

Bromine Incorporation in Regulated and Emerging DBPs and the Relative Predominance of Mono-, Di-, and Trihalogenated DBPs

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ABSTRACT

Previous research has shown that bromine incorporation into trihalogenated acetic acids (TXAAs) was similar to that of the trihalomethanes (THMs). Likewise, occurrence data for other trihalogenated DBPs (e.g., halonitromethanes [HNMs], haloacetaldehydes [HAs]) showed similar or somewhat lower bromine incorporation as that of the THMs. Moreover, bromine incorporation patterns into dihalogenated DBPs (e.g., haloacetic acids [HAAs], haloacetonitriles [HANs], HNMs, HAs) were similar or somewhat higher for the HANs. Some of the differences may have been due to steric hindrance (i.e., trihalogenated DBPs containing bromine), relative instability of some DBPs, and/or the presence of DBPs at low levels relative to their minimum reporting levels. However, even when there was lower bromine incorporation into some DBP subclasses, the trend was consistent (i.e., in most cases, the regression between DBP subclasses had a high correlation coefficient). The relative formation of dihalogenated HAAs (DXAAs) and TXAAs has been related to the nature of the organic matter and/or the disinfectant(s) used. This was also observed for various DBP classes. In addition, the relative degree of halogenation was related to the instability of certain DBP species. Understanding the relative formation of different DBP species can be used in predicting the formation of DBPs for which not all standards are available (e.g., haloacetamides) and in improving exposure assessments.

INTRODUCTION

Brominated disinfection by-products (DBPs) (in general) appear to be more cytotoxic and genotoxic than the chlorinated species, and some of the dihalogenated species are more toxic than the trihalogenated analogues (Plewa et al., 2008b); however, many of the more toxic species are not routinely measured. For example, there are nine halonitromethanes (HNMs), of which only one (chloropicrin [trichloronitromethane]) is routinely measured. Of the HNMs, the most genotoxic is dibromonitromethane, whereas chloropicrin was rank ordered fourth (Plewa et al., 2004). Likewise, there are nine haloacetaldehydes (HAs), where only chloral hydrate (trichloroacetaldehyde) is routinely measured. Trichloroacetaldehyde was found to not be genotoxic, whereas dibromoacetaldehyde was the most genotoxic in this class of DBPs (Plewa et al., 2008b).

Waller and colleagues (1998) found an association between high exposure to total trihalomethanes (TTHMs) and spontaneous abortion. Of the four individual THMs, only high bromodichloromethane exposure was associated with spontaneous abortions. However, an “association” in an epidemiology study does not mean “cause and effect.” Moreover, a water that is high in bromodichloromethane may also be high in other bromochloro DBPs, which may be of higher health concern.

Previous research has shown that bromine incorporation into trihalogenated acetic acids (TXAAs) was similar to that of the THMs and that the occurrence of brominated TXAAs could be predicted based on the occurrence of trichloroacetic acid and bromine incorporation into the THMs (Singer et al., 2002). Likewise, occurrence data for other trihalogenated DBPs (e.g., HNMs) showed similar bromine incorporation as that of the THMs (Krasner et al., 2006).

The relative formation of dihalogenated acetic acids (DXAAs) and TXAAs has been related to the nature of the organic matter and/or the disinfectant(s) used. Waters that are high in specific ultraviolet absorbance (SUVA) tend to form more TXAAs (Cowman and Singer 1996), whereas lower SUVA waters tend to form more DXAAs (Hwang et al., 2000). The use of chloramines or chlorine dioxide has been shown to minimize the formation of TXAAs (and THMs), whereas significant amounts of DXAAs have been found to form during chloramination (Karanfil et al., 2007) or chlorine dioxide treatment (Zhang et al., 2000).

The primary objective of this paper is an examination of bromine incorporation in emerging DBPs versus that of the regulated DBPs and a secondary objective is the study of the predominance of di- versus trihalogenated species in these different DBP classes, in order to better understand and characterize exposure to DBPs of health concern.

