CLEAN
Soil Air Water

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Review

A Review on Formation and Decay Kinetics of Trihalomethanes in Water of Different Qualities

Despite the many disadvantages associated with the use of chlorine for disinfecting drinking water, chlorination is still the main method used for this purpose worldwide. Low chlorine concentrations in water distribution systems increase health risks whereas high chlorine concentrations are associated with the formation of disinfection by-products such as trihalomethanes which are suspected carcinogens. Due to their negative health impacts, trihalomethanes occurrence in finished drinking water has received great attention from researchers and scientists worldwide. This manuscript critically reviews and discusses up to date knowledge on the occurrence of trihalomethanes in chlorinated drinking water and their associated health risks and identifies research gaps. The models for trihalomethane formation and decay have been compiled with special emphasis on the impact of the bromide ion on the total trihalomethane levels and speciation. Furthermore, the fate and transport of trihalomethanes in drinking water supplies and in groundwater have been investigated. Finally, management options for the reduction of trihalomethanes in chlorinated drinking water such as the removal of precursors from raw water, the use of alternative disinfectants and the removal of trihalomethanes from finished drinking water have been critically investigated and discussed.

1 Introduction

Drinking water must be disinfected before it is supplied to the consumers to minimize the risk of the breakout of water-borne diseases by inactivating the pathogens at the source and by protecting its quality against potential re-contamination during transport in the distribution systems and/or during storage in the utility storage tanks. Many chemicals have been used for disinfecting drinking water; chlorine, chlorine dioxide, and chloramines are the mostly preferred disinfectants due to their high effectiveness in inactivating pathogens and due to their persistence in water distribution systems (WDSs). Among the chlorine compounds, chlorine gas is the most commonly used disinfectant worldwide

due to its low cost, effectiveness, availability, persistence in WDSs, and ease of application.

Maintaining the adequate and acceptable water quality for drinking and for other uses as the water is transported, is a complicated task due to the complexity of WDSs, chlorine decay as the water travels in the distribution system, the vulnerability of WDSs to pollution, and the formation of chlorination by products. The spatial and temporal variability aspects of the problem increases the complexity of the drinking water safety several orders of magnitude. Management of chlorine concentrations in WDSs requires an optimum solution between two conflicting objectives that is; maintaining high chlorine residual concentrations adequate for disinfection and low enough to maintain the formation of the harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) within the acceptable limits as these DBPs are suspected carcinogens and pose other chronic and acute adverse health impacts to humans and animals [1–11].

Due to the severe health impacts of the DBPs, i.e., THMs, and due to the complexity of their formation mechanisms in finished drinking water, extensive research has been carried out to manage their levels in chlorinated drinking water all over the world since they were first identified in 1974 in the Netherlands and in the United States [12, 13]. This article critically reviews the literature on the different THM species formation mechanisms in finished drinking water and their fate in WDSs and groundwater. Furthermore, management options to maintain their concentrations within acceptable limits are discussed in detail. In addition, research gaps are identified.

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Abbreviations: AER, anion exchange resin; **BDCM**, bromodichloromethane; **BIF**, bromine incorporation factor; **DBCM**, dibromochloromethane; **DBP**, disinfection by-product; **DOC**, dissolved organic carbon; **DOM**, dissolved organic matter; **EC**, enhanced coagulation; **GAC**, granular activated carbon; **HAA**, haloacetic acid; **MCBR**, membrane bioreactor and membrane coagulation bioreactor; **MW**, molecular weight; **NOM**, natural organic matter; **PAC**, powdered activated carbon; **RO**, reverse osmosis; **SUVA**, specific UVA; **THM**, trihalomethane; **THMFP**, THM formation potential; **TOC**, total organic carbon; **TTHM**, total THM; **UVA**, ultraviolet absorbance; **WDS**, water distribution system

2 Formation of the different THM species in finished drinking water

2.1 Occurrence of THMs in public water supplies and their associated health risks

Chloroform, a DBP, was first identified in chlorinated drinking water in the Netherlands by Rook [12] and in the United States by Bellar et al. [13] in 1974 independently. As a consequence of Rook's and Bellars et al.'s finding, a survey was conducted in the United States by the National Organic Reconnaissance for the water supplies of 27 large cities by Symons et al. [14]. Their study revealed that four THMs are widespread in chlorinated drinking water at trace concentrations which are: chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform [15]. Since that date, many other DBPs have been identified in chlorinated drinking water such as haloacetic acids (HAAs), haloketones and halohallides. According to Richardson et al. [16], more than 700 confirmed DBP species have been identified in drinking water.

DBPs are formed by the reactions between disinfectants and naturally occurring organic matter in raw water. Natural organic matter (NOM) is a heterogeneous mixture of organic compounds with various physical and chemical properties [structure, functionality, molecular weight (MW), ultraviolet absorbance (UVA), fluorescence, etc.] [17, 18]. NOM consists mainly of humic and non-humic substances. Approximately 50% of dissolved organic carbon (DOC) is humic substances which can be classified into humic acid, fulvic acid, and humin which is the dominant group of organic compounds in water supplies [19, 20]. The remaining 50% are composed of non-humic substances. A major component of aquatic humic substances is fulvic acid with MW of <2000 Dalton (Da) which is present in dissolved form. In comparison, humic acid with a MW between 2000 and 5000 Da or greater is considered to be colloidal. Among the non-humic substances, about 60% of the DOC consists of hydrophilic acids [19].

NOM reacts with chlorine to produce chlorinated DBPs, such as THMs and other halogenated DBPs. The concentration and speciation of DBPs formed are influenced by the chemical and the structural characteristics of NOM such as aromaticity and functionality [21]. NOM is classified as hydrophobic and hydrophilic based on adsorption on XAD® resins and/or using spectroscopy. Hydrophobic NOM consists of compounds having high aromaticity. The molecules with activated aromatic structures account for most of the chlorine consumption in the chlorination process [18]. In addition, THM formation is strongly influenced by the hydrophobic fraction of the NOM. Furthermore, high THM formation potential (THMFP) is attributed to the high phenolic content of NOM [22, 23]. UV absorbance and specific UVA at 245 nm ($SUVA_{254}$) are two of the most strongly correlated NOM properties to the DBP formation potential [24–31]. UVA_{254}, a parameter of aromatic and/or hydrophobic matter, is related to THM formation. $SUVA_{254}$ is defined as the UV_{254} (m^{-1}) divided by the DOC concentration (mg/L). Correlations between DBP formation and SUVA appear particularly significant for NOM fractions from the same water source. SUVA can be determined quickly using a small sample volume with simple sample pretreatment and readily available instrumentation that is straightforward to operate. These features have made SUVA an attractive parameter to characterize dissolved organic matter (DOM) which has been used frequently over the past decade [31]. UVA_{254} and $SUVA_{254}$ are generally shown to correlate well with DBP formation in hydrophobic, aromatic and high MW NOM such as humic and fulvic acids [32, 33] especially in water with relatively high DOC concentration (>3 mg/L) and high $SUVA_{254}$ values ($>2-3$ L/mg Cm) [34]. Low-UV or non-UV absorbing NOM fractions are important in the formation of DBPs in water with low SUVA, low DOC and low bromide levels. SUVA and differential spectroscopy were not correlated well with the formation and speciation of THMs in water characterized by hydrophilic NOM, less aromaticity and low-SUVA values (<2 L/mg Cm) [34].

