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Total organic halogen (TOX) species formation at different locations in drinking water distribution systems†

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Total organic chlorine (TOCl), bromine (TOBr) and iodine (TOI) species and collectively total organic halide (TOX) concentrations were quantified quarterly at 11 US drinking water treatment plants (WTPs) and distribution systems. TOCl was the dominant halogen-specific TOX species in most plants. TOBr concentrations varied with source water bromide (Br^-) concentrations at WTPs. TOI was always below the minimum reporting level even though iodine species were present at $>1 \mu\text{g L}^{-1}$ in some source waters. Ratios of TOCl to TOBr varied seasonally. TOCl increased as intake DOC increased in some plants. Seasonal changes in raw water Br^- concentration did not lead to the corresponding variations in TOBr concentrations for most WTPs. For WTPs practicing chloramination, TOCl and TOBr concentrations did not increase significantly from the effluent into their distribution systems. Chlorine contact time for both pre-oxidation and post-chlorination prior to ammonia addition was the most important factor affecting the TOX formation in WTPs. On the other hand in distribution systems with free chlorine residuals, TOCl and TOBr concentrations increased as long as residual chlorine was available. Despite seasonal variations, the ratios of regulated brominated disinfection by-products to TOBr (*i.e.*, Br-DBP/TOBr) were lowest for chloraminated plants treating groundwater and generally higher for WTPs utilizing free chlorine. We observed TOBr levels as high as $116 \mu\text{g L}^{-1}$ in one distribution system, while the ratio of regulated brominated DBPs to TOBr was as low as 15% in some systems indicating that the major portion of TOBr in the finished water is unidentified and unmeasured. Given the higher toxicity of brominated DBPs than their chlorinated analogs, it is important to develop treatment and/or operational strategies to reduce the formation of TOBr in distribution systems in order to minimize exposure of the public to such DBPs.

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Water impact

While extensive data exists on specific DBPs after different retention times in distribution systems, there is paucity of information about the total organic halide (TOX) speciation. This work highlights that elevated bromide concentrations and long chlorine contact times promote formation of different TOX species in distribution systems, which vary seasonally and geographically.

1. Introduction

Microbial disinfection is an essential process in drinking water to protect public health against acute health risks. However, reactions between chlorine-based disinfectant

residuals with natural organic matter (NOM) plus inorganic halides unintentionally produce disinfection by-products (DBPs) that pose chronic carcinogenic, and potentially acute, human health risks.^{1,2} Trihalomethanes (THMs) and haloacetic acids (HAAs) are the major classes of regulated DBPs, but it is known that a large number of unregulated DBPs including haloacetaldehydes, haloacetonitriles, halo ketones, and halonitromethanes also occur at part per billion ($\mu\text{g L}^{-1}$) concentrations in United States (US) drinking water systems.^{1,3} To quantify the total halogenated DBPs (*i.e.*, regulated plus other known and unidentified halogenated DBPs), total organic halogen (TOX) can be used as a surrogate measure. Hundreds of other identified DBPs have been reported,⁴ but these identified and quantified DBPs in

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chlorinated waters account for only 16–70% of TOX,^{5–7} whereas identified DBPs account for less than 20% of TOX in chloraminated waters.^{8,9} As the identified DBPs do not fully account for the toxicity of chlorinated waters, unidentified fractions of TOX may contain a number of toxicologically significant compounds that contribute to the observed adverse health effects associated with drinking water DBPs.

Conventional TOX analysis can be modified to quantify pools of individual organo-halide species. A conventional TOX analysis consists of three steps; i) adsorption of organic compounds onto activated carbon (AC) cartridges, ii) pyrolysis of the AC cartridges in a furnace, and iii) absorption of produced gases (HX) into an aqueous solution that is titrated for halides. A chlorinated phenol is often used as a standard and TOX is reported as an equivalent concentration of organically-bound chloride ($\mu\text{g L}^{-1}$ as Cl) without differentiating chloride, bromide, and iodide. Thus the halogen-specific analysis has been further developed to distinguish different halogenated species; total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI). Halogen-specific TOX can be determined by adsorption of the effluent gas onto an on-line ion chromatography (IC) column¹⁰ or absorption in an aqueous solution that can be analyzed with off-line IC,^{11–15} ultra-performance liquid chromatography-electrospray ionization-mass spectrometry (UPLC-ESI-MS),^{16,17} or inductively coupled plasma-mass spectrometry (ICP-MS).¹⁸

Most studies report only TOX, not the halogen-specific TOX fractions, which provides limited ability to manage DBP exposure risks wherein brominated and iodinated DBPs are often reported to be more cyto- or geno-toxic than chlorinated analogs.¹ TOX data is often reported within water treatment plants (WTPs), but measuring TOCl, TOBr, and TOI has only been done in limited studies. Three decades ago, a wide range of TOX concentrations (*i.e.*, 152–1234 $\mu\text{g L}^{-1}$ as Cl) has been observed in finished waters of 6 drinking water utilities.¹⁹ Krasner *et al.* monitored the occurrence of DBPs in 35 US water utilities and found that TOX concentrations (up to $\sim 700 \mu\text{g L}^{-1}$) in the utilities using chlorine as a final disinfectant were higher than those (up to $\sim 400 \mu\text{g L}^{-1}$) in the utilities applying chloramines.²⁰ Singer *et al.* reported 171–289 $\mu\text{g L}^{-1}$ (median values) and 215–365 $\mu\text{g L}^{-1}$ (median values) of TOX in effluents and distribution systems, respectively, of 6 chlorinated utilities in North Carolina.²¹ According to the information collection rule (ICR) data analysis report providing a comprehensive survey of treatment and occurrence data related to DBPs at all large water utilities in US, <50 –1010 $\mu\text{g L}^{-1}$ of TOX with <50 , 102, and 242 $\mu\text{g L}^{-1}$ of 25th, 50th, and 90th percentiles, respectively, was observed in finished water samples collected from 496 plants.²² TOX concentrations in distribution systems having surface water supplies were <50 –935 $\mu\text{g L}^{-1}$ and <50 –811 $\mu\text{g L}^{-1}$ for the plants using chlorine and chloramine as secondary disinfectants, respectively, while TOX of ground water distribution systems ranged <50 –788 $\mu\text{g L}^{-1}$. An occurrence study conducted with chloraminated

and chlorinated drinking waters collected from 23 cities in US and Canada reported that TOX levels in finished waters ranged 19–683 $\mu\text{g L}^{-1}$ with great seasonal variations.²³

