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FEATURE ARTICLE

Disinfection byproducts in drinking water and regulatory compliance: A critical review

Xiaomao WANG[1], **Yuqin MAO**[1], **Shun TANG**[1], **Hongwei YANG (✉)**[1], **Yuefeng F. XIE**[1,2]

1 State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment,
Tsinghua University, Beijing 100084, China
2 Environmental Engineering Programs, The Pennsylvania State University, Middletown, PA 17057, USA

Abstract Disinfection by-products (DBPs) are regulated in drinking water in a number of countries. This critical review focuses on the issues associated with DBP regulatory compliance, including methods for DBP analysis, occurrence levels, the regulation comparison among various countries, DBP compliance strategies, and emerging DBPs. The regulation comparison between China and the United States (US) indicated that the DBP regulations in China are more stringent based on the number of regulated compounds and maximum levels. The comparison assessment using the Information Collection Rule (ICR) database indicated that the compliance rate of 500 large US water plants under the China regulations is much lower than that under the US regulations (e.g. 62.2% versus 89.6% for total trihalomethanes). Precursor removal and alternative disinfectants are common practices for DBP regulatory compliance. DBP removal after formation, including air stripping for trihalomethane removal and biodegradation for haloacetic acid removal, have gained more acceptance in DBP control. Formation of emerging DBPs, including iodinated DBPs and nitrogenous DBPs, is one of unintended consequences of precursor removal and alternative disinfection. At much lower levels than carbonaceous DBPs, however, emerging DBPs have posed higher health risks.

Keywords Disinfection byproducts (DBPs), drinking water standards, regulatory compliance, alternative disinfection, information collection rule (ICR), emerging DBPs

1 Introduction

Disinfection is the cornerstone for water treatment. Formation of disinfection byproducts (DBPs) is associated with water disinfection as an unintended consequence. A number of review papers/book chapters have been published in the last decade, covering DBP formation, occurrence and health effects [1–7]. Several DBPs, including trihalomethanes (THMs) and haloacetic acids (HAAs), have been regulated in a number of countries or regions. However, the maximum levels for each DBP and the calculation methods for regulatory compliance differ substantially among these countries and regions.

In China, a new standard for drinking water quality (GB5749) was promulgated in 2006 and has become effective since 2012 [8]. The new Standards regulated a total of 106 contaminants, including 14 DBPs. Many water utilities have reported various incompliance issues associated with the new Standards. However, little is known about the equivalency of the Chinese DBP regulation to other industrial nations, including the United States (US). The economic and compliance impacts of the Chinese DBP regulation on water utilities are not well understood. Therefore, there is a need to systemically assess the Chinese DBP regulations. In addition, the assessment of analytical methods and calculation methods for DBP compliance is also needed.

To comply with DBP regulations, water utilities commonly consider enhanced coagulation for precursor removal and chloramination as an alternative to chlorination to control DBPs in their finished water. In comparison, there is very limited information on removing DBPs after their formation. One of the unintended consequences of enhanced coagulation and chloramination is the increased formation of a group of emerging DBPs, including brominated/iodinated DBPs and nitrogenous DBPs. Although most of these DBPs are not regulated, emerging

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E-mail: yanghw@tsinghua.edu.cn

DBPs may have substantial adverse health impacts due to their high toxicities. In addition, a few of the emerging DBPs (e.g. *N*-nitrosodimethylamine (NDMA)) are being considered for future regulations in the US and other countries.

This review article covers analytical methods for both regulated DBPs and emerging DBPs, the typical DBP occurrence levels in the US and other parts of the world, DBP regulations in China and other industrial countries, the comparison of the US and the Chinese DBP regulations, DBP control technologies, and emerging DBPs. This review also compared the DBP compliance rates of Information Collection Rule (ICR) plants under the Chinese DBP regulation and the US DBP regulations, identified potential issues associated with the Chinese DBP regulations, and suggested potential solutions for future regulation revisions.

2 Analytical methods

The US Environmental Protection Agency (EPA) has issued and approved analytical methods for regulated DBPs under Disinfectants and Disinfection Byproducts (D-DBP) Rule and ICR [2,9], including Methods 502.2, 524.2 and 551.1 for THMs and other volatile DBPs such as haloaldehydes, haloacetonitriles (HANs), cyanogen halide (CNX), haloketones, haloamides and halonitromethanes, Methods 552.1, 552.2 and 552.3 for HAAs, Methods 300.1, 317.0 and 321.8 for bromate, Methods 300.0, 300.1, 317.0, 326.0 and 327.0 for chlorite, and Methods 554 and 556 for carbonyl compounds (Table 1). Most of these methods are gas chromatography (GC) with electron capture detector (ECD) based methods for organic DBPs and or ion chromatography (IC) with conductivity detector (CD) based methods for inorganic DBPs. The few exceptions are Method 524.2 based on GC-mass spectrometry (MS), Method 321.8 based on IC- inductively coupled plasma (ICP)-MS, Method 327 as a colorimetric method, and Method 554 based on liquid chromatography (LC) with ultraviolet (UV) detector. Sample pretreatment includes liquid-liquid extraction (LLE) or purge and trap (P&T) for organic DBP preconcentration, and chemical derivatization for polar DBPs like HAAs and carbonyl compounds. Similar standard methods, including Standard Method 6232 and 6251, are also approved by the U.S.EPA.