Although epidemiological studies have not proven strong relationship between THMs and cancer, there is some evidence that links rectal, intestinal and bladder cancer to long-term, low level exposure to THMs [35]. Llopis-González et al. [36] found possible association between bladder cancer in women and exposure to THMs at levels below the European Community legal limit. Besides, being suspected carcinogens [37–42] exposure to THMs is also linked to miscarriage in women. A study in California conducted by the State Health Department found out that women exposed to high levels of DBPs had a 17.5% risk of miscarriage, whereas women who had little exposure to THMs had a lower level risk of 9.5% [41]. In addition, several other studies suggested increased risks of bladder, stomach, large intestines and rectal cancer in places where the source of drinking water is surface water [43–45]. Other studies have suggested links between adverse reproductive outcomes and exposure to DBPs during pregnancy [46–48]. Furthermore, chloroform is suspected to be carcinogenic to animals too [49]. Tokmak et al. [50] estimated that each year, 1 of the 5 million Ankara residents is at risk of contacting cancer from the daily water intake, mainly because of the exposure to chloroform through oral ingestion.

Recently, extensive research has been conducted worldwide by many researchers independently to estimate the risks associated with the exposure to THMs through paths other than direct ingestion such as inhalation and dermal contact during bathing, showering and swimming. Uyak [51] studied the cancer risk to Istanbul residents through direct ingestion of chlorinated drinking water, dermal absorption and inhalation during bathing, showering and swimming. It was concluded that Istanbul residents are at higher cancer risk from direct ingestion rather than from dermal contact and inhalation. Each year, approximately 5 of the 8 million Istanbul residents are at risk of contacting cancer from the direct ingestion of tap water. Mallika et al. [52] found out that swimmers are exposed to high risk of contacting-skin cancer from swimming pools in Nakhon Pathom Municipality in Thailand. Chowdhury et al. [10] found out that 700 cancer cases in Canada might have been caused by exposure to THMs in drinking water through direct ingestion, inhalation and dermal contact. Villanueva and Font-Ribera [53] found out that no epidemiological evidence of increased risk of reproductive outcomes as a consequence of swimming during pregnancy exists. However, an epidemiological study suggested an increased risk of bladder cancer from swimming pools, although, this finding is not conclusive. In addition, there is evidence that associates asthma risk and swimming. However, the risk depends on the target population [54]. It was found that those who are occupationally exposed to the pool environment are at high risk of respiratory symptoms including asthma, although the causality of this association is uncertain. Furthermore, the health impacts of swimming pools on children are less conclusive as Font-Ribera et al. [55] study indicates that asthma risk is not increased by swimming pool attendance by children. Venkataraman and

Venkatesh [56] quantified and mapped the toxicological risks associated with exposure to THMs during showering in the Gulf Coast region of Texas. It was found that the areas with the highest estimated cancer risk are metro- and micropolitan areas. Lourencetti et al. [57] found that the chloroform predominates over the other THMs in the air of the chlorinated swimming pool which can be explained by the fact that chloroform has higher vapor pressure than the other THMs. However, bromoform dominated in the air of brominated pool. Reghi et al. [58] studied exposure of swimmers to DBPs in indoor swimming pools in Italy. THMs were detected in all collected pool samples at an average concentration of ($36.9 \pm 28.2\,\mu g/L$). Hira et al. [59] found out that the average life time cancer risk by exposure to drinking water through ingestion, inhalation, and dermal contact is 0.74×10^{-4} and 1.24×10^{-4} for Rawalpindi and Islamabad inhabitants in Pakistan, respectively. The number of expected cancer cases per year was estimated at two cases per city. Lee et al. [60] found out that the mean lifetime cancer risks in South Korea by exposure to THMs and HAAs in tap water through ingestion, dermal contact, and inhalation are $7.23–10.06 \times 10^{-6}$, $2.19–3.63 \times 10^{-6}$, and $5.22–7.35 \times 10^{-5}$, respectively. In addition, it was found that the main exposure route to THMs is inhalation during showering. Furthermore, sensitivity analysis showed that shower time and frequency had high impact on the lifetime cancer risk by the exposure to THMs in tap water. Chowdhury [61] took water temperature into consideration while estimating exposure to total THMs (TTHMs) through different exposure paths. Exposure through ingestion was estimated using cold water, while exposure through inhalation and dermal contact during showering was estimated using warm water. Inhalation of THMs was estimated by partitioning THMs into the shower air, while dermal uptake was estimated for steady and unsteady states type of exposure during showering. It was found out that inhalation and dermal contact during showering contributed 25–60% of total exposure. Chowdhury [62] found out that the steady-state assumption in estimating dermal uptake of THMs during showering resulted in lower exposure estimates.

2.2 Mathematical modeling of the formation of different THM species

Since the different THM species have been first identified in chlorinated drinking water, many mathematical models have been developed worldwide to predict their concentrations and/or their formation potential for the ultimate objective of understanding their formation mechanisms and controlling their levels in chlorinated drinking water [24, 48, 63–78]. Chowdhury et al. [4], in a recent review article, mentioned that 118 different mathematical models that predict the concentrations of the different DBPs in finished drinking water are reported in 48 scientific publications. Table 1 summarizes some of the models that predict THM concentrations in chlorinated drinking water in terms of the employed predictors, water type, and location. Table 1 shows that the main THM predictors are organic content, chlorine dose, temperature, pH, contact time, and bromide ion concentration. However, Walker [81], Palmstorm et al. [82], Karimi and Singer [83], and Martin et al. [84] reported strong correlation between algal productivity and THMFP. Furthermore, Canale et al. [85] related THMFP to chlorophyll, zooplankton, secchi disk depth, dissolved oxygen, and total phosphorus. Others related THM levels to ammonia concentration [86, 87]. In addition, Table 1 shows that