More recent research studies have found value in differentiating TOCl, TOBr and even TOI pools within TOX by relating them to known, unregulated DBPs. Echigo *et al.* compared the formation of TOCl and TOBr in simulated water samples treated with chlorine (4.5 mg L^{-1}), chloramine (5.0 mg L^{-1}), and chlorine dioxide (6.0 mg L^{-1}) for 5 days in the presence of Br^- (100 mg L^{-1}) and NOM (Suwanee river fulvic acid, 3 mg L^{-1} dissolved organic carbon).¹¹ TOCl concentrations after chlorination, chloramination, and chlorine dioxide treatment were 511, 131, and 23 $\mu\text{g L}^{-1}$, respectively, while TOBr levels were 36, 11, and 33 $\mu\text{g L}^{-1}$ as Cl. Hua measured TOCl and TOBr in finished waters collected from 6 different geographic locations applying various disinfection practices.²⁴ Relatively low TOX (*i.e.*, the sum of TOCl and TOBr) levels (38–70 $\mu\text{g L}^{-1}$ as Cl) were observed in chloraminated finished waters treated with pre-ozonation, while chloraminated or chlorinated finished waters without pre-oxidation showed 160–443 $\mu\text{g L}^{-1}$ of TOX. The chlorinated finished water with higher DOC (7.6 mg L^{-1}) showed the highest TOX concentration. The percentages of unknown TOX (UTOX) in 6 finished waters were 48–67%. In another study using two chlorinated natural waters fortified with various levels of Br^- and iodide (I^-), Hua *et al.* found that at higher Br^- the formation of unknown TOX and unknown TOCl decreased while unknown TOBr increased.²⁵ The extent of iodine substitution was much lower than that of bromine substitution when comparing identical initial concentrations because a substantial amount of I^- was oxidized to iodate (IO_3^-) by chlorine. In another DBP occurrence survey at 12 drinking water treatment plants, 21–284 $\mu\text{g L}^{-1}$ of TOX was observed with a median 178 $\mu\text{g L}^{-1}$.³ Known TOX determined by the sum of the halogenated DBPs accounted for $\sim 30\%$ (*i.e.*, $\sim 70\%$ remained unknown). The effluent TOCl and TOBr ranged 87–206 $\mu\text{g L}^{-1}$ (a median of 161 $\mu\text{g Cl L}^{-1}$) and 16–102 $\mu\text{g L}^{-1}$ as Cl (a median of 35 $\mu\text{g L}^{-1}$), respectively.

TOX has been monitored as an indicative parameter in previous DBP occurrence studies. In addition, substantial DBP studies have shown that TOX is positively correlated with the overall toxicity of chlorinated and chloraminated waters.^{1,15,18,26–28} Nevertheless, the formation of TOX is not fully understood related to source water characteristics or types of disinfection, and limited datasets on the occurrence and seasonal variations of halogen-specific TOX species exist in the literature for drinking water distribution systems. This study monitored the occurrence of TOCl, TOBr, and TOI in effluents and distribution systems of selected drinking water plants using different oxidants and showing low to elevated Br^- concentrations in their influents. In order to gain additional insights on the formation of halogen-specific TOX in distributions systems, holding experiments which simulate typical and extended distribution retention times were also conducted to examine the formation of TOCl, TOBr, and TOI

and to compare their formation patterns in different distributions systems.

2. Materials and methods

2.1. Collection of water samples and *in situ* halogen-specific TOX occurrence

To monitor the occurrence of TOCl, TOBr, and TOI, finished water samples were collected at the plant effluent and the locations with average and maximum residence time in the distribution system of the selected 11 drinking water plants in US according to their historical intake Br[−] concentrations and disinfection methods. Plants 1–3 which treated surface water with moderate Br[−] levels (*ca.* 120 µg L^{−1}) applied chloramines (*i.e.*, chlorine followed by ammonia hereafter) at the beginning of the treatment without pre-oxidation. Plants 4–9 are also chloraminated plants with pre-chlorination (except for plant 6 with chlorine dioxide (ClO₂)), while plants 10 and 11 applied chlorine after pre-ozonation. The highest Br[−] level (*ca.* 480 µg L^{−1}) was observed in the intake water of plant 6, while low levels (21–65 µg L^{−1}) of Br[−] were observed in plants 7–11. Only plants 4 and 5 treated 100% or partial groundwater. During the collection of finished waters, intake water samples were concurrently collected and water quality parameters such DOC, specific UV absorbance at 254 nm (SUVA₂₅₄), Br[−], I[−], and IO₃[−] were measured. Especially, the determination of total iodine, I[−] and IO₃[−] in intake and effluent samples during one or two sampling campaigns was conducted in a commercial laboratory (Eurofins Eaton Analytical, LLC., Monrovia, CA) using a LC/MS/MS. Samples for halogen-specific TOX analysis were collected in amber glass bottles quarterly from October 2018 to capture a possible seasonal trend and the residual chlorine was quenched immediately by adding ascorbic acid at the time of sampling. Occurrence samples were shipped in coolers with blue ice packs to the laboratory overnight and analyzed within 24 hours of arrival. Table 1 summarizes selected intake water quality parameters along with water treatment information (type of source water, pre-oxidation, and final disinfectant) and average and maximum residence time in

the distribution system of each plant. An overview of 11 plants' operational configurations is presented in Fig. 1.