In China, a series of standard methods were also issued and recommended for DBP measurement (Table 1), which were all included in GB/T 5750.10-2006 [10]. Head space (HS) was suggested as the pretreatment for the determination of THMs in the samples. When packed column is used for analyte separation, the detection limits are relatively high, which are 0.6, 1, 0.3 and 6 $\mu g \cdot L^{-1}$ for chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform, respectively. The method may not be suitable for measurement of bromoform in drinking water due to the high detection limit. The method for dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) measurement is essentially identical to Methods 552.2 and 552.3. The method for CH measurement is an indirect method, which is based on the enhanced hydrolysis of chloral hydrate (CH) under alkaline condition over that under neutral condition. The hydrolysis product of CH is chloroform, which is then measured by the standard HS-GC-ECD method. Our results however showed that the enhanced hydrolysis of other trichlorinated DBPs (notably 1,1,1-trichloropropanone (TCP) and TCAA) under alkaline conditions can lead to substantial over-estimation of the CH levels [11]. Measurement of samples collected from south China indicated that the over-estimation was about 1.9 times. The IC-CD methods for bromate, chlorite and chlorate determination are the same with that approved by the U.S.EPA, respectively. Moreover, chlorite and chlorate could be measured by the titration method after reacting with potassium iodide. The influence of other oxidizing agents in the water samples need be precluded. Formaldehyde is determined by the colorimetric method after reacting with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole and potassium iodate. The detection limit of the method is 50 $\mu g \cdot L^{-1}$ which is unacceptably higher than the typical formaldehyde concentration in ozonated drinking water. Cyanogen chloride (CNCl) is determined colorimetrically by reacting with isonicotinic acid and barbituric acid. The detection limit is 10 $\mu g \cdot L^{-1}$, much higher than that reported in the literature using GC-ECD or GC-MS method [12,13].

Conventionally, GC-MS method is widely used for the identification of unknown DBPs in disinfected water. ECD and other detectors may then be used for routine quantification of the identified DBPs. However, as Method 524.2, GC-MS based methods were widely used for the determination of HAAs, haloaldehydes, HANs, haloketones and CNXs [2,12–15] in the literature.

Recently, LC-MS methods are increasingly used for the determination of relatively polar DBPs such as HAAs [16]. One of the advantages of LC-based methods is the facilitation of direct injection of water samples. The detection limits of the LC-MS-MS method [17] for most HAAs were low enough (0.16–0.99 $\mu g \cdot L^{-1}$), except that for DBCAA and TBAA, which were 1.44 $\mu g \cdot L^{-1}$ and 8.87 $\mu g \cdot L^{-1}$, respectively, primarily due to their chemical instability (hydrolysis) in water. A similar method recommended by EPA for HAA measurement is Method 557, in which IC is employed for HAA separation. The detection limits for the nine HAAs are from 0.015 $\mu g \cdot L^{-1}$ to 0.20 $\mu g \cdot L^{-1}$. Method 557 can also be used for bromate determination. The method is more sensitive than Method 321.8 with the detection limit as low as 0.020 $\mu g \cdot L^{-1}$.

Similar to GC-MS methods, the LC-MS methods can be used for the identification of unknown DBPs, especially those with high polarity or molecular weight [18,19]. One special utilization of the LC-electrospray ionization (ESI)-

MS-MS instrument is the fast selective detection of chlorinated and/or brominated DBPs by using precursor ion scan mode [20–22]. Both chlorine and bromine atoms have two natural isotopes with the abundance ratio at 3:1 and 1:1, respectively, and as such can be selected as product ions for DBP identification.

Other methods for DBP determination in the literature include capillary electrophoresis (CE) [23–25], and high-field asymmetric waveform ion mobility spectrometry (FAIMS)-MS [17,26,27] for HAA measurement, membrane introduction mass spectrometry (MIMS) [26] for CNX measurement and IC-ECD [28] for bromate measurement.

3 Occurrence levels

The commonly measured DBPs in drinking water include THMs, HAAs, CH, HANs, TCP, 1,1-dichloropropanone (DCP) and trichloronitromethane (TCNM) as well as CNCl (when chloraminated), bromate and aldehydes (when ozonated), and chlorite and chlorate (when ClO_2 is used). These DBPs are generally present at low-to-mid-$\mu g \cdot L^{-1}$ or sub-$\mu g \cdot L^{-1}$ levels in drinking water [14]. Usually, THM and HAA concentrations are substantially higher than other organic DBP classes. Haloacetaldehydes represent the third highest concentration by class [29], followed by haloketones, halonitriles, haloamides, and halonitromethanes [30]. Within each DBP class, the formation potential followed the general trends: Cl > Cl–Br > Br-DBPs, and trihalo > dihalo > monohalo-DBPs [31].

ICR is probably the most comprehensive DBP occurrence survey by far. ICR required all large-scale drinking water treatment plants (serving a population of at least 100,000) across the US to report sampling results for DBP parameters for six quarters. A total of 500 plants were covered under the ICR. An ICR database was subsequently established to facilitate ICR data retrieval and analysis [32–34]. A statistical analysis of the ICR data showed that the median THM4 level was 29.7 $\mu g \cdot L^{-1}$ (Table 2), which was higher than the median HAA9 level at 22.6 $\mu g \cdot L^{-1}$ (although bias might exist because only approximately 22% of the samples were determined for all of the nine HAAs). The median levels for HAA5, CH, HAN4 and DCP&TCP were approximately 60%, 8%, 9% and 4% of that for THM4. TCNM was generally at low levels and the median value was below the detection limit. Approximately 11% of all ICR samples were determined for CNCl concentration, and the median level was 2 $\mu g \cdot L^{-1}$. Approximately 12% and 5% of all ICR samples were determined for bromate and formaldehyde concentrations, respectively, and the median levels were both below the detection limits. Approximately 14% and 19% of all ICR samples were determined for chlorite and chlorate, respectively, and the median levels were 170 $\mu g \cdot L^{-1}$ and 66 $\mu g \cdot L^{-1}$, respectively.