different quality parameters were used to express and to quantify the organic content of the raw water which are: total organic carbon (TOC), UVA$_{254}$, DOC, NOM, and DOM. It was found that the observed THM levels are directly proportional to the organic matter content, chlorine dose, temperature, pH, contact time, and bromide ion concentration; however, the breakdown between chloroform and the different brominated THM species is strongly affected by the bromide ion concentration [48, 63, 74]. Zhao et al. [75] found out that the low MW DOM is the major THMs precursor in the disinfection process with chlorine and chlorine dioxide from Guangzhou section of the Pearl River in New York. Rodrigues et al. [76] ranked the precursors for each THM species: they found out that the chloroform concentration is mostly affected by the fulvic acid concentration, temperature and pH; the BDCM formation is mostly affected by the fulvic acid concentration and the chlorine dose; the DBCM formation is mostly affected by the fulvic acid concentration and the chlorine dose and to a lesser degree by the bromide ion concentration, pH and temperature and the bromoform concentration is mostly affected by the chlorine dose and the bromide ion concentration and to a lesser degree by the fulvic acid concentration. Di Cristo et al. [88] investigated the applicability of 18 THM formation models for the Aurunci-Valcanneto WDS in Southern Lazio (Italy). It was found that the models developed based on field data were more suitable for reproducing THMs formation for the Southern Lazio WDS.

The impact of pipe material on chlorine decay rate and THM formation was modeled by Li et al. [89]. It was found that the rate constant for chlorine decay is highest for stainless steel and decreases for ductile iron pipe and polyethelene pipe. Consequently, THM formation followed the reverse order, i.e., highest for polyethelene pipe and lowest for stainless steel pipe. Chowdhury et al. [90] found out that THMs concentrations can increase significantly within the pipe plumbing system and hot water tanks beyond the WDS, i.e., within the consumer plumbing system. Based on a study on the plumbing system and hot water tanks of six houses in Quebec (Canada), THMs in pipe plumbing and hot water tanks were observed to be 1.4–1.8 and 1.9–2.7 times that of the THMs concentration in the WDS. Three linear models and two nonlinear models were developed based on the data collected in this study to simulate DBPs concentrations in the consumer pipe plumbing and in the hot water tank. The developed models were capable of predicting DBPs in the pipe plumbing and water heating tanks.

2.3 Impact of bromide ion concentration on TTHM levels and speciation

It has been reported by many researchers that the THM concentration increases with increasing bromide ion concentration [48, 91, 92]. According to Hutton and Chung [93], the presence of bromide ion in THMs has two significant features. The first feature is that the atomic mass of the bromide ion is about twice that of the chloride ion. Because of this mass difference, brominated THMs increase the TTHMs concentration in chlorinated drinking water significantly and hence reduce the ability of water authorities to meet the standards. The second feature is that the health impacts of the individual THM species are specific to the different species. It was found by Hong et al. [94] that the cancer risk of TTHMs peaks at a bromide concentration ranging between 218 and 262 mg/L [with a bromide to DOC molar ratio (Br$^-$/DOC) ranging between 15 and 18 mM/mM]. Wang et al. [86] reported that brominated THMs are

Table 1. Summary of selected mathematical THM models

Predictor	Type of water	Location	Advantage	Limitation	Reference
TOC, UV absorbance, temperature	Water from thirteen treatment plants	North Carolina	Seasonal variations in THMs were taken into consideration. Geographic distribution of THMs formation was observed	Correlation coefficients of applied linear regression analyses were relatively poor; bromide concentrations and water residence time were not included as predictors in the developed models	Singer et al. [64]
UV_{254} nm absorbance, pH, chlorine consumption, and temperature	Raw water from Grasse River and Glenmore Reservoir	Massena, New York	UVA as a surrogate parameter for TOC and TTHM formation potential was used in the study	Reaction time was not considered as a predictor	Edzwald et al. [24]
TOC, UV absorbance, temperature, chlorine dosage, bromide concentration, reaction time and pH	Natural water	Different states in the US	The models were developed by linear and nonlinear regression to predict THMs formation. The models were based on robust database that took variable water quality characteristics into consideration. The R^2 was pretty good	Database for this study was obtained from laboratory chlorination experiments on raw water. Water characteristics of real water supply systems were different from raw water characteristics, so the models may not represent reality	Amy et al. [65]
TOC, pH, temperature, chlorine concentration, bromide ion concentration and contact time	Natural water	Denver, CO	Validation of the developed models was carried out using different databases	This study was carried out using laboratory scale databases which did not represent the water characteristics in real water distribution systems	Montgomery Watson [67]
TOC, pH, temperature and chlorine residual level	Different source water and water treatment plants	Fairfield, CA	The developed model is based on second-order kinetics and links the formation of TTHMs to chlorine consumption. In addition, it allows the characterization of TTHMs formation as a function of initial chlorine concentration and chlorine decay kinetics	Data used in developing this model were collected under laboratory conditions which may affect predictions in real water supply systems	Clark [70]
Chlorine concentration, temperature and bromide ion concentration	Desalinated drinking water	United Arab Emirates	The model used nonlinear optimization to characterize kinetics of TTHMs formation which allowed estimating differences in TTHMs at different nodes of water distribution systems	Important parameters such as TOC and pH were not among the predictors used in the developed model	Elshorbagy [63]
Chlorine dose, chlorophyll a, temperature, pH and bromide ion concentration	Finished water reservoirs for Menidi Treatment Plant	Athens, Greece	Multiple regression models that took the seasonal variations in THMs were developed based on data observed from actual water treatment plant	Chlorophyll a was considered as the only index of the organic matter of raw water. In addition, the performance of the developed models was relatively poor	Golfinopoulos and Arhonditsis [71]
DOC and UVA_{254} with THMFP	Korean drinking water	Korea	Variable water quality characteristics of different sources were taken into consideration in the study	A model developed by other authors for another water source was used in the study, so the predictions were very poor	Youn et al. [72]
Residual chlorine and temperature	Finished drinking water in the distribution system	Quebec, Canada	Multivariate regression models were developed in order to estimate seasonal and spatial variations in THMs for five water utilities which have different surface sources and undergo different treatments. Seasonal and spatial variations in THMs at the sampling points were predicted knowing the THMs concentration at the outlet of the treatment plant and chlorine consumption between the outlet of the treatment plant and the sampling points by the use of the developed models which is a practical procedure for water utility managers	Modeling results were relatively poor due to the limited information available about water residence times at the sampling points	Rodriguez et al. [79]

(Continued)

Table 1. (*Continued*)