DBP DATABASES

Occurrence data on emerging halogenated DBPs of health concern from various studies were evaluated. Specific DBPs that were considered included the four regulated THMs, the nine bromine- and chlorine-containing haloacetic acids (HAAs), the three dihaloacetonitriles (DHANs), the three dihalo- and four trihalonitromethanes (DHNMs, THNMs), the three dihalo- and the four trihaloacetaldehydes (DHAs, THAs). Although (in theory) there should be nine

DBPs for many classes of DBPs (two mono-, three dihalo-, and four trihalogenated species), some of the subclasses are typically not present in drinking water. For example, trichloroacetonitrile was rarely detected (McGuire et al., 2002) because it readily undergoes base-catalyzed hydrolysis (Croué and Reckhow, 1989). The occurrence of the brominated analogues of TCAN was also infrequent and very low in concentration (Weinberg et al., 2002). Thus, for certain DBP subclasses, which are not readily formed or stable in drinking water, they were not included in this study. For some DBP classes (e.g., haloacetamides), occurrence studies only included those species for which standards were available (Weinberg et al., 2002; Krasner et al., 2006). Thus, a complete examination of bromine incorporation into those species can not be conducted. Nonetheless, some of those data will be discussed.

Data on DBP occurrence in finished waters from full-scale facilities in the U.S., which treated a range of water qualities with a diversity of treatment/disinfection scenarios, were examined. The databases included a U.S. nationwide DBP occurrence study (Weinberg et al., 2002; Krasner et al., 2006), a U.S. nationwide wastewater DBP study (Krasner et al., 2008), and a U.S. nationwide study on nitrogenous (N) DBPs (Mitch et al., 2008). For the preliminary evaluation of data in the nationwide occurrence study, only sample events in which total organic halogen (TOX) was measured were examined, as that database also provided DBP concentrations on a molar basis (see data analysis below). The wastewater study included results for well nitrified wastewater treatment plants (WWTPs) in which the addition of chlorine formed a free chlorine residual (in most poorly nitrified wastewaters, the addition of chlorine forms chloramines with the ambient ammonia). In addition, the latter study included drinking water treatment plants (DWTPs), some of which were impacted by WWTP discharges. The N-DBP study focused on DWTPs impacted by treated wastewater and/or algae, which are both sources of organic nitrogen. Note that not all of the target DBPs were measured in each of the studies from which data were obtained. For example, HAAs were not measured in the N-DBP study, whereas THMs and HAs, which are carbonaceous DBPs, were. Moreover, data were obtained from Barcelona (Spain), which due to an extensive drought, was highly impacted by bromide and, thus, the water formed many brominated DBP species.

Finally, the total organic carbon (TOC) of one U.S. surface water was concentrated ~130-fold with reverse osmosis (RO), was spiked with bromide to replace bromide lost in the concentration process, and was chlorinated, which formed DBPs at levels orders of magnitude higher than in the ambient water. The DBP speciation of the chlorinated RO concentrates was also evaluated.

DATA ANALYSIS

The bromine incorporation factor (n , BIF) for THMs is defined as follows (Gould et al., 1983; Symons et al., 1993):

$$\text{BIF} = \frac{\text{TTHM-Br}}{\text{TTHMs}} = \frac{0 \times \text{CHCl}_3 + 1 \times \text{CHCl}_2\text{Br} + 2 \times \text{CHClBr}_2 + 3 \times \text{CHBr}_3}{\text{CHCl}_3 + \text{CHCl}_2\text{Br} + \text{CHClBr}_2 + \text{CHBr}_3}$$

where the THM concentrations are on a molar basis

For the THMs, BIF values range from 0 (all chloroform [CHCl_3] to 3 (all bromoform [CHBr_3]). A BIF of 1.0 corresponds to a water in which the “average” species is bromodichloromethane (CHCl_2Br). A similar equation was used to determine the BIF for other trihalogenated DBPs (e.g., TXAAs, THNMs, THAs).