Compared with that reported by previous US nationwide surveys [29,36], the THM and HAA occurrence levels in the plant effluent were significantly reduced during the ICR survey period. The previous THM4 and HAA5 median concentrations were 39 $\mu g \cdot L^{-1}$ and 19 $\mu g \cdot L^{-1}$, respectively. The reduction was likely due to the promulgation of the Trihalomethanes Rule and various DBP control processes implemented by the water utilities. Further DBP concentration reduction is expected due to the promulgation of the Stage 1 and Stage 2 D-DBP Rules.

A later survey in the US was conducted by Krasner et al.

Table 1 Comparison of the approved methods for the measurement of regulated DBPs in the US and China

	ethods issued by the US.EPA	methods in GB/T 5750.10−2006
THMs	Method 502.2 (P&T-GC-PID-ELCD), Method 524.2 (P&T-GC-MS), Method 551.1 (LLE-GC-ECD)	HS-GC(packed column)-ECD, HS-GC(capillary column)-ECD
HAAs	Method 552.1 (SPE-derivatization-GC-ECD), Method 552.2 (LLE-derivatization-GC-ECD), Method 552.3 (LLE-derivatization-GC-ECD)	LLE-derivatization-GC-ECD
CH	Method 551.1 (LLE-GC-ECD)	Hydrolysis-HS-GC-ECD
bromate	Method 300.1 (IC-CD), Method 317.0 (IC-PCR-UV/VIS), Method 321.8 (IC-ICP-MS)	IC-CD
formaldehyde	Method 554 (LSE-HPLC-UV), Method 556 (LLE-derivatization-GC-ECD)	Colorimetry
chlorite	Method 300.0 (IC-CD), Method 300.1 (IC-CD), Method 317.0 (IC-CD), Method 326.0 (IC-CD), Method 327.0 (colorimetry)	Titrimetric, IC-CD
chlorate	Method 300.0 (IC-CD), Method 300.1 (IC-CD), Method 317.0 (IC-CD)	Titrimetric, IC-CD
CNCl	–	Colorimetry
2,4,6-trichlorophenol	–	LLE-derivatization-GC-ECD, HS-GC-ECD

Table 2 The occurrence levels of the commonly measured DBPs obtained by the several nationwide surveys in the United States (unit: $\mu g\cdot L^{-1}$)

	Krasner et al., 1989 [29]	ICR	Krasner et al., 2006 [30]	Mitch et al., 2009 [35]
THM4	37	29.7	31	36
HAAs	18 14.4 (HAA5)	22.6 * 17.7 (HAA5)	34	
haloacetaldehydes	2.2 (CH)	2.3 (CH)	4	4.5 (THA)
haloacetonitriles	3.2	2.8 (HAN4)	3	4 (DHAN)
haloketones	1.3 (DCP&TCP)	1.1 (DCP&TCP)	2	
haloacetamides			1.4	
halonitromethanes	0.12 (TCNM)	0 (TCNM)	1	0.5 (TCNM)
halogenated furanones			0.31	
CNCl	0.6	2		
bromate		0		
formaldehyde	2.7	0		
acetaldehyde	1.8			
chlorite		170		
chlorate		66		

[30] on the DBP occurrence levels in the finished water (plant effluent) of 12 water treatment plants. These plants were selected due to relatively high total organic carbon (TOC) content and bromide concentration in the raw waters. The survey results were generally consistent with that obtained by ICR, although the median level for HAA9 was found slightly higher than that for THM4. THM4, HAAs, HANs accounted for 14%, 12% and 2% of the total organic halides (TOX). Because of the increased concern of nitrogenous DBPs, a later survey covering 11 US drinking water treatment plants was later conducted with a focus on the treated water impacted by wastewater or algae [35]. Results showed that nitrogenous DBP levels were significantly higher than that obtained previously, with dihaloacetonitrile (DHAN) and TCNM median levels to be 4 $\mu g\cdot L^{-1}$and 0.5 $\mu g\cdot L^{-1}$, respectively.

Approximately in the same time period with of the ICR data collection, a number of DBP surveys were conducted in other countries. Results indicated that the DBP occurrence levels differed substantially among the different countries. The 1993 Canadian survey, covering 53 drinking water plants [37], revealed that the THM4 and HAA5 occurrence levels were consistent with that in the US [29]. In contrast, the THM4 and chloro-HAA concentrations in the Australian water distribution systems were significantly higher than that in the US, which ranged from 6 $\mu g\cdot L^{-1}$to 191 $\mu g\cdot L^{-1}$ and from 18 $\mu g\cdot L^{-1}$to 252 $\mu g\cdot L^{-1}$, respectively [38]. These high levels have been attributed to source water with a high organic content and a high chlorine demand. When surface water was treated, the HAA6 concentration on a median basis was found significantly higher than the THM4 concentration according to the Finnish survey [39]. It was attributed to the enhanced formation of TCAA from the humic materials with high specific UV absorbance. According to the Korean survey conducted during 1996–1998 [40], the median THM4 and DCAA&TCAA& dibromoacetic acid (DBAA) concentrations were as low as 9.05 $\mu g\cdot L^{-1}$ and 6.96 $\mu g\cdot L^{-1}$, respectively, which were only approximately one third of the respective values in North America. A study also indicated that the DBP precursor levels in Korean river waters are lower than those in the US [41]. The most recent Chinese survey obtained similar results, which revealed that the median THM4 and HAA9 concentrations were as low as 10.5 $\mu g\cdot L^{-1}$ and 11.0 $\mu g\cdot L^{-1}$, respectively [42].