Predictor	Type of water	Location	Advantage	Limitation	Reference
Initial chlorine concentration, bromide ion concentration, TOC, pH and Temperature	Raw surface water and finished drinking water	Amman, Jordan	A regression model to predict THMs formation was developed. Water age in the distribution system was also estimated using hydraulic modeling software. The model results showed good agreement between model predictions and observations of THMs	The model was developed for a constant temperature of 20°C	Al-Omari et al. [74]
TOC, temperature and chlorine dose	Finished drinking water in the distribution system	Istanbul, Turkey	A regression model that predicts THMs formation which took seasonal variability into consideration was developed. The model showed relatively good results	pH and reaction time were not considered as predictors in the model	
Low MW DOM	Guangzhou section of the Pearl River	New York	The impact of chlorine dioxide and chlorine gas on THM formation was examined. The study showed that MW of dissolved organic matter was the main THMs precursor	The dataset for this study was obtained from laboratory chlorination experiments on raw water. This data set might not have represented the real water supply systems	
Chloroform: Fulvic acid concentration, temperature and pH, BDCM: Fulvic acid concentration and chlorine dose DBCM: Fulvic acid concentration, chlorine does and to a lesser degree bromide ion concentration, pH and temperature Bromoform: Chlorine dose and bromide ion concentration and to a lesser degree fulvic acid concentration	Surface water, Caldeirão dam	Guarda, Portugal	THMs formation models were developed by the use of statistical techniques. These models assessed the interactions among the different THMs predictors	The model was not validated, nor did it represent the real situation	
Water temperature, TOC, chlorine dose, UV absorbance and turbidity	Barcelona's water works plant	Barcelona, Spain	Four different multivariate linear regression models were developed to predict THMs. Multi-linear regression and partial least square regression models showed good results	Residence time was not taken into consideration. The predictions of individual THMs were relatively poor	
Chlorine dose, SUVA absorbance, UVA_{254}, TOC, bromide ion concentration, contact time and temperature	Finished drinking water	Lebanon	The developed models which used a database obtained from laboratory and field-scale experiments provided flexibility for model selection. Seasonal variability of THMs formation was taken into consideration	The coefficient of determinations of the developed models was too poor	

proved to be more carcinogenic than their chlorinated analogues. Chowdhury et al. [48] mentioned that BDCM has stronger link to stillbirths and neural tube defects than other THMs species. Hutton and Chung [95] presented a mathematical model that evaluates alternative methods for reducing THMFP in Sacramento-San Joaquin delta which is an important drinking water source for California. Their model related THMFP to two parameters which are bromine incorporation factor (BIF) and bromine distribution factor. These factors describe the effect of the bromide ion on the distribution of compounds measured by California department of water resources.

Hypobromous acid (HOBr) is a strong oxidant compared to hydrochlorous acid (HOCl) [96]. HOBr role in the formation of DBPs is analogous to that of HOCl [97]. Symons et al. [98] indicated that HOBr reacts with NOM faster than HOCl. In addition, the ratio of HOBr/ HOCl plays an important role in the THMs speciation [97]. The presence of the bromide ion shifts the distribution of THMs towards brominated species [99–101]. In addition, the distribution of chlorinated and brominated DBPs is affected by $HOCl/Br^-$ ratio [102], Br^-/NOM ratio, and $Br^-/$free chlorine ratio [97, 103, 104].

The speciation of the different THM species in the presence of bromide ion was investigated by Chang et al. [104] as depicted in Fig. 1. As can be observed from this figure, TTHM concentration increases slowly with i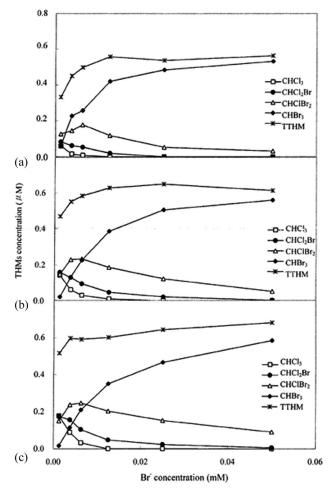ncreasing Br^- concentration. In addition, at low chlorine dosage a slight decrease in TTHM is observed with increasing Br^- concentration. Furthermore, Fig. 1 shows that the concentration of chloroform and BDCM decrease with increasing Br^- concentration. However, the concentration of DBCM increases initially with increasing Br^- concentration and then decreases. The peak concentration occurs at a bromide concentration between 0.0038–0.0063 mM which is equivalent to 0.3–0.5 mg/L, whereas the concentration of bromoform increases continuously as Br^- concentration increases [104]. The observed patterns of the different THM species were similar for different chlorine dosages in this particular study. In addition, THM speciation was observed to shift from chlorinated species to mixed bromochloro species to brominated species with increasing Br^- concentration. Mixed bromochloro and brominated THM species were produced even at the lowest Br^- concentration of 0.0013 mM [104].

Duong et al. [87] investigated the speciation of the different THMs in ground water of different bromide levels in Hanoi water supply. Water with high bromide ion concentration, water with low bromide ion concentration, and water with high bromide ion concentration along with high ammonia and high DOC concentrations were investigated. They found that the concentration of the brominated THMs was highest for the water with high bromide ion concentration and lowest for the water with high bromide ion concentration associated with high ammonia and high DOC concentrations. Sorlini and Collivignarelli [105] investigated the formation of the different THM species for natural water that contain NOM and bromide ion. They found that the TTHM concentration is proportional to the bromide ion concentration; in addition, chloroform is the main THM species for water without bromide ion which increases with increasing TOC. Furthermore, higher bromide ion concentrations resulted in higher concentrations of the brominated THMs. Mok et al. [106] modeled the impact of bromide ion on the speciation of the different THM species. The results indicated that shifting of the dominant THM species from chlorinated to brominated one occurs at a very low bromide ion concentration which reflects the significant impact of the bromide ion on the speciation of the different THM species. Farré and Knight [101] found out that the speciation of the different DBPs is impacted by the DOC/Br ratio. Hong et al. [94] made chlorination experiments on samples from Dongjiang River which is the major drinking water source for Hong Kong. They found that TTHM and chloroform are strongly correlated with Cl_2/DOC ratio, while total brominated THMs and BDCM has no correlation with the Cl_2/DOC ratio. It is rather strongly correlated with the bromide ion concentration. In addition, it was found that chloroform has negative correlation with the bromide ion concentration. BDCM reached its maximum molar percentage at $[Br^-]$ of 210 mg/L and $Br^-/$ DOC of 14.4 mM/mM, whereas maximum fraction of DBCM and bromoform occurred at $[Br^-]$ of 310 mg/L and Br^-/DOC of 21.3 mM/mM. Nokes et al. [107] showed that the percentage fractions of the four THM species are controlled by the relative rates of the competing halogenations reactions. Chang et al. [104] indicated that the peak concentration of DBCM occurred at bromide concentrations of 300–500 mg/L. Chellam and Krasner [108] showed that, the competing halogenation reactions may result in peak BDCM and DBCM at Br^-/DOC levels of 12 and 25 mM/mM, respectively. Wang et al. [86] investigated the factors that impact the formation of brominated THMs in chlorinated drinking water. High correlation between the BIF and Br^-/Cl_2 ratio was observed whereas no correlation between BIF and TTHM formation was observed at