2.2. Halogen-specific TOX formation experiments

To investigate the formation of halogen-specific TOX species in the distribution system as a function of residence time, a holding experiment was conducted with the selective effluent water samples. The collected samples without adding quenching reagent were shipped to the laboratory and stored at room temperature. Then the bottles were opened after average and maximum residence time of each plant (Table 1) and then quenched with ascorbic acid for further DBP and TOX analysis. For selected samples, additional effluent waters which were spiked with Br[−] (600 µg L^{−1}) were also collected and opened after the extended residence time (504 h) to examine TOX formation/speciation under an extreme condition. At plant 10 and 11, conventionally treated water samples which were pre-ozonated were collected before chlorination and dosed with either chlorine (3.2 mg L^{−1} as Cl₂) or preformed monochloramine (3.2 mg L^{−1} as Cl₂) in the laboratory to further examine the formation of TOX species in the same type of water under two different disinfection conditions. Once transferred to eight 250 mL amber glass bottles, four bottles were chlorinated and the other four bottles were chloraminated. One bottle (*t* = 0 h) was opened within 5 minutes after either chlorination or chloramination and then quenched with ascorbic acid. The other bottles were opened and quenched after designated reaction times (*i.e.*, 150, 300, and 504 h for average, maximum, and extended residence time, respectively).

2.3. Analysis of water samples

2.3.1. UV absorbance, DOC, and bromide. Before determination of water quality parameters, collected water samples were filtered through 0.45 µm glass fiber membranes (Whatman, Clifton, NJ). UV absorbance was measured using a Cary 50 UV-vis spectrophotometer (Varian) based on Standard Method 5910B.²⁹ Samples were placed in a 1 cm quartz cuvette and measured at a wavelength of 254 nm. DOC was determined using a Shimadzu TOC-VCHS or

Table 1 Selected water quality parameters along with the treatment information and average and maximum residence time in the distribution system of each plant. ND: not detected

	Source water	DOC (mg L ^{−1})	SUVA ₂₅₄ (L mg ^{−1} m ^{−1})	Br [−] (µg L ^{−1})	I [−] (µg L ^{−1})	IO ₃ [−] (µg L ^{−1})	Pre-oxidation	Final disinfection	Ave. RT (hour)	Max. RT (hour)
Plant1	Lake A	3.3–4.4	1.9–2.6	97–140	1.2	1.0	None	Chloramines	120	336
Plant2		3.4–4.7	1.8–2.6	92–140	1.5	ND	None	Chloramines	144	384
Plant3	Lake B	3.3–4.8	1.7–2.6	90–153	2.6	ND	None	Chloramines	96	264
Plant4	Groundwater (GW)	0.3–1.4	0.1–1.1	89–119	ND	28–30	Cl ₂	Chloramines	90	200
Plant5	GW + Lake C	1.3–2.6	1.0–1.2	150–171	5.4–7.1	37–79	Cl ₂	Chloramines	90	200
Plant6	Lake D	3.2–4.8	0.9–1.4	444–513	3.6	9	ClO ₂	Chloramines	90	200
Plant7	River A	2.2–5.3	2.0–4.2	13–30	ND	ND	Cl ₂	Chloramines	46	169
Plant8	River B	1.7–3.7	1.8–3.3	45–70	ND	1.1	Cl ₂	Chloramines	59	117
Plant9		1.6–3.4	1.9–3.6	33–61	ND	ND	Cl ₂	Chloramines	26	96
Plant10	Lake E	2.7–3.9	1.6–2.0	58–69	ND	1.7	O ₃	Chlorine	150	300
Plant11							O ₃	Chlorine	150	300

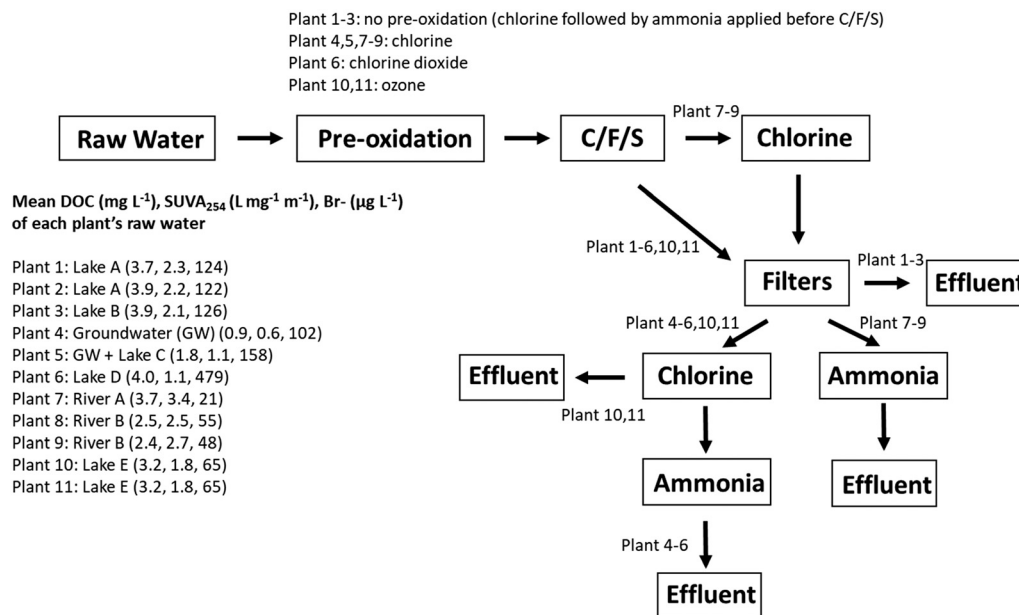


Fig. 1 An overview of the operational configurations of 11 drinking water treatment plants where finished waters were collected at effluent and distribution system. C/F/S: coagulation, flocculation, and sedimentation.

TOC-LCHS high temperature combustion analyzer (Shimadzu Corp., Kyoto, Japan) according to Standard Method 5310B.²⁹ TOC standards were prepared by diluting 1000 mg C L^{-1} potassium hydrogen phthalate solution in the range of 0.2–15 mg C L^{-1} . The minimum reporting level (MRL) for DOC was determined to be 0.15 mg L^{-1} . A Dionex ICS-2100 ion chromatography system (Dionex, Sunnyvale, CA) was used to determine chloride, bromide and iodide concentrations in aqueous solutions. The mobile phase for the system was 20 mM KOH and a Dionex AS-19 column coupled with an AG-19 guard column was used for separation. The MRLs for chloride (Cl^-), bromide (Br^-), and iodide (I^-) was 10, 10, and 25 $\mu\text{g L}^{-1}$, respectively.

