66:703–6.
- Bull RJ, Meier JR, Robinson M, Ringhand HP, Laurie RP, Stober JA. Evaluation of the mutagenic and carcinogenic properties of brominated and chlorinated acetonitriles: by-products of chlorination. Fundam Appl Toxicol 1985;5:1065–75.
- Bull RJ, Sanchez IM, Nelson MA, Larson JL, Lansing AL. Liver tumour induction in B6C3F1 mice by dichloroacetate and trichloroacetate. Toxicology 1990;63:341–59.
- Cantor KP, Lynch CF, Hildesheim M, Dosemeci M, Lubin J, Alavanja M, et al. Drinking water source and chlorination by-products in Iowa: 1. Risk of bladder cancer. Epidemiology 1998;9:21–8.
- Chang EE, Chao S, Chiang P, Lee J. Effects of chlorination on THM formation in raw water. Toxicol Environ Chem 1996;56:211–25.
- Chang EE, Chiang PC, Ko YW, Lan WH. Characteristics of organic precursors and their relationship with disinfect ion by-products. Chemosphere 2001;44:1231–6.
- Chen WJ, Weisel CP. Halogenated DBP concentrations in a distribution system. J Am Water Works Assoc 1998;90(4):151–63.
- Chlorine Chemistry Council. Drinking water chlorination: a review of disinfection practices and issues. Chlorine Chemistry Council 2003, Arlington, VA; 2003.
- Chowdhury S, Champagne P. An investigation on parameters for modeling THMs formation. Global NEST J 2008;10(1):80–91.
- Chowdhury S, Champagne P. Risk from exposure to trihalomethanes during shower: probabilistic assessment and control. Sci Total Environ 2009;407(5):1570–8.
- Chowdhury S, Husain T. Evaluation of drinking water treatment technology: an entropy-based fuzzy application. J Environ Eng 2006;132(10):1264–71.
- Chowdhury S, Champagne P, Husain T. Fuzzy approach for selection of drinking water disinfectants. J Water Supply: Res Technol (AQUA) 2007;56(2):75–93.
- Clark RM, Rice G. Characterizing microbial and DBP risk tradeoffs in drinking water: application of CRFM. In: Surampalli RY, Tyagi KD, editors. Advances in water and wastewater treatment. ASCE; 2004. p. 456–71.
- Clark RM, Sivaganesan M. Predicting chlorine residuals and formation of TTHMs in drinking water. J Environ Eng 1998;124(12):1203–10.