For DXAAs, the BIF was calculated as follows:

$$\text{BIF} = \frac{0 \times \text{DCAA} + 1 \times \text{BCAA} + 2 \times \text{DBAA}}{\text{DCAA} + \text{BCAA} + \text{DBAA}}$$

where the DXAA concentrations are on a molar basis

For the DXAAs, BIF values range from 0 (all dichloroacetic acid [DCAA] to 2 (all dibromoacetic acid [DBAA]). A BIF of 1.0 corresponds to a water in which the average species is bromochloroacetic acid (BCAA). A similar equation was used to determine the BIF for other dihalogenated DBPs (e.g., DHANs, DHNMs, DHAs).

For the monohalogenated acetic acids (MXAAs), a similar equation was used for those two species, where the BIF values range from 0 to 1. In other research, the BIF for mono-, di-, and trihalogenated species was normalized by the number of halogens to get a common range of values, however that was not done in this study.

Finally, the relative proportion of tri- and dihalogenated species (e.g., TXAAs/DXAAs) and the relative proportion of di- and monohalogenated species (e.g., DXAAs/MXAAs) was determined. Those calculations were done on a molar basis.

RESULTS

U.S. Nationwide DBP Occurrence Study

Figure 1 shows a comparison of the BIFs for THMs and TXAAs in the U.S. nationwide occurrence study. The slope of the regression line was less than 1 (i.e., 0.73), which indicates that there was somewhat less bromine incorporation into TXAAs than into THMs on a central tendency basis. There may have been less apparent bromine incorporation in the TXAAs for two reasons. Because of the presence of the carboxylic acid group in the TXAAs, there may have been steric interference in incorporating too many bromine atoms. Alternatively, brominated TXAAs may have formed but degraded to some extent. In other research, brominated TXAAs were found to be decomposed to varying degrees by light at room temperature (Pormoghaddas and Dressman, 1993).

Figure 2 shows a comparison of the BIFs for DHANs and DXAAs in the nationwide occurrence study. When all of the data were considered, the correlation coefficient (R^2) was fair (i.e., 0.64). There was a significant outlier with BIF values of 1.0 for DHANs and 0.06 for DXAAs. This sample was from a lime-softening plant, where the high pH resulted in base-catalyzed hydrolysis of most of the DHANs (Weinberg et al., 2002). There was some bromochloroacetonitrile detected (i.e., 0.2 $\mu\text{g/L}$), whereas the other DHAN species were not detected at or above their minimum reporting levels (MRLs) (i.e., 0.1-0.2 $\mu\text{g/L}$). Thus, when the

DBPs in a particular class are present near their MRL values, determination of the BIF is probably not reliable. When this data point was removed, it resulted in a higher R^2 (i.e., 0.78). Nonetheless, the slope was less than 1.0 (i.e., 0.62). This indicates that there was more bromine incorporation into DHANs than into DXAAs. Obolensky and Singer (2005) also saw more bromine incorporation into DHANs when data from the U.S. Information Collection Rule were examined.

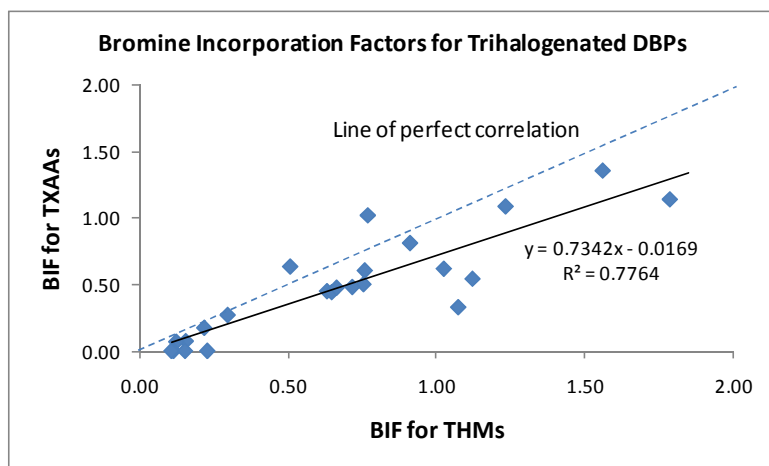


Figure 1. Comparison of BIFs for THMs and TXAAs in U.S. nationwide DBP occurrence study