2.3.2. Halogen-specific TOX species. TOCl, TOBr, and TOI were determined using an Analytik Jena Multi-X 2500 TOX Analyzer coupled with off-line ion chromatography (Analytik Jena, Germany). After acidified with sulfuric acid adjusted to $\text{pH} \leq 2$, 80 mL of sample was passed through two activated carbon microcolumns in series using a sample adsorption unit (APU; Analytik Jena, Germany). The activated carbon columns were then rinsed with aqueous sodium nitrate solution (20 mL, 6.85 g L^{-1} NaNO_3) to remove inorganic halides. Both columns were manually transferred into the furnace and burned for 20 minutes at 950 °C. After that, off-gas was collected in 20 mL of distilled and deionized water and analyzed using an off-line ion chromatography (Dionex ICS-2100) for Cl^- , Br^- , and I^- concentrations which are finally divided by a concentration factor of 4 to determine the concentrations of TOCl, TOBr, and TOI. All halogen-specific TOX samples were analyzed in duplicate and the concentrations of TOCl, TOBr, and TOI were presented as Cl equivalent herein. The MRLs for TOCl, TOBr, and TOI were 2.5, 2.5, 6.3 $\mu\text{g L}^{-1}$, respectively, which are equivalent to 2.5,

1.1, and 1.7 $\mu\text{g Cl L}^{-1}$. Concentration <MRL does not necessarily mean “no formation”.

2.3.3. THMs and HAAs. THMs (chloroform (TCM), dichlorobromomethane (DCBM), dibromochloromethane (DBCM), and bromoform (TBM)) were extracted by liquid/liquid extraction with methyl *tertiary*-butyl ether (MtBE) and quantified by an Agilent 6890 gas chromatography and electron capture detection (GC/ECD) according to US Environmental Protection Agency (EPA) Method 551.1. HAAs (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA)) were extracted with MtBE followed by derivatization with acidic methanol and analyzed using a GC/ECD according to US EPA Method 552.2. More details of DBP analysis can be found elsewhere.¹⁵ The sum of THMs and HAAs were considered as a known TOX fraction in this study.

3. Results and discussion

3.1. Source water characteristics and operational configuration of water treatment plants

The lowest Br^- levels were observed in the intake waters of plants 7–9 (13–70 $\mu\text{g L}^{-1}$) followed by plants 10 and 11 (58–69 $\mu\text{g L}^{-1}$), while more than 100 $\mu\text{g L}^{-1}$ of Br^- was measured in the other plants (Table 1). DOC and SUVA₂₅₄ of all monitored intake water samples remained relatively constant over different seasons. The lowest levels of DOC (0.3–2.6 mg L^{-1}) and SUVA₂₅₄ (0.1–1.2 $\text{L mg}^{-1} \text{m}^{-1}$) were observed in plants 4 and 5 which were treating groundwater. I^- (5.4–7.1 $\mu\text{g L}^{-1}$) was observed in the intake water of plant 5, while I^- concentrations in the other plants were very low or not

detected (Table S1†). In most surface waters, IO_3^- was below $2 \mu\text{g L}^{-1}$, but its concentration was high in pure and blended groundwater ($28\text{--}79 \mu\text{g L}^{-1}$). It has been known that the composition of iodine species in groundwater is related with the redox potential; IO_3^- is a dominant species at $>0 \text{ mV}$ of the redox potential (Eh), while I^- is the most abundant under reducing condition.^{30,31} While I^- can be transformed *via* the reaction with NOM to TOI, IO_3^- is a sink for I^- .³²

TOX formation could be affected by not only the source water characteristics, but also the plant treatment train configuration such as disinfection method, residence time in the distribution system, and other specific operational parameters (Fig. 1). The sequential chloramination (*i.e.*, chlorination prior to ammonia addition with various chlorine contact times) was used in plants 1–9 and chlorine was used as the final disinfectant in plants 10 and 11. Pre-oxidation was conducted with chlorine, chlorine dioxide, or ozone in all plants except for plants 1–3. Depending on their distribution systems, the average and maximum water residence times vary from plant to plant (Table 1).

3.2. Occurrence of halogen-specific TOX in finished waters

Fig. 2a shows the seasonal occurrence of TOCl and TOBr in the water samples collected from each plant's effluent, and average and maximum residence points of the distribution system. TOCl was the dominant TOX species in most samples and TOI was not detected in any sample. Pre-oxidation with ozone or chlorine (and possible chlorine dioxide) can transform I^- to IO_3^- and, thus, minimize TOI formation.³² In plants 1–3 where chloramination was applied at the beginning of the treatment trains without pre-oxidation, TOCl was low ($49\text{--}65 \mu\text{g L}^{-1}$) in fall and higher ($97\text{--}117 \mu\text{g L}^{-1}$) in winter, while TOBr increased during summer (up to $45 \mu\text{g L}^{-1}$). Although Br^- levels in the intake water decreased in winter and increased in fall, there was no significant difference between TOBr values observed in fall and in winter. DBP speciation shifted from brominated to chlorinated ones during winter as TOCl increased. Increases in temperature account for the enhanced TOBr formation during summer, which was also observed for plants 4–6. All these plants treated waters having moderate to high Br^-