- Clark RM, Sivaganesan M. Predicting chlorine residuals in drinking waters: second order model. J Water Resour Plan Manage 2002;128(2):152–61.
- Clark RM, Adams JQ, Lykins BW. DBP control in drinking water: cost and performance. J Environ Eng 1994;120(4):759–82.
- Clark RM, Adams JQ, Sethi V, Sivaganesan M. Control of microbial contaminants and disinfection by-products for drinking water in the US: cost and performance. J Water Supply: Res Technol, AQUA 1998;47(6):255–65.
- Clark RM, Thurnau RC, Sivaganesan M, Ringhand P. Predicting the formation of chlorinated and brominated by-products. J Environ Eng 2001;127(6):493–501. Connel GF. The chlorination/chloramination hand book. Water disinfection series.
- Connel GF. The chlorination/chloramination hand book. Water disinfection series. Denver, Colo: Am. Water Works Assoc. (AWWA); 1997.
- Croue JP, Gorshin GV, Leenheer JA, Benjamin MM. Isolation, fractionation and characterization of natural organic matter in drinking water. Am. Water Works Assoc. Res. Foundation (AWWARF) report; 1998.
- Dempsey BA, Ganbo RM, O'Melia CR. The coagulation of humic substances by means of aluminium salts. J Am Water Works Assoc 1984;74(4):141–50.
- Edzwald JK. Coagulation in drinking water: particles, organics and coagulants. Water Sci Technol 1993;27(11):21–35.
- Edzwald JK, Becker WC, Wattier KL. Surrogate parameters for monitoring organic matter and THM precursors. J Am Water Works Assoc 1985;77(4):122–32.
- Elshorbagy W, Abu-Qdais H, Elsheamy MK. Simulation of THMs species in water distribution systems. Water Res 2000;34(13):3431–9.
- Engerholm BA, Amy GL. A predictive model for chloroform formation from humic acid. J Am Water Works Assoc 1983;75(8):418–23.
- Gallard H, Von-Gunten U. Chlorination of natural organic matter: kinetics of chlorination and of THM formation. Water Res 2002;36:65–74.
- Gang DD, Segar Jr RL, Clevenger TE, Banerji SK. Using chlorine demand to predict THM and HAA9 formation. J Am Water Works Assoc 2002;94(10):76–86.
- Gang D, Clevenger TE, Banerji SK. Relationship of chlorine decay and THMs formation to NOM size. J Hazard Mater 2003;A96:1-12.
- Garcia-Villanova RJ, Garcia C, Gomez JA, Garcia MP, Ardanuy R. Formation, evolution and modelling of trihalomethanes in the drinking water of a town: I. At the municipal treatment facilities. Water Res 1997a;31(6):1299–308.
- Garcia-Villanova RJ, Garcia C, Gomez JA, Garcia MP, Ardanuy R. Formation, evolution and modelling of trihalomethanes in the drinking water of a town: II. In the water distribution system. Water Res 1997b;31(6):1405–13.
- Gates D. The chlorine dioxide handbook, water disinfection series. Denver, Colorado: Am. Water Works Assoc.; 1998.
- Ginasiyo M, Dietz J, Arevalo J, Taylor JS. Combined chlorine dissipation: pipe material, water quality and hydraulic effects. J Am Water Works Assoc 2007;99(10):96-106.
- Golfinopoulos SK, Arhonditsis GB. Multiple regression models: a methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics. Chemosphere 2002a;47:107-1018.
- Golfinopoulos SK, Arhonditsis GB. Quantitative assessment of trihalomethane formation using simulations of reaction kinetics. Water Res 2002b;36:2856–68.
- Golfinopoulos SK, Xilourgidis K, Kostopoulou N, Lekkas TD. Use of a multiple regression model for predicting trihalomethane formation. Water Res 1998;32(9):2821–9.
- Haas CN, Karra SB. Kinetics of wastewater chlorine demand exertion. J Water Pollut Control Federation 1984;56(2):170–3.
- Harrington GW, Chowdhurry ZK, Owen DM. Developing a computer model to simulate DBP formation during water treatment. J Am Water Works Assoc 1992;84(11): 78–87.
- Health Canada. Guidelines for Canadian drinking water quality; 2007. Website. http:// www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/guidelines_sixth-rec_e.html.
- Hellur-Grossman L, Manka J, Lamoni-Relis B, Rebhun M. THM, haloacetic acids and other organic DBPs formation in disinfect ion of bromide rich Sea of Galilee (Lake Kinneret) water. Water Sci Technol: Water Supply 2001;1(2):259–66.
- Hong HC, Liang Y, Han BP, Mazumder A, Wong MH. Modeling of trihalomethane (THM) formation via chlorination of the water from Dongjiang River (source water for Hong Kong's drinking water). Sci Total Environ 2007;385:48–54.
- Huang JJ, McBean EA. Using Bayesian statistics to estimate the coefficients of a twocompartment second-order chlorine bulk decay model for a distribution system. Water Res 2007;41:287–94.
- Huixian Z, Sheng Y, Xu X, Ouyong X. Formation of POX and NPOX with chlorination of fulvic acid in water: empirical models. Water Res 1997;31(6):1536–41.
- Ibarluzea JM, Goni F, Santamaria J. Trihalomethanes in water supplies in the San Sebestian area Spain. Bull Environ Contam Toxicol 1994;52:411–8.
- IRIS (Integrated Risk Information System). The Integrated Risk Information System online database. Washington DC: US Environmental Protection Agency; 2006. Website: http://www.epa.gov/iris/subst/index.html.
- Jo WK, Weisel CP, Lioy PJ. Chloroform exposure and the health risk associated with multiple uses of chlorinated tap water. Risk Anal 1990;10(4):581–5.
- King WD, Marrett LD. Case-control study of bladder cancer and chlorination by products in treated water (Ontario, Canada). Cancer Causes Controls 1996;7:596–604.
- King WD, Marrett LD, Woolcott CG. Case-control study of colon and rectal cancers and chlorination by-products in treated water. Cancer Epidemiol Biomark Prev 2000;9:813–8.
- Kolla, R.B., 2004. Formation and modeling of disinfect ion by-products in Newfoundland communities. Masters Thesis; Memorial University of Newfoundland, NL, Canada. Korn C, Andrews RC, Escobar MD. Development of chlorine di-oxide related by-product
- models for drinking water treatment. Water Res 2002;36:330–42. Krasner SW, Weinberg HS, Richardson SD, Pastor SJ, Chinn R, Sclimenti MJ, et al.
- Occurrence of a new generation of disinfection byproducts. Environ Sci Technol 2006;40(23):7175–85.
 Lekkas TD, Nikolaou AD. Development of predictive models for the formation of
- trihalomethanes and haloacetic acids during chlorination of bromide ion rich water. Water Qual Res J Can 2004;39(2):149–59.