4 Regulations and guidelines

Shortly after the detection of THMs in the disinfected drinking water, THMs were regulated by the U.S.EPA with a maximum contaminant level (MCL) for TTHM at 100 $\mu g\cdot L^{-1}$ [2]. The MCL reflected analytical and treatment technologies that were available and affordable at the time for water utilities to meet the MCL requirement. The Stage 1 D-DBP Rule [43] lowered the MCL for TTHM to 80 $\mu g\cdot L^{-1}$, and also regulated HAA5, bromate and chlorite at MCLs of 60 $\mu g\cdot L^{-1}$, 10 $\mu g\cdot L^{-1}$, and 1000 $\mu g\cdot L^{-1}$, respectively. The Rule stated that the determination of the regulatory compliance of TTHM, HAA5 and bromate was based on the running annual average (RAA) of all samples from all monitoring locations across the water distribution system. RAA reduced the effects of the DBP seasonal and locational variations in the distribution system. The U.S. EPA further promulgated the Stage 2 D-DBP Rule in 2006

[44], which did not change the MCLs for regulated DBP. Rather, the Rule stated that MCL compliance of THM4 and HAA5 should be calculated using the locational running annual average (LRAA) for each monitoring location in the distribution system. LRAA only reduces the effects of the seasonal variation of the DBP concentrations, and targets at reducing the variability of exposure and providing equal protection for people at various points in the distribution system. The DBP guidelines in Canada [45] are similar to that in the US, although the maximum acceptable concentrations (MACs) for TTHM and HAA5 are 100 $\mu g \cdot L^{-1}$ and 80 $\mu g \cdot L^{-1}$, respectively, and more DBP species are regulated. The regulatory compliance of TTHM and HAA5 is also based on LRAA. The MCLs for both chlorite and chlorate are 1 $mg \cdot L^{-1}$. Canada is among the few countries where nitrosamines are included in the Standards or Guidelines. The MCL for NDMA in Canada is as low as 40 $ng \cdot L^{-1}$. NDMA was first detected in chlorinated drinking waters from Ontario, Canada [3], and is one of the most potent carcinogens among the various DBPs detected by far. The European Union (EU) only list two DBPs in their Drinking Water Directives [46]. The guideline values for chloroform and bromate are 100 $\mu g \cdot L^{-1}$ and 10 $\mu g \cdot L^{-1}$, respectively, identical to that in Canadian Guidelines. However, the EU member countries may set more stringent DBP standards than the EU Directives. For example, the THM4 regulatory limits are 50 $\mu g \cdot L^{-1}$, 30 $\mu g \cdot L^{-1}$ and 25 $\mu g \cdot L^{-1}$ in Germany, Austria and Switzerland, respectively [47].

Since 1958 the World Health Organization (WHO) has periodically published International Standards for Drinking-Water and later Guidelines for Drinking Water Quality. The WHO guidelines are currently adopted by many countries and regions, including the Hong Kong Special Administrative Region of China. The latest edition [48] was published in 2011, and set guideline values for TTHM and 14 individual DBPs. Each of the four THMs has its guideline value, with the MCLs for chloroform, BDCM, DBCM and bromoform at 300 $\mu g \cdot L^{-1}$, 60 $\mu g \cdot L^{-1}$, 100 $\mu g \cdot L^{-1}$ and 100 $\mu g \cdot L^{-1}$, respectively. TTHM is not calculated on a concentration basis. Rather, it is denoted as the sum of the ratio of the concentration of each THM to its guideline value. Only the three solely chlorinated acetic acids are in the DBP lists. The guideline values for monochloroacetic acid (MCAA), DCAA and TCAA are 20 $\mu g \cdot L^{-1}$, 50 $\mu g \cdot L^{-1}$ and 200 $\mu g \cdot L^{-1}$, respectively. The WHO Guidelines did not cover CH, formaldehyde or CNCl. No guideline value is set for formaldehyde, as it was believed the formaldehyde levels in drinking water are below the level at which adverse health effects may occur. Rather, two HANs (dichloroacetonitrile (DCAN) and dibromoacetonitrile (DBAN) at 20 $\mu g \cdot L^{-1}$ and 70 $\mu g \cdot L^{-1}$, respectively), one nitrosamine (NDMA) at 0.1 $\mu g \cdot L^{-1}$ and 2,4,6-trichlorophenol at 0.2 $mg \cdot L^{-1}$ are included in the Guidelines.

In mainland China, the first national Standards for Drinking Water Qualities (TJ 20−76) was promulgated in 1976 then revised in 1985 (GB5749−1985). The only DBP regulated by GB5749−1985 was chloroform with an MCL at 60 $\mu g \cdot L^{-1}$. The Standards was further revised in 2006 and the new Standards (GB5749−2006) [8] regulates TTHM and 13 individual DBPs (Table 3). Similar to the WHO Guidelines, TTHM denotes the sum of the ratio of the concentration of each THM to its respective MCL under the New Standards. All the four individual THMs are regulated by GB5749−2006, but with the MCL for chloroform at 60 $\mu g \cdot L^{-1}$. DCAA and TCAA, two most common HAAs in disinfected drinking water, are regulated with MCLs at 50 $\mu g \cdot L^{-1}$ and 100 $\mu g \cdot L^{-1}$, respectively. The MCLs for bromate, chlorite, chlorate and 2,4,6-trichlorophenol by GB5749−2006 are the same with the respective WHO guideline values. However, GB5749−2006 also regulates CH, formaldehyde and CNCl. CNCl normally accumulates during chloramination and is regulated with an MCL at 70 $\mu g \cdot L^{-1}$. A water system is out of compliance when more than 5% of the measured samples collected from the system exceed the MCL (termed 5% method hereafter). GB5749−2006 requires the sampling frequency no less than once every month for chloroform, bromate, chlorite, chlorate and formaldehyde, and no less than once every half year for the remaining regulated DBPs.