Figure 1. The impact of bromide concentration on THM formation and speciation under various Cl_2 concentrations [80]. (a) $Cl_2 = 2.0$ mg/L (0.028 mM), (b) $Cl_2 = 4.0$ mg/L (0.056 mM), (c) $Cl_2 = 6.0$ mg/L (0.085 mM).

constant DOC, pH, Br⁻/DOC ratio, and bromide concentration. Furthermore, high Br⁻/DOC and Br⁻/Cl₂ favor the formation of brominated THMs over chlorinated THMs. In addition, ammonia reduces TTHM formation which is consistent with the findings of Doung et al. [87].

Huang et al. [109] investigated the impact of NOM characteristics on the formation of brominated THMs by ozonation. It was found that carboxylic/phenolic acidity, aromatic/aliphatic content, and UVA of the aquatic organic matter impact the formation of halogenated organics. Generally, hydrophobic organics characterized by high phenolic acidity, aromatic content, and UVA are higher ozone consumers and produce higher concentrations of brominated organics than hydrophilic organics. It was also found that humic acid showed the highest bromoform ($CHBr_3$), dibromoacetic acid, and 2,4-dibromophenol formation, whereas hydrophilic neutral produced less bromoform and 2,4-dibromophenol than the other organic fractions but produced the highest dibromoacetone and dibromoacetonitrile. Westerhoff et al. [110] ozonated well-characterized NOM fractions, they found that different NOM fractions are characterized by different rate constants. Furthermore, the reactions followed first-order kinetics. In addition, they showed that NOM of high aromaticity and high MW acted as an OH radical promoter and as an OH radical scavenger.

Zhao et al. [75] investigated the impact of DOM molecular size distribution on THMs formation when disinfecting the Pearl River water with chlorine and chlorine dioxide. The results showed that the reverse osmosis (RO) fraction was the main THM precursor which is consistent with the findings of Amy et al. [111] who showed that THMFP was highest for the fraction with molecular size of <500 Da for two raw water samples. Moreover, $SUVA_{254}$ and the THMs concentrations gradually decreased when the MW increased during the chlorine disinfection process which indicates that the small size DOM is more reactive to form THMs during the disinfection process. Gang et al. [112] reported that TTHM yield coefficients increased as the MW of the fractions decreased. Overall yields of TTHMs varied from 26.2 to 47.9 µg/L per mg/L TOC in the disinfection process. Furthermore, it was found that 65% of the THMs formed during disinfection by chlorine were converted from RO fraction of DOM, accumulation of THMs from fractions with MW <1000 Da was >77%. Similar trends were observed when using chlorine dioxide for disinfection, 64% of the THMs were from RO fraction of DOM, and accumulation of THMs from fractions with MW < 1000 Da were >72%. These results indicated that DOM with MW < 1000 Da was important in the formation of THMs during the disinfection process by both chlorine and chlorine dioxide.

2.4 Fate and transport of THMs in water distribution systems

Despite the fact that drinking water meets the biological quality standards as it leaves the water treatment plant, it must be disinfected before it is pumped to the consumers to guard against biological re-growth as the water travels in the WDS. However, there is a clear conflict between maintaining the biological drinking water quality up to the standards as the water travels in the WDS and the formation of disinfection byproducts, i.e., THMs. High chlorine dose reduces the risk of the deterioration of the biological quality of drinking water, however, it increases the risk of THMs concentration exceeding the permissible limits at the consumers' tap, especially at the WDS extremities. Poleneni [113] and Poleneni and Innis [114]

investigated chlorine residual and THM formation in small WDSs under different operational conditions of normal chlorine dosing, booster dosing, and high chlorine dosing. It was found out that the high chlorine dosing maintained chlorine residual concentration in the WDS, however, it elevated TTHM concentration significantly. It was also found out that booster chlorination before the storage tank elevated the TTHM concentration in the WDS due to the increased contact time, which means that booster chlorine dosing should be practiced after the storage tank. For these reasons, researchers all around the world studied the spatial and the temporal variations in TTHM concentrations for specific WDSs where different disinfectants were used to maintain the biological quality of the drinking water up to the standards. Significant temporal and spatial variations in TTHM concentrations in WDSs were observed [115–117]. Rodriguez et al. [79] studied the occurrence of the different THM species in five drinking WDSs in greater Quebec in Canada. They found that the TTHM concentrations in the systems' extremities were 1.3- to 2.5-fold of those at the outlet of the water treatment plant. In addition, the average TTHM concentrations during summer at the systems' extremities were 2.5- to 5-fold of those observed during winter. The high seasonal variations in the observed TTHM concentrations were attributed firstly to the high variation of the raw water quality between summer and winter, and secondly to the higher temperature during summer. The higher TTHMs concentration at the systems' extremities is mainly attributed to the longer contact time between the chlorine and the different THM precursors. Toroz and Uyak [80] investigated TTHM concentrations in Istanbul WDS. It was found out that TTHM levels in the distribution system were 1.2- to 1.8-fold of those in the finished water at the outlet of the water treatment plant in summer when the temperature exceeded 24°C. However, TTHM levels in the distribution system extremities rarely exceeded 100 µg/L when water temperature was below 15°C during fall and spring. The spatial and the temporal variations in the different TTHM species' levels, indoor and outdoor, were investigated by Al-Mudhaf and Abu-Shady [118] in the finished drinking water from a thermal desalination plant in Kuwait. Significant spatial variations were observed between the indoor and the outdoor samples. It was found that TTHM levels were higher in the outdoor samples. In addition, brominated THMs were the dominant species with the bromoform having the highest concentration among the other THM species. Thacker et al. [119] found high THM levels in Mombai, India, WDS and service reservoirs during post monsoon, winter and summer seasons. The correlation between the different THM species' levels in three UK WDSs were investigated by Whitaker et al. [120]. They found out that chloroform levels declined in 1995 in three water supplies of UK during drought. Furthermore they also found out that there was a moderate positive correlation between the THMs of similar structure (chloroform and BDCM, BDCM and DBCM, and DBCM and bromoform) and a slight negative correlation between chloroform and bromoform levels. Jodeh et al. [121] investigated TTHM in Nablus water supply in Palestine where sodium hypochlorite is used for disinfection. The water source for Nablus water supply is groundwater. In addition, due to water shortage, the pumping in Nablus WDS is intermittent. It was found that TTHM concentration through Nablus WDS is less than the maximum contaminant level set by the United States Environmental Protection Agency (US EPA) of 80 µg/L except for one sample where the concentration was 153 µg/L. Shabani [122] investigated the effect of polymeric pipes and desalinated water on the formation of