Author's personal copy

4206

S. Chowdhury et al. / Science of the Total Environment 407 (2009) 4189-4206

Liang L, Singer PC. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking waters. Environ Sci Technol 2003;37:2920–8.

Lou JC, Chiang PC. A study of trihalomethanes formation in water distribution system. Hazard Waste 1994;11(2):333-43.

Louvar JF, Louvar BD. Health and environmental risk analysis. Upper Saddle River, NJ 07458: Prentice-Hall Inc.; 1998.

Lykins Jr BW, Koffskey WE, Patterson KS. Alternative disinfectants for drinking water treatment. J Environ Eng 1994;120(4):745–58.

Malcolm Pirnie Inc. Water Treatment Plant Simulation Program, Version 1.21, User's manual. Washington, D.C.: U.S. Environmental Protection Agency (EPA); 1992.

- Malcolm Pirnie Inc. Bay-Delta water quality modeling report No. 15-041. Los Angeles: Metropolitan Water District of Southern California; 1993.
- Mills CJ, Bull RJ, Cantor KP, Reif J, Hrudey SE, Huston P, et al. Health risks of drinking water chlorination by-products. Chronic Dis Can 1998;19(3):91-102.
- Milot J, Rodriguez MJ, Serodes J. Modelling the susceptibility of drinking water utilities to form high concentrations of trihalomethanes. J Environ Manag 2000;60:155–71.
 Milot J, Rodriguez MJ, Sérodes J. Contribution of neural networks for modelling THM
- occurrence in drinking water. J Water Resour Plan Manage 2002;128(5):370–6.
- Miltner RJ, Speth TF, Richardson SD, Krasner SW, Weinberg HS, Simmons JE. Integrated disinfection by-products mixtures research: disinfection of drinking waters by chlorination and ozonation/postchlorination treatment scenarios. J Toxicol Environ Health, Part A 2008;71(17):1133–48.
- Minear RA, Morrow CM. Raw water bromide in finished drinking water, research report 9. Water Resources Research Center, University of Tennessee; 1983.

Mitch WA, Sedlak DL. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. Environ Sci Technol 2002;36:588–95.

- MOE (Ministry of Environment, Ontario, Canada), 2006. Drinking Water Surveillance Program (DWSP) monitoring data for 2000–2004 on 179 municipal water Supply systems (MWSS) in Ontario. (Personal communication with Dave Fellowes, MOE, Ontario, Canada and website http://www.ene.gov.on.ca/envision/water/dwsp/0002/index.htm).
- Montgomery W. Disinfection/disinfection byproducts database and model project. Denver, Colorado: Am. Water Works Assoc.; 1991.
- Montgomery W. Mathematical modelling of the formation of THMs and HAAs in chlorinated natural waters. Denver . Colorado: Am. Water Works Assoc.: 1993.

Montgomery DC, Runger GC. Applied statistics and probability for engineers. 4th ed. New York, USA: John Wiley and Sons; 2007.