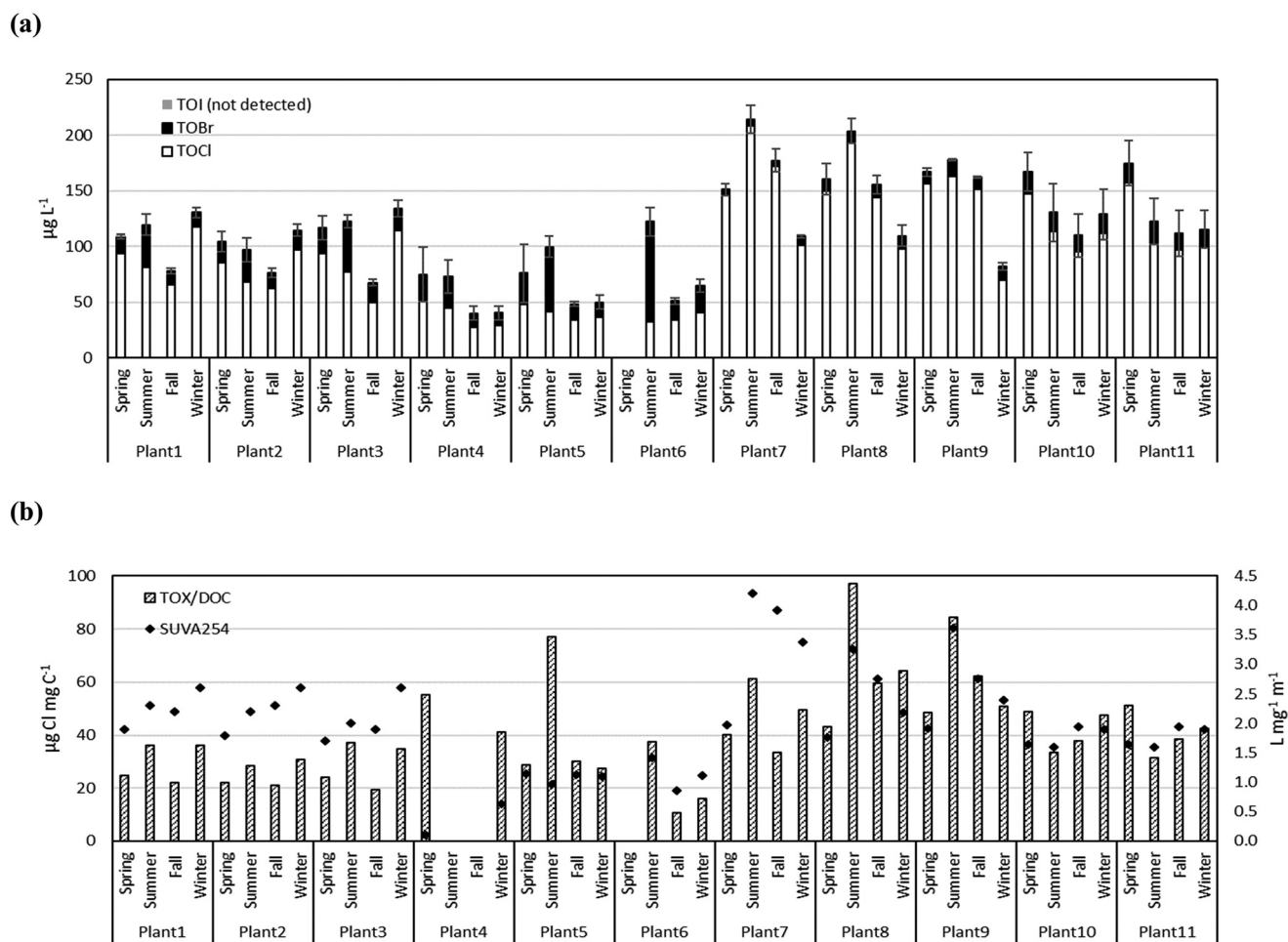


Fig. 2 Seasonal TOX species (*i.e.*, TOCl, TOBr, and TOI) occurrence (a) and DOC-normalized TOX (*i.e.*, (TOCl + TOBr)/DOC) along with SUVA₂₅₄ (b) in finished waters (collected at effluent and in distribution system) of eleven drinking water plants.

levels. Seasonal trends of TOBr formation, however, were not clear at the other plants whose intake waters had relatively low Br^- concentrations. THMs and HAAs in effluent and distribution system samples were high in fall and low in winter, which is opposite to the seasonal pattern of TOCl at plants 1–3 (Tables S2 and S3†). The average known TOX fraction (*i.e.*, (THMs + HAAs)/TOX) ranged from 52% to 59% which is far greater than previous results in chloraminated waters.⁸ TOCl/TOX ranged from 63% to 90% at plants 1–3. Since the intake water characteristics were similar for all three plants, their TOX occurrence patterns were also similar to one another. Minor differences may be a result of different retention times in each distribution system.

The TOCl formation at plants 4 and 5 was consistently low due to low DOC and SUVA_{254} of their intake waters. Low TOCl was also observed at plant 6 probably because of the use of ClO_2 as a pre-oxidant. TOCl/TOX ratios ranged from 63% to 73% in fall to spring, while the ratios dropped to 27–61% in summer due to the elevated TOBr formation (up to $58 \mu\text{g L}^{-1}$). The formation of brominated THM species and the total THM formation were also elevated in summer. However, the total HAA concentrations did not increase despite enhanced formation of brominated HAAs especially at plant 6. This indicates that the impact of pre-oxidation with ClO_2 on the THM formation is not the same as on the HAA formation. Despite high Br^- concentrations (up to $513 \mu\text{g L}^{-1}$) and high TOBr occurrence in these three plants, TOI was not detected which was expected because the intake I^- concentrations were very low (Table 1). Instead, up to $80 \mu\text{g L}^{-1}$ of IO_3^- , which is sink for I^- , was detected in the intake waters of plants 4–6.

The highest levels of TOCl (up to $208 \mu\text{g L}^{-1}$) were observed at plants 7–9. TOBr occurrence was consistently low (*i.e.*, $5\text{--}12 \mu\text{g L}^{-1}$) during the monitoring period, while TOCl dropped about 50% in winter, which trend is opposite to the case in plants 1–3. The reduced TOCl formation was accompanied with the DOC decrease in the intake waters in winter. Since Br^- concentrations ($13\text{--}30 \mu\text{g L}^{-1}$) in the intake of plant 7 were always lower than those ($33\text{--}70 \mu\text{g L}^{-1}$) of plants 8 and 9, TOBr occurrence in the effluent and distribution system of plant 7 was always lower than those of plants 8 and 9. TOCl/TOX ratios ranged 92–97% during spring to fall, while it decreased to 85–93% in winter.

At plants 10 and 11, chlorinated plants, more TOCl (up to $157 \mu\text{g L}^{-1}$) formed in spring than the other seasons, while seasonal changes in TOBr were insignificant. TOCl/TOX ranged 85–90% at these plants. Since plants 10 and 11 receive water from the same source and the water retention times are similar in each distribution network, the seasonal patterns of TOCl and TOBr occurrence were almost identical.