Drinking water quality standards or guidelines were promulgated in some other countries or regions in Asia. The Drinking Water Quality Standards in Japan [49] regulate TTHM and the four individual THMs, the three solely chlorinated HAAs, bromate, CNCl and formaldehyde. The regulated DBP species are almost identical to GB5749−2006, except for that chlorite, chlorate and 2,4,6-trichlorophenol are not regulated but MCAA is regulated. The other differences between the two Standards are that the Japanese Standards are more stringent for BDCM, formaldehyde and CNCl but less stringent for TCAA, and the Japanese Standards regulate TTHM by a concentration basis. The Australian Guidelines is probably the one which includes the largest number of DBP parameters (a total of 24), although no guideline values were set for chlorate, 3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone (MX), the four chloroketones, TCNM and the four HANs due to the lack of sufficient data from the health aspect [50]. Except for TTHM (the guideline value of which is on a centration basis (250 $\mu g \cdot L^{-1}$)), the DBP parameters of Australian Guidelines are similar to that of WHO Guidelines, although the former is generally less stringent than the latter in terms of the guideline values except for those for the taste- and odor-causing chlorophenols. In addition to 2,4,6-trichlorophenol, two more chlorophenols are included in the Australian Guidelines, primarily due to their lower taste thresholds [48]. In the Taiwan region of China, very few DBP parameters are regulated and the MAC for TTHM is 150 $\mu g \cdot L^{-1}$.

The assessment of the Chinese DBP regulations was conducted by comparing with the U.S.EPA D-DBP Rules by using the same ICR DBP database. Under the Stage 1 D-DBP Rule, 3.8% and 3.6% of the water systems included in ICR database will be out of compliance with the TTHM and HAA5 requirements, respectively (Table 4). Under the Stage 2 D-DBP Rule 10.4% and 5.1%, of the ICR plants will be out of compliance with the TTHM and HAA5 requirements, respectively. The increase in percentage of plant out of compliance is due to the compliance calculation method. The Stage 1 D-DBP Rule uses RAA, but the Stage 2 D-DBP Rule uses LRAA. The greater increase in out of compliance percentage for THMs than that for HAAs indicates that a great spatial variation in THM levels than that in HAAs in the water distribution systems. Under the Chinese Standards, 37.8%, 24.5%, 18.1% and 9.8% of the ICR plants would be out of the compliance with THMs, CH, HAAs and bromate, respectively. The much higher percentages of out-of-compliance ICR plants under the Chinese Standards are also mainly due to compliance calculation methods. Under the Chinese Standards, the water plants are out of compliance when 5% of samples have the DBP levels higher than the Standards. Further analysis indicates that most of out of compliance samples are samples collected in summer or fall seasons. The RAA calculation method used under the US Stage 1 D-DBP regulation reduces the effects of high DBP levels samples collected in summer and fall.

Considering the chronic toxicity of DBPs and critical role of water disinfection, especially in summer and fall seasons, the authors suggested the RAA calculation be adopted under the Chinese Standards to maintain water disinfection. Using the RAA calculation, the percentages for the out of compliance ICR plants under the Chinese Standards will be reduced to 13.8%, 3.5%, 0.4%, 0, 4.0% and 0 respectively, for the TTHM, chloroform, DCAA, TCAA, CH and bromate parameters. This proposed change could better protect public health by promoting effective water disinfection during summer and fall seasons and reduce the regulatory burden of water utilities.

The Chinese Standards also regulated formaldehyde at $0.9\ \mathrm{mg \cdot L^{-1}}$ and specified an analytical method with a detection limit at $50\ \mu\mathrm{g \cdot L^{-1}}$ [10]. Generally, formaldehyde occurs at levels less than $50\ \mu\mathrm{g \cdot L^{-1}}$ in ozonated water. The aldehyde requirement has little impact on the regulatory compliance but will result in analytical and reporting burdens for water utilities. Moreover, the high detection limit of the analytical method will prevent the water utilities from using the formaldehyde data to potentially assess taste and odor, or biologic stability of treated water. The authors suggest that both MCL and analytical method for formaldehyde be revised. U.S.EPA Method 556 is suggested for analyze several common aldehydes, including formaldeghyde, acetaldehyde, glyoxal and methyl glyoxal. In addition, the authors also suggest that U.S.EPA Method 551.1 be adopted for the measurement of CH, along with THM4, CNCl and other volatile DBPs, and GC-ECD methods for the measurement of CNX [12] in drinking water.

5 DBP control

Common DBP control strategies include DBP precursor removal and alternative disinfectants. Organic DBP precursors can be effectively removed by several treatment processes such as enhanced coagulation, activated carbon adsorption, biologic treatment, nanofiltration (NF), anion exchange and advanced oxidation processes (AOPs) [5,14,51–54]. Enhanced coagulation and granular activated carbon (GAC) process are two best available technologies (BATs) for DBP control under the Stage 1 D-DBP Rule [2]. For alternative disinfectants, chloramination is commonly practiced by water utilities for THM and HAA control.

Both enhanced coagulation and chloramination are effective in reducing the formation of THMs, HAAs, and other carbonaceous DBPs. However, enhanced coagulation of water containing bromide may result in a higher level of brominated DBPs [2]. Chloramination can also result in a higher level of nitrogeneous DBPs, including CNCl and NDMA, and iodinated DBPs [55–57]. Formation of these emerging DBPs may offset the benefits in reduction of THMs and HAAs.