disinfection byproducts in three laboratory scale WDSs of different polymeric pipe materials namely: polyvinyl chloride, polyethylene, and polypropylene. Different combinations of TOC and initial calcium hypochlorite concentrations were used. The results showed that polyvinyl chloride pipes have the highest potential for THMs formation followed by polyethylene and polypropylene pipes, respectively. Basiouny et al. [123] modeled the formation of the different THM species for Benha water supply in Egypt. Mathematical models that express the different THM species in terms of their predictors were developed by performing regression analysis on monitoring data. The mathematical models were used along with EPANET to predict the concentration of the different THM species in Benha water supply in Egypt. Good agreement was found between modeled and measured THM concentrations.

The use of alternative disinfectants and/or pre-oxidants such as chlorine dioxide, chloramines, and ozone has proven to reduce TTHM concentration in finished drinking water. Guay et al. [124] assessed the use of ozone as a pre-oxidant and chloramines as secondary disinfectant in a small Quebec water utility for DBP reduction. The results showed that THMs concentration was significantly reduced when ozone was used as pre-oxidant as compared to chlorine. However, the reduction in THMs concentration was higher when chloramines were used as a secondary disinfectant as compared to chlorine. The reduction in THMs concentration as a result of using ozone as a pre-oxidant is attributed to the oxidation of organic matter which is a THM precursor as evidenced by the reduction in TOC. However, the disadvantage of ozone is that brominated THMs can form which is another DBP if the ozonated water contains bromide ion [15]. The use of chloramines as a secondary disinfectant reduces the THM levels significantly; however, the disinfection power of chloramines is much less than that of free chlorine. Furthermore, it was found that the use of ozone as a pre-oxidant followed by slow sand filtration in addition to chloramines as secondary disinfectant resulted in high microbial inactivation efficiency. Furthermore, chloroform and BDCM were detected in this case. However, no information was given regarding the impact of the alternative disinfectants on the speciation of the different THM species, nor about the bromide ion concentration.

Sorlini and Collivignarelli [105] showed that alternative disinfectants, i.e., chlorine dioxide and ozone, reduced the formation of THMs by 97% as compared to chlorine applications. These experiments were based on different oxidation batch tests that employed chlorine or chlorine dioxide or ozone on natural surface water from ten different drinking water sources (seven artificial lakes and three rivers). However, bromate is produced as a by-product of ozonation of bromide containing water. Adams et al. [125] showed that the use of chloramines significantly reduced both THM and HAA levels for the systems that treated their own water. However, they did not have significant impact on systems which purchased their water from primary systems. Zhao et al. [75] found out that chlorine dioxide produced less THMs than chlorine when disinfecting river water samples from Guangzhou section of the Pearl River. Jo et al. [126] showed that chloroform concentrations during winter were significantly lower in the ozone–chlorine-treated water than in the chlorine-treated water. However, the summer water chloroform concentrations and summer and winter concentrations of the other two THMs (BDCM and DBCM) exhibited no significant difference between chlorine and ozone–chlorine-treated water. Thapsingkaew et al. [127] investigated the efficiency of ozonation as compared to

chlorination for the removal of microcystins and the production of THMs in Thailand tap water. The results showed that THM level is significantly lower in ozonated water than in chlorinated water which is consistent with the finding of Guay et al. [124]. In addition, the results showed that chloroform is the dominant species. Among the brominated THMs, BDCM was detected. However, the bromide ion concentration was not mentioned. It was found that the TOC level in the ozonated water is much less than that in the chlorinated water. In addition, the microcystin level in all water samples was below the World Health Organization guideline of (1 mg/L) for drinking water.

2.5 THMs in groundwater

As an important and a primary drinking water resource, the fate and transport of THMs in groundwater was studied by many researchers. Stuart et al. [128] investigated the THMFP in ground water as affected by the infiltration of wastewater and landfill leachate. They proposed that the THMFP provides a sensitive measure of low levels of organic contamination and can be used as a surrogate for DOC as certain difficulties are encountered in measuring this parameter in groundwater. Pavelic et al. [129] investigated the behavior of DBPs during aquifer storage and recovery in an anoxic aquifer in South Australia. They found that the half life of the different THM species varied from less than 1 day to 65 days, with the persistence of chloroform being the highest and the persistence of bromoform being the lowest. Further, the rates of THM attenuation were shown to be highly dependent on the geochemical environment.

Groundwater samples from drinking water wells across the United States were analyzed for THMs by Moran et al. [130] in order to understand THM occurrence in drinking water supplies at a national scale. Chloroform was the most frequently detected THM species. In addition, the sources of THMs in groundwater are believed to be primarily anthropogenic whereas the most likely source of THMs in groundwater from urban public wells is the recycling of chlorinated drinking water, which may contain THMs from the treatment process. It is also believed that biodegradation is the primary process that contributes to the occurrence of THMs in ground water where dissolved oxygen strongly influences the microbiological activity responsible for the transformation of THMs which explains the strong correlation between THMs and dissolved oxygen levels in groundwater. The fate of THMs in leaked water from WDSs in Amman Jordan was investigated by Salameh et al. [131]. The results showed that the predominant THM species in the investigated groundwater is chloroform among the other measured species. In addition, it was found that the average THM concentration is higher during winter than during summer. Furthermore, the high THM levels in groundwater are associated with high TOC which was attributed to leakages from sewer lines and chlorinated drinking water from the WDS which makes a suitable environment for the formation of THMs.

2.6 Management of THM levels in chlorinated drinking water

In their efforts to provide effective management options to keep THM levels in chlorinated drinking water within the permissible limits, researchers and scientists investigated different approaches. These approaches include the removal of THM precursors from the raw water; the removal of THMs from the finished drinking water;

the use of alternative disinfectants such as ozone, chloramines and chlorine dioxide, and supplying low chlorine concentration at the source while providing booster stations for chlorine dosing within the WDS. Chlorine simulation models are used to optimize the last approach. However, this approach is beyond the scope of this article. The use of alternative disinfectants and/or pre-oxidants was discussed in Section 2.4. This section focuses on the removal of THMs precursors from the raw water by different technologies and talks briefly about the removal of THMs from finished drinking water.