To further assess the seasonal change in the intake DOC reactivity toward TOCl or TOBr formation, the DOC-normalized TOX (expressed in units of $\mu\text{g as Cl mg C}^{-1}$) is plotted along with SUVA_{254} in Fig. 2b. In general, TOX/DOC increased apparently in summer at chloraminated plants (*i.e.*, plants 1–9), while it decreased in summer at plants 10

and 11, chlorinated plants suggesting that the temperature dependency of TOX yields may be impacted by disinfection method. However, TOX/DOC was also high in winter at some plants and in spring at others. TOX/DOC trend at a plant is well correlated with seasonal SUVA_{254} changes. TOX/DOC increased as SUVA_{254} increased with a few exceptions. Given seasonal variations of TOX/DOC at eleven plants, the occurrence of halogen-specific TOX which was highly site-specific would be affected by multiple factors including temperature, pH and operational parameters such as chlorine dose and contact time. In a laboratory study, Hua *et al.* found that chloramination of NOM produced much higher UTOX (calculated as the differences between TOX and the sum of halogen equivalent concentrations of THMs, HAAs, dihaloacetonitriles, haloketones, and chloropicrin) percentages than chlorination, and UTOX was strongly correlated with SUVA_{254} .³³ In other studies, good linear regression correlation coefficient (R^2) values of THM and HAA yields *vs.* DOC were observed with slightly weaker correlations for HAAs.^{34,35} However, in the present study, any strong correlation was not observed between TOX and any single water quality parameter. Nevertheless, DOC and SUVA_{254} of an influent water may be used to predict TOX formation in the distribution system of either a chlorinated or chloraminated plant.

Fig. 3 shows the levels of TOCl and TOBr occurrence in box-and-whisker plots for the samples collected at the effluent and the distribution system of eleven plants. The TOBr formation in finished waters apparently depended on the intake Br^- concentrations of the plants. Higher TOBr was observed in plants 1–6 treating waters with moderate to high levels of Br^- than in plants 7–11 with relatively low Br^- in their source waters. To show how much of Br^- was utilized in TOBr formation, TOBr/ Br^- was plotted in Fig. S1†. TOBr/ Br^- was highest in summer at plants 1–6 indicating more Br^- conversion into TOBr at higher temperature. However, such trend of TOBr/ Br^- was not observed at plants 8–11. Interestingly, almost Br^- was utilized in TOBr formation in spring and winter at plant 7. On the other hand, the TOCl formation seems to be governed by little more complicated reasons. The lowest DOC and SUVA_{254} accounted for the lowest TOCl observed in plants 4 and 5. Considering DOC levels ($3.2\text{--}4.8 \text{ mg L}^{-1}$) in the intake water of plant 6, an application of ClO_2 for pre-oxidation at plant 6 might lead to low TOCl formation in its finished water. TOCl in chlorinated plants (*i.e.*, plants 10 and 11) were slightly higher than chloraminated plants (*e.g.*, plants 1–3). However, even higher TOCl formation was observed in plants 7–9 where chloramines were applied as the final disinfectant. This was likely due to a longer chlorine contact time. Prior to ammonia addition, hours of chlorine contact time were applied at plants 7–9, while minutes at the other chloraminated plants. The longer chlorine contact time produced the higher TOCl in finished waters. Moreover, higher SUVA_{254} and lower Br^- at plants 7–9 also account for more TOCl formation than at plants 1–3 (Table 1). Therefore,

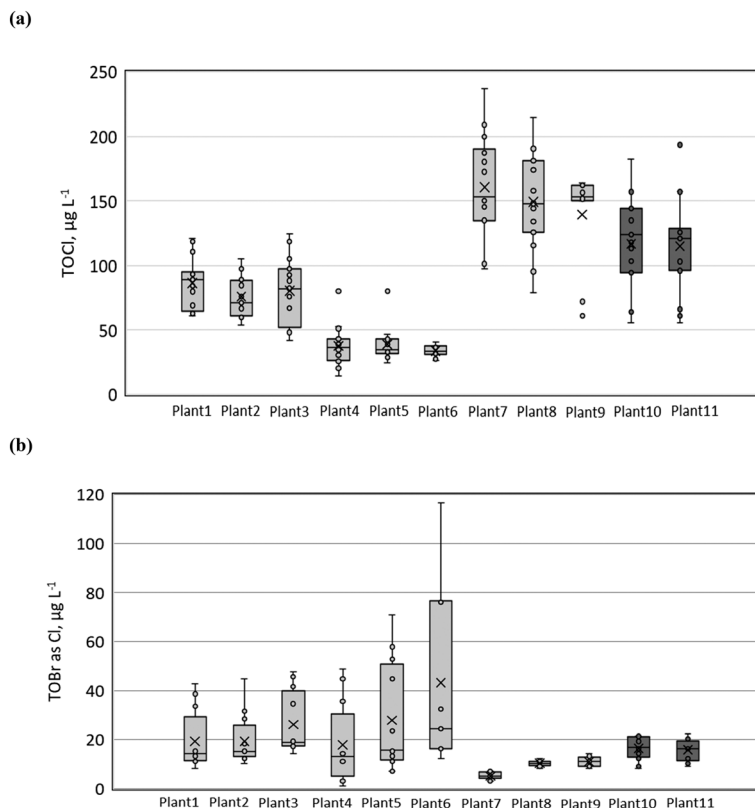


Fig. 3 TOCl (a) and TOBr (b) occurrence in finished waters (collected at effluent and in the distribution systems, $n = 12$ for each plant) of eleven plants.

the formation of halogen-specific TOX in the distribution system of drinking water treatment plants would be dependent on multiple elements such Br^- , DOC, SUVA_{254} in intake waters as well as pre-oxidation, final disinfectant and chlorine contact time which may change seasonally.