Another effective DBP control and regulatory compliance strategy is the DBP removal after formation. Prechlorination and/or intermediate chlorination are commonly practiced by water utilities to control Fe/Mn and taste and odor compounds, to improve coagulation or filtration efficiency, or to meet disinfection CT requirement. DBPs formed can be removed by treatment processes in the treatment plants, or treatment processes in the clear wells or distribution systems. Both THMs and HAAs can be removed by activated carbons, in point-of-use or point-of-entry carbon adsorption devices. However, frequent GAC replacement (e.g., every other month or every quarter) makes the process unpractical in treatment plants [58].

Although the GAC adsorption capacity for DBPs is limited, bioactivities on the GAC surface are effective in removing biodegradable DBPs, including HAAs, CH, aldehydes, and ketoacids. Biologically active carbon (BAC) is effective in removing HAAs formed during prechlorination or intermediate chlorination [59,60]. At 10°C, an empty bed contact time (EBCT) of 7–8 min was required to remove 50% of mono- and di-haloacetic acids [60]. A higher removal could be achieved at higher water temperatures or longer EBCTs. Mixing with 5% of acclimated GAC can enhance bioactivity development on the GAC surface and the removal efficiency of HAAs after

Table 3 A comparison of the maximum contaminant levels for the various disinfection by-products regulated by the Chinese and US drinking water standards, and suggested by the WHO guidelines (unit: mg·L^{-1})

DBP species	Chinese standards	WHO guidelines	US regulations	Canadian guidelines	EU directive	Japanese standards	Australian guidelines
TTHM	1[a]	1[a]	0.08	0.1 LRAA	0.1	0.1	0.25
chloroform	0.06	0.3	–	–	–	0.06	–
BDCM	0.06	0.06	–	–	–	0.03	–
DBCM	0.1	0.1	–	–	–	0.1	–
bromoform	0.1	0.1	–	–	–	0.09	–
HAA5	–	–	0.06	0.08 LRAA	–	–	–
MCAA	–	0.02	–	–	–	0.02	0.15
DCAA	0.05	0.05	–	–	–	0.04	0.1
TCAA	0.1	0.2	–	–	–	0.2	0.1
CH	0.01	–	–	–	–	–	0.02
bromate	0.01	0.01	0.01	0.01	0.01	0.01	0.02
formaldehyde	0.9	–	–	None required	–	0.08	0.5
chlorite	0.7	0.7	1	1	–	–	0.8
chlorate	0.7	0.7	–	1	–		N.D.
CNCl (as CN-)	0.07	–	–	–	–	0.01	0.08
DCAN	–	0.02	–	–	–	–	N.D.
DBAN	–	0.07	–	–	–	–	N.D.
2-chlorophenol	–	–	–	–	–	–	0.0001
2,4-dichlorophenol	–	–	–	–	–	–	0.0003
2,4,6-trichlorophenol	0.2	0.2	–	–	–	–	0.002
NDMA	–	0.0001	–	0.000 04	–	–	0.0001

Note: a) the sum of the ratio of the concentration of each trihalomethane to its respective MCL/guideline value

Table 4 The regulation violence rates of the ICR plants based on the China standards and the US standards

DBP species	Chinese regulations		US regulations	
	5% method	RAA	RAA	LRAA
TTHM	37.8%	13.8%	3.8%	10.4%
chloroform	18.1%	3.5%	–	–
BDCM	0	0	–	–
DBCM	0	0	–	–
bromoform	0	0	–	–
HAA5	–	–	3.6%	5.1%
MCAA	–	–	–	–
DCAA	2.7%	0.4%	–	–
TCAA	0.5%	0	–	–
CH	24.5%	4.0%	–	–
bromate[b]	9.8%	0	0	N.A.
formaldehyde	0	0	–	–
chlorite[c]	39.5%	38.1%	19.0%	N.A.
chlorate[c]	4.2%	4.2%	–	–
CNCl (as CN-)	0	0	–	–

Note: b) when ozone is used as the disinfectant; c) when chlorine dioxide is used as the disinfectant

GAC was replaced. HAAs can also be reduced by the biologic activity in the distribution systems [61]. It is also the reason why the lowest level of HAAs is often observed at the end of the distribution systems [62].

Air stripping can be used for THM (and other volatile DBP) removal [63,64]. Recently, the use of air stripping in water storage tanks has been investigated as a cost-effective technology for THM removal, especially in small water systems or a THM hot spot in a large water distribution system [65–67]. Because of the high Henry's law constant, air stripping is the most effective in summer months when the formation of THMs is highest. Because of the lower Henry's Law constants, however, air striping will be less efficient when dominant THMs are brominated THMs. In comparison to enhanced coagulation and chloramination, air stripping for THM removal and BAC for HAA removal, will not form other known byproducts with potential health risks. Both technologies are more effective in summer or fall seasons when the formation of THM and HAAs are highest. However, the effective of these two processes on other DBPs are not comprehensively investigated.

Recently, zero-valent iron (ZVI) reduction of halogenated DBPs has attracted a lot of interest [68–73]. Cast iron scraps were effective in reducing TCAA, which is much less biodegradable than mono- and di-halogenated HAAs. A combination of ZVI filtration and a subsequent BAC filtration would be a viable process for HAA removal [74].