Removal of THMs precursors which depends on the nature of NOM and characteristics of raw water, such as turbidity and hardness, is very important to minimize the formation of THMs [132, 133]. Recommended methods for the removal of THMs precursors from raw water are enhanced coagulation (EC), granular activated carbon (GAC) adsorption, and membrane filtration [134–136]. US EPA has specified the best available technology to be effective in controlling maximum contaminant level and maximum disinfectant residual level in drinking water while remaining economically feasible for drinking water systems [137]. EC and media filtration which uses the conventional treatment processes of chemical addition, coagulation, and dual media filtration is referred to as the best method to reduce DBP precursors by the US EPA. Studies showed that it is cost effective and reliable, while its limitations are reported as extensive operator care and sludge disposal [117, 137–139]. Less [140] studied the efficiency of EC and three anion exchange resins (AERs) in removing NOM and consequently reduce THMs in finished drinking water. The results showed that all tested AERs were efficient in removing NOM, especially the moieties that absorb UV light at 254 and 272 nm over 75 min of contact time. However, differences in the removal rate were observed among the three AERs tested. Alum coagulation was also found to be effective in removing NOM and consequently reduce THMs concentration in the finished drinking water. However, Farre and Knight [101] showed that EC and EC with powdered activated carbon (PAC), in bromide rich water, led to increases in brominated THM species, which was attributed to the increase in Br/DOC ratio for the treated water relative to the raw water. Dunn [141] and Dunn and Kanappe [142] studied the impact of PAC base material, i.e., bituminous coal, lignite, coconut shell, wood, and PAC particle size on the performance of PAC in the removal of NOM. It was found that the removal of THMs precursor from North Carolina water was highest with a chemically activated wood-based PAC. In addition, it was found that the super fine PAC for all base material type increases the removal efficiency of NOM significantly which was attributed to faster adsorption kinetics and higher adsorption capacity.

Enhanced coagulation and microfiltration or ultrafiltration for the removal of NOM which uses membrane filtration of coagulated NOM is other method with high operation and maintenance cost and relatively low capital costs. Nanofiltration, which is a physical process, can be used for NOM removal from water. Nanofiltration requires less operator care and chemical usage than microfiltration. In addition, it is a reliable process in producing water with respect to NOM levels; however, membrane fouling, high operation, and maintenance costs along with concentrate disposal problems are the limitations of this technique. RO which produces high quality water uses semi permeable membrane. High cost, membrane fouling, pretreatment and feed pump requirements, and concentrate disposal are the main limitations of RO process [137]. Decreasing membrane pore size and increasing charge density on the

membrane surface and in the pores improved the efficiency of NOM removal. Hybrid processes, i.e., coupling membrane processes with other unit processes enhance NOM removal [143]. Another alternative method for NOM removal is lime softening which uses $Ca(OH)_2$ to raise pH to >10 to help precipitate NOM and carbonate hardness. It is a reliable method that has low capital cost while the limitations are pH readjustment, sludge disposal, chemical usage, and extensive operator care [137].

GAC which uses extremely porous carbon media in a process known as adsorption is another best available technology to remove NOM in water. GAC is effective in the removal of NOM and other chemicals through adsorption and catalytic degradation [144]. Application of the well-established GAC method increases the operational and maintenance costs by 30–50% [145]. Farre and Knight [101] found that MIEX® resin and GAC were able to adsorb bromide and DOC which resulted in lower DBP formation as compared to EC and combined EC and PAC. They also found that EC combined with silver impregnated activated carbon resulted in improved DOC and halides removal and consequently lowered DBPs.

Mosteo et al. [146] investigated the effectiveness of alternative pretreatments for the degradation of THM precursors in raw water. The pretreatments consisted of different pre-oxidation processes (chlorination and advanced oxidation processes: O_3, O_3/H_2O_2, O_3/TiO_2, and $O_3/H_2O_2/TiO_2$), adsorption with PAC, and coagulation–flocculation. The results showed that the coagulation–flocculation process can be mentioned as the major process responsible for the THMs reduction. Recommended pretreatments were pre-oxidation by ozonation, adsorption by PAC, coagulation–flocculation using aluminum sulfate followed by decantation and final post chlorination. Musikavong et al. [147] found that TOC, DOC, and SUVA were significantly reduced by alum and ferric chloride. In addition, maximum THMFP percentage reduction of 25 and 28 were achieved by alum and ferric chloride dosages of about 80 mg/L at pH 5.5 and 5.0, respectively. Page et al. [148] found that conventional alum treatment was unsuccessful in removing DOM from water at five reservoirs and "synthetic water" prepared using terrestrially derived DOM extracted from vegetation and reservoir catchment soils. Wong et al. [149] investigated the removal efficiency of NOM by ultra filtration. The results showed low DOC removal, whereas 50% removal efficiency was achieved for humic substances and THM precursors which were quantified by measurements of UV_{254} and THMFP, respectively. Tian et al. [150] tested the performance of membrane bioreactor and membrane coagulation bioreactor (MCBR) for the removal of organic matter from raw water. They found that the MCBR achieved much higher removal efficiencies of organic matter as quantified by TOC, permanganate index (CODMn), DOC and UVA_{254}. Further the removal efficiencies for corresponding THMFP and HAAs formation potential were better for MCBR due to polyaluminum chloride coagulation in the bioreactor. Reckhow and Singer [66] found that alum coagulation of a moderately colored surface water resulted in the removal of 50–90% of several chlorination by-product precursors tested which were THMs, total organic halide, trichloroacetic acid, dichloroacetic acid, trichloroacetone, and dichloroacetonitrile.

Removal of NOM from raw water by isolation and fractionation which is a method that separates NOM into different fractions based on hydrophilicity and hydrophobicity of these fractions was investigated by many researchers among whom are Leenheer [151] and Leenheer and Croué [152]. Studies based on this method showed that the hydrophilic fractions of NOM are composed mostly of

aliphatic carbon and nitrogenous compounds while hydrophobic NOM primarily consists of humic and fulvic acids and is rich in aromatic carbon, phenolic structures and conjugated double bonds [22, 136, 153–157].