- Morrow CM, Minear RA. Use of regression models to link raw water characteristics to trihalomethane concentrations in drinking water. Water Res 1987;21(1):41–8. MWH (Montgomery Watson Harza). Water treatment: principles and design. NJ, USA: John
- Wiley & Sons; 2005. National Cancer Institute of Canada. Canadian cancer statistics; 1998. Web Address:
- http://www.cancer.ca/stats. Nikolaou AD, Kostopoulou MN, Lekkas TD. Organic by-products of drinking water
- chlorination. Global Nest, Int J 1999;1(3):143.
- Nikolaou AD, Lekkas TD, Golfinopoulos SK. Kinetics of the formation and decomposition of chlorination by-products in surface waters. Chem Eng J 2004;100:139–48. Nokes CJ, Fenton E, Randall CJ. Modelling the formation of brominated trihalomethanes
- in chlorinated drinking waters. Water Res 1999;33(17):3557–68.
- Ozekin K., 1994. Modelling bromate formation during ozonation and assessing its control, Ph.D. Dissertation, University of Colorado, USA.
- Pereira MA. Carcinogenic activity of dichloroacetic acid and trichloroacetic acid in the liver of female B6C3F1 mice. Fundam Appl Toxicol 1996;31:192–9.
 Peterborough Utilities Commission (1998) http://www.puc.org/hist.htm.
- Rathbun RE. Speciation of trihalomethane mixtures for the Mississippi, Missouri and
- Ohio rivers. Sci Total Environ 1996a;180:125–35. Rathbun RE. Regression equations for disinfection by-products for the Mississippi, Ohio
- and Missouri Rivers. Sci Total Environ 1996b;191:235-44. Reckow DA, Singer PC. The removal of organic halide precursors by preozonation and alum coagulation. Am Water Works Assoc 1984:76:151.
- Reiff FM. Balancing the chemical and microbial risks in the disinfection of drinking water supplies in developing countries. Assessing and managing health risks from
- drinking water contamination: approaches and applicationsIAHS Pub.; 1995. Richardson SD. New disinfection by-product issues: emerging DBPs and alternative
- routes of exposure. Global Nest, Int J 2005;7(1):43–60. Richardson SD, Simmons JE, Rice G. Disinfection byproducts: the next generation. Environ Sci Technol 2002;36(9):198–205.
- Richardson SD, Thruston Jr AD, Krasner SW, Weinberg HS, Miltner RJ, Schenck KM, et al. Integrated disinfection by-products mixtures research: comprehensive characterization of water concentrates prepared from chlorinated and ozonated/postchlorinated drinking water. J Toxicol Environ Health, Part A 2008;71(17):1165–86.

Rodrigues MSM, Silva JCG, Antunes MCG. Factorial analysis of the trihalomethane

- formation in water disinfection using chlorine. Anal Chim Acta 2007;595:266–74. Rodriguez MJ, Sérodes JB. Spatial and temporal evolution of trihalomethanes in three
- water distribution systems. Water Res 2001;35(6):1572–86. Rodriguez MJ, Serodes J, Morin M. Estimation of water utility compliance with trihalomethane
- regulations using modelling approach. J Water Supply: Res Technol 2000;49(2):57–73. Rook JJ. Formation of haloforms during chlorination of natural waters. Water Treat Exam 1974:23:234–43.