6 Emerging DBPs

The DBPs of emerging concerns generally include bromo- and iodonitromethanes, iodo-THMs, iodoacids, haloamides, brominated trihaloacetaldehydes, MX, brominated MX (BMX) and analogs, and NDMA [14,30]. These emerging DBPs are generally of relatively high occurrence levels among a list of about 50 priority DBPs which were selected by an expert toxicological review [75]. The priority DBPs were those not included in the ICR survey but received the highest ranking for potential toxicity among the vast number of DBPs reported in the literature. NDMA, as an emerging DBP, was set guideline values by WHO as well as Canadian and Australian authorities.

The volatile halogenated emerging DBPs (including bromo- and iodonitromethanes, iodo-THMs, haloamides and brominated trihaloacetaldehydes) can be measured by methods similar to that for THM4 (e.g. EPA Method 551.1). However, one must be aware of the co-elution problem when determining iodo-THMs [14]. Results showed that LLE-GC-ECD is more effective than HS-GC-ECD and P&T-GC-ECD in determining iodo-THMs. The detection limits for iodo-THMs are in the range of $0.01\ \mu g \cdot L^{-1}$–$0.03\ \mu g \cdot L^{-1}$ [76]. Trihalonitromethanes might decompose during GC analysis [77] and a GC injector temperature $\leqslant 170°C$ should be used. Similarly, iodoacids can be determined by the same methods for HAAs. Recent methods for measuring MX, BMX and the analogs have included LLE, derivatization with BF_3/methanol or acidic methanol, and analysis using GC-ECD [2,14]. NDMA and other nitrosamines are more suitably measured by an MS detector, with details that can be found in the EPA Method 521. Method 521 is a GC-MS-MS method with solid-phase extraction (SPE) pretreatment. Nitrosamine concentrations in drinking water normally are extremely low and measurement requires low detection limits. Tandem MS satisfies the requirement, and the detection limits for the 7 nitrosamines range from $0.26\ ng \cdot L^{-1}$ to $0.66\ ng \cdot L^{-1}$. LC-MS-MS methods were also developed for nitrosamine determination with analyte preconcentration by using SPE or LLE [78]. The detection limit for NDMA of SPE-LC-MS-MS method could be as low as to $1\ ng \cdot L^{-1}$, a level similar to that of SPE-GC-MS-MS method. Compared with GC-MS methods, an LC-MS method may be more suitable for the measurement of thermal-labile nitrosamine species, e.g. N-nitrosodiphenylamine and N-nitrosoopiperidine [79].

According to the few surveys conducted on the occurrence levels of the emerging DBPs and other priority DBPs in the drinking water [30,31], the iodo-THM concentrations were in the sub-$\mu g \cdot L^{-1}$ level and the ratio of iodo-THMs to THM4 was 2% on a median basis. The highest formation of iodo-THMs was observed in water from the plants which added chlorine and ammonia simultaneously to form chloramines with a moderate amount of bromide (and probably iodide). Iodoacids were found in finished drinking water also having relatively high levels of iodo-THMs. Haloacetamides were in a concentration range comparable to CH and the median value was $1.4\ \mu g \cdot L^{-1}$. The main species of haloacetamides was 2,2-dichloroacetamide.

The median level for halogenated furanones was $0.31\ \mu g \cdot L^{-1}$, and MX only constituted a minor component of halogenated furanones (with a median level at $20\ ng \cdot L^{-1}$). BMXs and BEMXs could occur at relatively high concentrations in some high-bromide waters. Other studies showed that the MX concentration was usually less than $60\ ng \cdot L^{-1}$ [14], although in some occasions the concentration might be much higher [38,39,80].

The NDMA concentration in drinking water was found varying from $< 2.4\ ng \cdot L^{-1}$ to $130\ ng \cdot L^{-1}$ [81], but in most cases its concentration was less than $10\ ng \cdot L^{-1}$ [55]. However, NDMA may account for only 5% of all nitrosamines in chloraminated drinking waters [82].

Enhanced coagulation was suggested by U.S.EPA as BAT for the removal of DBP precursors. However, coagulation has little effect on either bromide or iodide ions, resulting in increased Br/ dissolved organic carbon (DOC) and I/DOC ratios. In addition, coagulation generally exhibits better removal ability for high molecular weight (MW) and hydrophobic organics [83–85]. The remaining low MW and hydrophilic natural organic matter

(NOM) fractions are more reactive to hypobromous and hypoiodous acids than the hydrophobic fractions [85,86]. Therefore, coagulation can potentially cause a shift to more brominated and iodinated DBPs. In actuality, any processes that remove organic DBP precursors more than bromide and iodide would favor the formation of brominated or iodinated DBPs during subsequent chlorination or chloramination [87–89]. Recently, Watson et al. reviewed the strategies for the removal of these inorganic DBP precursors from drinking water sources and their applicability in DBP minimization [54]. NF process is normally effective in rejecting bromide and iodide ions [90]. Bromide and iodide can also be removed by electrochemical and adsorptive techniques. Moreover, the low MW (<1 kDa) and hydrophilic fractions remained after enhanced coagulation had a higher NDMA yield than the other fractions [91]. Furthermore, some polymeric coagulants (e.g. polyamine and poly DADMAC) may form NDMA when in contact with a number of chemical disinfectants including ozone, free chlorine and chloramines [92].

Though chloramination in lieu of chlorination can substantially reduce the levels of regulated DBPs, it favors the formation of emerging DBPs, including iodinate DBPs, NDMA, and other nitrosamines [3]. The rate of NDMA formation through reaction of monochloramine with secondary amines (e.g. the amine-based polymers used for coagulation) is approximately an order of magnitude higher than that observed with free chlorine [93,94]. In contrast to the commonly measured THM4, bench- and plant-scale studies showed that iodo-THM formation was favored by chloramination, especially if the ammonia was added first [95]. Similar phenomenon was found for iodo-acids [96]. Chloramines are weak oxidants that oxidize iodide only to hypoiodite rather than to iodate [14].