3.3. Controlled TOCl and TOBr formation experiments

To investigate the formation of TOX in the distribution system as a function of residence time, holding experiments were conducted with the selective effluent water samples. The TOCl and TOBr formations in chloraminated finished waters (*i.e.*, plants 1–9) were relatively constant as the holding time increased (Fig. S2†). This indicates that TOX forms already within these plants and additional TOX formation is insignificant as the residence time increases in the distribution systems. Spiking of Br^- to the effluent water increased only TOBr formation (for example, from $39 \mu\text{g L}^{-1}$ to $132 \mu\text{g L}^{-1}$ at plant 1), while TOCl remained almost same over 504 h of extended residence time. In addition, the formation of THMs and HAAs was not significantly elevated by the presence of high Br^- suggesting that other types of unknown DBPs might have formed over a simulated extended residence time. Unlike chloraminated plants, however, the TOCl and TOBr formations in plants 10 and 11 apparently increased as the residence time increased in the distribution systems (Fig. 4a and b) during the monitoring period. Since the pre-ozonation was applied at this utility, the

TOX formation would be initiated only by the chlorine addition before the product water leaves the plants. TOCl and TOBr, reported in comparable unit, were $46 \mu\text{g L}^{-1}$ and $8 \mu\text{g L}^{-1}$ at $t = 0$ and increased up to $200 \mu\text{g L}^{-1}$ and $20 \mu\text{g L}^{-1}$, respectively, at $t = 504 \text{ h}$ (Fig. 4c). Therefore, this indicates that the TOX formation in the chlorinated water keeps increasing in the distribution system as long as the residual chlorine is available. The ratio of known TOX (*i.e.*, THMs + HAAs as Cl equivalent concentration) to the total TOX (*i.e.*, TOCl + TOBr + TOI) was 55–60% for chlorination. In contrast, TOCl and TOBr formations under chloramination were much less and slower than chlorination. TOCl and TOBr in chloraminated waters were $25 \mu\text{g L}^{-1}$ and $3 \mu\text{g L}^{-1}$, respectively, at $t = 0$ and increased to $39 \mu\text{g L}^{-1}$ and $5 \mu\text{g L}^{-1}$ at $t = 300 \text{ h}$. Then TOCl and TOBr remained constant for further retention time ($t = 504 \text{ h}$). The ratio of known TOX to the total TOX for chloramination was only 24–28%. The percentages of UTOX for chlorination and chloramination were in good agreement with previous findings although water matrix and experimental conditions were not exactly same.³⁶

3.4. Implications of measuring halogen-specific TOX occurrence

Halogen-specific TOX (especially TOI) occurrence in drinking water distribution systems has not been widely studied. Most previous studies have not reported and/or considered crucial

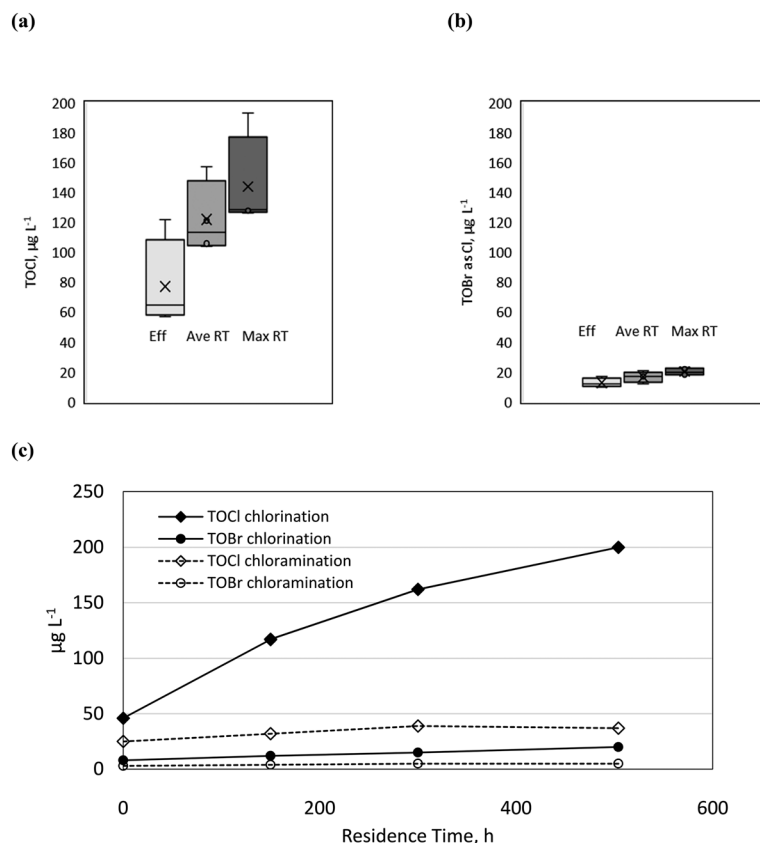


Fig. 4 TOCl (a) and TOBr (b) occurrence at effluent (Eff) and in distributions system (ave. RT and max. RT) of plant 10. The holding experiment results (c) under chlorination and chloramination with the treated water samples collected just before chlorination from plant 10.

parameters such as DOC, SUVA_{254} , and Br^- of intake waters and their seasonal variations in addition to pre- and post-disinfectant, and chlorine contact time within the treatment plants in spite of their important roles in understanding the formation and speciation of TOX in the distribution system. TOI has not been measured and reported in any previous occurrence study. In this study, TOI formation was also examined with product waters but always less than the MRL. The highest TOX (*i.e.*, $\text{TOCl} + \text{TOBr} + \text{TOI}$) level in this study was $242 \mu\text{g L}^{-1}$ in the effluent of a chloraminated drinking water plant (plant 7) where pre-chlorination was applied and the intake Br^- level was relatively low (about $23 \mu\text{g L}^{-1}$). Since this plant treated the water with the highest SUVA_{254} , more than one factor likely contribute to the TOX formation. Pre-chlorination plus a long chlorine contact time (hours) prior to ammonia addition caused such high levels of TOX in the distribution system of the plant (Fig. 1). On the other hand, the lowest TOX was $26 \mu\text{g L}^{-1}$ in the effluent of a chloraminated plant (plant 4) using groundwater as a source. This plant also had the lowest DOC and SUVA_{254} which accounted for the lowest TOX formation. Moreover, some plants showed greater seasonal variations of halogen-specific TOX occurrence than the others, suggesting that the effects of temperature, DOC, Br^- , operational parameters, *etc.* on the formation of halogen-specific TOX species in the distribution system are site-specific. Modeling based on a suite of

multiple parameters can help to predict TOX formation if more variables such as temperature, influent and effluent water pH are available. Furthermore, due to the lack of information regarding water quality and/or operational parameters in the previous studies, it is not easy to directly compare the findings in the present study with the reported TOX values in the literature.