Lu et al. [158] investigated the removal of THM from finished chlorinated drinking water by commercial carbon nanotubes and PAC. They found that commercial carbon nanotubes have high potential for the removal of THMs from finished drinking water. Uyak et al. [159] found that nanofiltration membranes are effective in removing THMs from the finished chlorinated drinking water.

3 Discussion

Due to their projected health impacts, THMs in chlorinated drinking water have been a source of serious concern for water authorities and an area of extensive and interesting research for scientists and researchers all over the world since THMs were first identified in chlorinated drinking water. Extensive research to estimate health risks associated with THMs through routes of exposure other than direct ingestion by drinking is ongoing. Exposure to THMs through inhalation and dermal contact in swimming pools was investigated by several independent researchers [10, 42, 51, 56–62]. It was found that THMs in municipal water poses cancer risks to humans through inhalation and dermal contact during showering and swimming as well as through direct ingestion. Many mathematical models were developed worldwide to predict the concentrations of the different THM species in chlorinated drinking water. A close investigation of these models reveals that there is agreement among researchers on the THM predictors; however, the large number of models suggests that no mathematical model seems to be universally accepted. In addition, despite the fact that most of the models use the same predictors, some researchers have identified strong correlation between THMs and other quality parameters such as chlorophyll, Secchi disk depth, zooplankton, dissolved oxygen, and total phosphorus [81–85]. However, these parameters are dependent and may be represented by a single variable or are probably directly related to an already included variable such as the organic content of the raw water.

The THM predictors can be divided into two groups: the precursor's group and the environmental conditions group. The precursor's group, which includes organic content and bromide ion, refers to the substances that react with chlorine to form the different THM species. The environmental conditions group refers to temperature, pH, and contact time which characterize the environment within which the reaction takes place. The impact of the environmental conditions group on the formation of the different THM species is better understood than the impact of the precursors group as the environmental conditions impacts all reactions in almost a similar way. However, the impact of the organic content is not well understood as different quality parameters were selected by different researchers to express and quantify the organic content of raw water without enough explanation or justification. This brings up the need for further in depth research to establish sound and scientific bases for the selection. Regarding the impact of bromide ion, there seems to be an agreement among researchers that the bromide ion concentration increases THM levels significantly and strongly affects the speciation of the different THM species [86, 87, 91, 92]. Wang et al. [86] and Duong et al. [87] found out that the presence of ammonia in raw water reduces the THMs concentration which was attributed to the

formation of chloramines that do not cause the formation of the different THM species. However, when ammonia is present in the raw water, great care should be taken not to create conditions that promote the formation of dichloramines as they cause taste and odor problems in chlorinated drinking water.

WDSs pose suitable environments that further enhance THMs formation due to the prolonged contact time between the different THM precursors in these distribution systems. The fate and transport of THMs in WDSs received due attention by researchers worldwide. It was found that the concentration of the TTHM is higher in the WDS extremities due to the longer contact time between the chlorine and the THM precursors. In addition, it was also found that the THM concentration is usually higher in summer than in winter due to the higher temperature during summer and due to the seasonal raw water quality changes. Furthermore, it was found by Several researchers, as, e.g., Li et al. [89] and Shabaneh [122] that the pipe material impacts chlorine decay and consequently THM concentration in WDSs. Moreover, it was found by Chowdhury et al. [90] that THMs concentrations can increase significantly within the consumer pipe plumbing system and hot water tanks beyond the WDS. Poleneni [113] and Poleneni and Innis [114] found that booster chlorination should be practiced after utility storage tanks as practicing booster chlorination at the utility storage tanks increases TTHM significantly. Management of THM levels in drinking WDSs has not been easy due to the reasons mentioned earlier in this article.

Several researchers recommended different pretreatments to reduce THM levels in chlorinated drinking water. More specifically, coagulation–flocculation was found effective in removing the precursors from raw water which resulted in reducing the TTHM concentrations. However, the added chemicals for the removal of the THMs precursors create problems themselves as they need to be removed at a certain stage from the sludge which brings the need for more research on using physical processes for this purpose, i.e., membrane filtration. Furthermore, it was found that the use of disinfectants, other than chlorine gas, resulted in lower THM levels in the finished drinking water; however, other DBPs were produced. Sorlini and Collivignarelli [105] showed that the use of ozone resulted in lower THM levels; however, bromate was produced as a by-product when the raw water contains bromide ion [38]. Zhao et al. [75] showed that the use of chlorine dioxide also resulted in lower THM levels in the finished drinking water; however, other DBPs were produced such as chlorate and chlorite [15]. Furthermore, the removal of THMs from finished drinking water was investigated by Uyak et al. [159] and Lu et al. [158]. This option should be investigated more thoroughly especially when physical processes such as membrane filtration are used. The feasibility of this option, both technical and economical, should be investigated especially at the household level to remove THMs that have been formed in the WDS. Finally, many researchers related the THMFP in ground water to leaks from sewer lines and chlorinated drinking water leakage from WDS in addition to landfill leachate.

4 Concluding remarks

Despite the extensive research that took place in the past four decades to understand and control the formation of the different THM species in chlorinated drinking water, many aspects of THM formation need further investigation to better understand them. The way NOM of the raw water impacts the formation of the

different THM species is not fully understood and needs further research to determine more specifically which fraction of the organic content impacts the formation and speciation of the different THM species. The use of alternative disinfectants and or pre-oxidants, i.e., ozone, chlorine dioxide, and chloramines resulted in lower THMs in the finished drinking water; however, other by-products are produced. Bromate is produced as a result of using ozone for disinfecting bromide containing water, the health impacts of which are not well understood. The use of chlorine dioxide does not cause the formation of THMs. However, many other DBPs are produced such as chlorate and chlorite, the health impacts of which need to be investigated thoroughly. The use of chloramines for disinfection proved to reduce disinfection byproducts significantly, however, the disinfection efficiency of chloramines is much less than that of free chlorine which increases the risk of re-growth of pathogens in the distribution system. In addition, the risk of taste and odor generation is a serious concern in WDSs if dichloramine is formed as a result of chlorinating ammonia containing water. This is mainly due to the difficulty in controlling the chlorine to ammonia ratio within the WDS as it is dependent on the hydraulics of the WDS which can't be controlled as it is demand dependent.

Pretreatment of the raw water for the removal of THMs' precursors has proved to be effective in reducing the level of the different THM species. However, the use of chemical processes for this purpose such as coagulation and flocculation brings the need for removing the chemicals used at a later stage. The use of physical processes such as nanofiltration and microfiltration for this purpose deserve further investigation. Furthermore, little research on the removal of THMs from finished drinking water was carried out; this area deserves more investigation especially at the household level.

Acknowledgments

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