- Rossman LA, Brown RA, Singer PC, Nucklos JR. DBPs formation kinetics in a simulated distribution system. Water Res 2001;35(14):3483–9.
- Sadiq R, Rodriguez M. (2004) Disinfection byproducts (DBPs) in drinking water and predictive models for their occurrences: a review. Sci Total Environ 2004;321:21–46. Semerjian L, Dennis J, Ayoub G. Modeling the formation of trihalomethanes in drinking
- waters of Lebanon. Environ Monit Assess 2008, doi:10.1007/s10661-008-0219-4. Serodes JB, Rodriguez MJ, Li H, Bouchard C, Occurrence of THMs and HAAs in experimental
- chlorinated waters of the Quebec City area (Canada). Chemosphere 2003;51:253–63. Shorney HL, Randtke S, Hargette P, Knocke W, Dietrich A, Hoehn R, et al. Removal of
- DBPs precursors by enhanced coagulation and lime softening. Denver CO: AWWA Research Foundation; 1999.
- Siddiqui M, Amy G, Ozekin K, Westerhoff P. Empirically and theoretically based models for predicting brominated ozonated by-products. Ozone: Sci Eng 1994;16:157–78. Singer PC. Control of disinfection by-products in drinking water. J Environ Eng 1994;120
- (4):727-37. Singer PC, Chang SD. Correlations between trihalomethanes and total organic halides
- formed during water treatment. J Am Water Works Assoc 1989;81(8):61–5. Singer PC, Obolensky A, Greiner A. DBPs in chlorinated North Carolina drinking water.
- Am Water Works Assoc 1995;87(10):83–92. Sohn J, Amy G, Cho J, Lee Y, Yoon Y. Disinfectant decay and disinfection by-products
- formation model development: chlorination and ozonation by-products. Water Res 2004;38:2461–78. Sohn J, Amy G, Cho J, Yoon Y. Bromide ion incorporation into brominated disinfection
- Song R, Donohoe C, Minear R, Westerhoff P, Ozekin K, Amy G. Empirical modeling of bromate formation during ozonation of bromide-containing waters. Water Res 1996;30(5):1161–8.
- Smith MK, Randall JL, Tocco DR, York RG, Stober JA, Read EJ. Teratogenic effects of trichloroacetonitrile in the Long-Evans rat. Teratology 1988;113:20.
- Stevens AA, Slocum CJ, Seeger DR, Robeck CB. Measurement of THM and precursor concentration changes. Am Water Works Assoc 1976;68:546–54.
- Sung W, Matthews BR, O'Day K, Horrigan K. Modeling DBP formation. Am Water Works Assoc 2000;92(5):53–63.Tyrovola, Diamadopoulos. Bromate formation during ozonation of groundwater in
- coastal areas in Greece. Desalination 2005;176:201–9.
- UK Water supply (water quality), 2000. Regulations for England and Wales. Web site address: www.dwi.detr.gov.ukyregsysi3184y3184.htm.
- Urano K, Wada H, Takemassa T. Empirical rate equation for trihalomethane formation with chlorination of humic substances in water. Water Res 1983;17(12):1797–802.
- USCDC (U.S. Centers for Disease Control and Prevention). Summary of notifiable diseases; morbidity and mortality weekly report. CDC surveillance summaries: surveillance for waterborne disease outbreaks USA; 1997.
- USEPA (US Environmental Protection Agency). Human health risk assessment protocol. EPA-530-D-98-001A. USA: USEPA Office of Solid Waste; 1998a.
- USEPA (US Environmental Protection Agency). National primary drinking water regulations: disinfectants and disinfection byproducts notice of data availability. Fed Regist 1998b;63(61):15673–92.
- USEPA (US Environmental Protection Agency). National primary drinking water standards. USEPA; 2001 a. 816-F-01-007.
- USEPA (US Environmental Protection Agency). Controlling disinfection by-products and microbial contaminants in drinking water. USEPA; 2001b. 600-R-01-110.
- USEPA (US Environmental Protection Agency). National primary drinking water regulations: stage 2 disinfectants and disinfection by products rule: final rule. Fed Regist 2006;71(2).
- Uyak V, Toroz I. Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City. Desalination 2005;176:127–41.
- Uyak V, Toroz I. Investigation of bromide ion effects on disinfection by-products formation and speciation in an Istanbul water supply. J Hazard Mater 2007;149:445–51.
- Uyak V, Toroz I, Meric S. Monitoring and modeling of trihalomethanes (THMs) for a water treatment plant in Istanbul. Desalination 2005;176:91-101.
- Vasconcelos JJ, Rossman LA, Grayman WM, Boulos PF, Clark RM. (1997) Kinetics of chlorine decay, Am. Water Works Assoc 1997;89(7):54–65.
- Villanueva CM, Cantor KP, Cordier S, Jaakkola JJK, King WD, Lynch CF, et al. Disinfection byproducts and bladder cancer: a pooled analysis. Epidemiology 2004;15(3):357–67.
- Waller K, Swan SH, DeLorenze G, Hopkins B. Trihalomethanes in drinking water and spontaneous abortion. Epidemiology 1998;9(2):134–40.Westerhoff P, Debroux J, Amy GL Gatel D, Mary V, Cavard J. Applying DBP models to full-
- scale plants. Am Water Works Assoc 2000;92(3):89-102.
- White DM, Garland DS, Narr J, Woolard CR. Natural organic matter and DBP formation potential in Alaskan water supplies. Water Res 2003;37:939–47.
- WHO (World Health Organization), Guidelines for drinking-water quality. Recommendations, 3rd eds.Geneva; 2004.
- Wigle DT. Safe drinking water: a public health challenge. Chronic Dis Can 1998;19(3):103-7.
- Xu X, Weisel CP. Human respiratory uptake of chloroform and haloketones during showering. J Expo Anal Environ Epidemiol 2005;15:6-16.