Although the concentrations of THMs and HAAs in finished drinking waters can be well maintained below the regulated levels, unmeasured brominated and iodinated DBPs may contribute further significantly to the water toxicity with respect to the public health.³⁷ To assess TOBr as an indicator of underestimated potential water toxicity, therefore, the regulated TOBr fractions were calculated by adding brominated THMs (*i.e.*, DCBM, DBCM, and TBM) to brominated HAAs (*i.e.*, MBAA and DBAA) which are currently regulated by US EPA, and taking the ratios of the regulated brominated DBPs (Br-DBPs) as Br^- to TOBr. Despite some seasonal variations, Br-DBP/TOBr was the lowest in the chloraminated plants treating groundwater and generally higher in chlorinated plants (Fig. 5). Since absolute TOBr values were very low at plants 7–11 due to their low intake Br^- concentrations, contributions of unknown TOBr fractions to the water toxicity would be insignificant. However, the impact of unknown TOBr fractions on the water toxicity can be more significant at plants treating source waters having

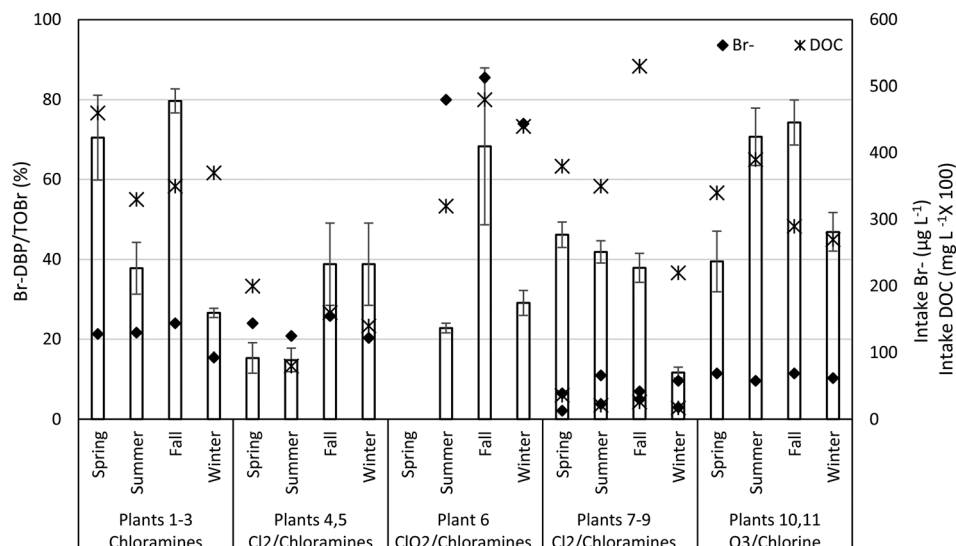


Fig. 5 Seasonal changes in the ratios of the regulated brominated DBPs (the sum of DCBM, DBCM, TBM, MBAA, and DBAA as Br) to TOBr along with intake DOC and Br⁻ concentrations of eleven plants.

elevated Br⁻ such as plants 1–6. Especially at plants 4 and 5 receiving groundwater with 100 µg L⁻¹ or greater Br⁻, Br-DBP/TOBr in spring and summer was only about 15%, indicating that the major portion of TOBr in the finished water is unidentified and unmeasured and the water toxicity may be underestimated while complying with the current DBP regulations. Using the data reported in a previous nationwide DBP occurrence study, Br-DBP/TOBr was calculated for 8 plants in US and compared with our results (Fig. S3†).³⁸ Br-DBP/TOBr of chloraminated plants (24–38%) was slightly lower than that of a chlorinated plant (52%), and the lowest levels (2–3%) were observed in the plants treating groundwater. Krasner *et al.* found that the percentage of TOBr accounted for by the halo-DBPs ranged from 6 to 58%, with a median value of 39%, while the percentage of TOCl accounted for by the halo-DBPs ranged from 12 to 33%, with a median value of 24%.³

4. Conclusions

Halogen-specific TOX species formation in the distribution system of all chloraminated plants was not significantly affected by the residence time since most TOCl and TOBr already formed within the plants by pre-chlorination and/or chlorine contact prior to ammonia addition, while TOCl and TOBr in chlorinated plants increased as the residence time increased in the distribution system. The results from the holding experiment support that the halogen-specific TOX species formation keeps increasing in the chlorinated distribution system as long as the residual chlorine is available. Nevertheless, the highest total TOX formation (*i.e.*, TOCl + TOBr + TOI) was observed in the distribution system of a chloraminated plant where a relatively long chlorine contact time was allowed prior to ammonia addition. Seasonal variations in DOC, Br⁻ concentration, and

temperature may lead to TOCl and TOBr dynamics in the distribution system, but any single parameter was not strongly correlated with TOCl or TOBr formation since it must be a multivariable process. Indeed, the utility operational conditions such as pre-oxidation, final disinfectant, and chlorine contact time prior to ammonia addition can play more important roles in the halogen-specific TOX species formation in the distribution system than intake water quality or the type of source water. TOBr levels were as high as 116 µg L⁻¹ in one distribution system treating the water having the highest Br⁻, while the values ranged in the other plants between 2–71 µg L⁻¹. Furthermore, the ratio of regulated brominated DBPs to TOBr was as low as 15% in some systems indicating that the major portion of TOBr in the finished water can be overlooked while complying with the current DBP regulations. Given higher toxicity of brominated DBPs than their chlorinated analogs, it is important to develop treatment and/or operational strategies to reduce the formation of TOBr in distribution systems in order to minimize exposure of public to such DBPs.

Conflicts of interest

There are no conflicts of interest to declare.

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