Ozonation destroys the precursors of a number of emerging DBPs. Ozone achieved the greatest reduction among preoxidants in NDMA formation [97,98], although a small amount of NDMA would be formed from reaction of polyelectrolytes with ozone [99]. No iodo-THMs were formed by ozonation [95]. However, preozonation was found to increase the formation of trihalonitromethanes (e.g., TCNM and tribromonitromethane (TBNM)) [30,35,98,100,101]. Oxidation by ozone of the NOM amine groups to nitro groups is the primary cause of the enhancement of trihalonitromethane formation during the subsequent chlorination or chloramination. UV radiation was believed a safe disinfection method yielding little DBPs. However, similar to ozonation, medium-pressure UV radiation would enhance the formation of trihalonitromethanes, although low pressure UV had no impact [102]. The TCNM formation was nearly doubled when post-chlorination rather than post-chloramination was coupled with medium pressure UV [103].

NDMA is neither biodegradable nor volatile, which however can be degraded by UV radiation using medium-pressure mercury lamps [55]. The dosage of UV radiation is however much higher than that for disinfection purpose. Because of the polarity and hydrophilicity, adsorption capacity of activated carbon for NDMA was relatively small and GAC is required to be replaced in few months.

7 Conclusions

Due to the potential health risks and widespread occurrence of DBPs in drinking water, many countries regulate DBPs in their drinking water. Analytical methods based on GC-ECD are most commonly used for the determination of organic DBPs, while the methods based on IC-CD for the determination of inorganic DBPs. Recently, MS and tandem MS are increasingly used as the detectors for DBP determination, primarily owing to their higher selectivity and lower matrix inference. Several nationwide surveys in the United States showed that the median THM4 and HAA9 concentrations in the distribution systems were both at 30 $\mu g \cdot L^{-1}$.

The DBP Regulations in the US and DBP Guidelines in Canada are similar, while the DBP Regulations/Guidelines in China, Japan and Australia are similar to the WHO DBP Guidelines. Based on the same set of DBP data (ICR database), a comparison study indicated that the regulatory compliance rate for ICR plants under the Chinese GB5749-2006 is much lower than the US Stage 1 and Stage 2 D-DBP Rule. This difference is primarily due to the compliance calculation methods used in the US and China. DBP control can be achieved by removing DBP precursors (e.g., enhanced coagulation) and/or using alternative disinfectants (e.g., chlormination). In recent years, removing DBPs after their formation, including aeration for THM removal and biodegradation for HAA removal, is also practiced for DBP control. One unintended consequences of precursor removal and chloramination is the formation of emerging DBPs, including brominated/iodinated DBPs and nitrogenous DBPs. In comparison to THMs and HAAs, these emerging DBPs occur at much lower levels but may pose equal or higher health risks due to their higher toxicity.

We suggest that the annual average calculation method (e.g., RAA or LRAA) be adopted for DBP compliance under the Chinese regulation, GB5749-2006. We also suggest that the revision of DBP analytical methods based on the current analytical technology. For DBP control, water utilities should consider DBP removal, as well as precursor removal and alternative disinfectants.

Abbreviations

AOP	advanced oxidation process
BAC	biologically active carbon
BAT	best available technology

BCAA	bromochloroacetic acid
BCAN	bromochloroacetonitrile
BDCAA	bromodichloroacetic acid
BDCM	bromodichloromet hane
BEMX	brominated EMX
BMX	brominated MX
CD	conductivity detector
CH	chloral hydrate (trichloroacetaldehyde hydrate)
CNCl	cyanogen chloride
CNX	cyanogen halide
D-DBP	disinfectants and disinfection by-products
DBP	disinfection by-products
DBAA	dibromoacetic acid
DBCAA	dibromochloroacetic acid
DBCM	dibromochloromet hane
DBAN	dibromoaceto nitrile
DCAA	dichloroacetic acid
DCAN	dichloroaceto nitrile
DCP	1,1-dichloropropanone
DHAA	dihaloacetic acid
DHAN	dihaloacetonitrile
DOC	dissolved organic carbon
ECD	electron capture detector
EMX	(E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid
EPA	Environmental Protection Agency
ESI	electrospray ionization
GAC	granular a ctivated carbon
GC	gas chromatography
HAA	haloa cetic acid
HAA5	sum of MCAA, DCAA, TCAA, MBAA and DBAA
HAA9	sum of HAA5, BCAA, BDCAA, DBCAA and TBAA
HAN	haloa cetonitrile
HAN4	sum of DCAN, BCAN, DBAN and TCAN
HS	head space
IC	ion chromatography
ICP	inductively coupled plasma
ICR	information collection rule
LC	liquid chromatography
LLE	liquid -liquid extraction
LRAA	locational running annual average
MAC	maximum acceptable concentration
MBAA	monobromoacetic acid
MCAA	monochloroacetic acid
MCL	maximum contaminant level
MS	mass spectrometry
MW	molecular weight
MX	3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone
NDMA	N-nitrosodimethylamine
NF	nanofiltration
NOM	natural organic matter
P&T	purge and trap
RAA	running annual average
SPE	solid-phase extraction
TBAA	tibromoacetic acid
TBNM	tribromonitromethane
TCAA	trichloroacetic acid
TCNM	trichloronitromethane
TCP	1,1,1-trichloropropanone
THM	trihalomethane
THM4	sum of chloroform, BDCM, DBCM and bromoform
TOC	total organic carbon
TOX	total organic halide
TTHM	THM4
UF	ultrafiltration
UV	ultraviolet
ZVI	zero -valent iron

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