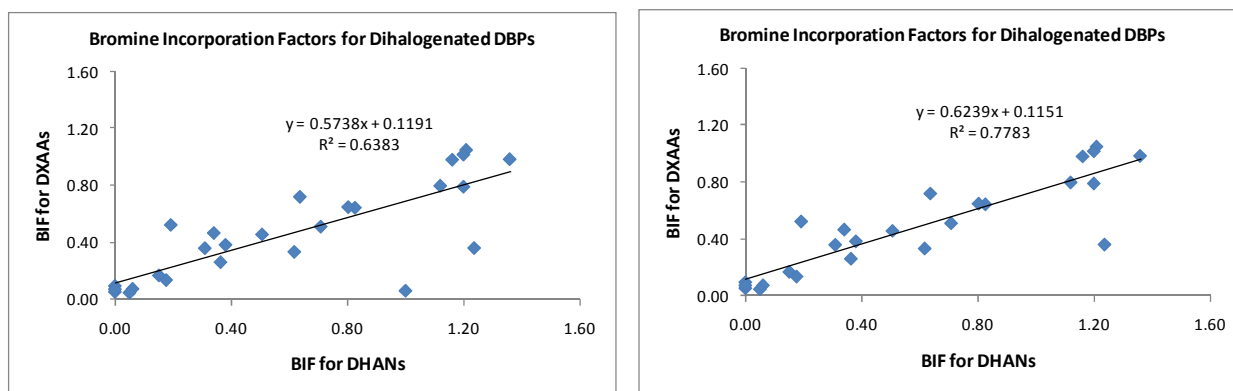


Figure 2. Comparison of BIFs for DHANs and DXAAs in U.S. nationwide DBP occurrence study: (a [left]) all data; (b [right]) excluding outlier with BIF values of 1.0 for DHANs and 0.06 for DXAAs

Figure 3 shows a comparison of the BIFs for THMs and THNMs in the nationwide occurrence study. There was a fair amount of scatter for this correlation. In some cases, this was due to the low occurrence of the THNMs (e.g., low occurrence of chloropicrin and brominated analogues not detected). Nonetheless, there was a good correlation for a number of points. For example, there were two plants in the study, which treated water from the same source. One used ozone and chloramines, whereas the other used chlorine and chloramines. Moreover, the ozone plant did not add chlorine or chloramines until the filtered water, whereas the other plant added chlorine to the raw water. The ozone plant had BIFs for THMs and THNMs of 1.8 and

2.3, respectively, whereas the chlorine plant had BIFs of 1.0 and 1.3, respectively (Krasner et al., 2006).

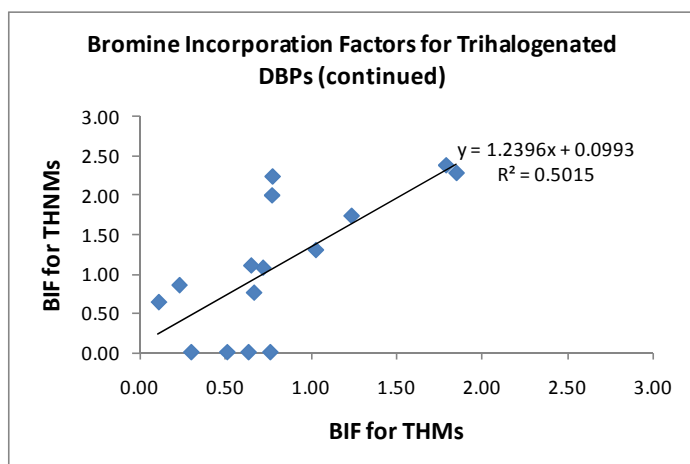


Figure 3. Comparison of BIFs for THMs and THNMs in U.S. nationwide DBP occurrence study

Figure 4 shows a comparison of the BIFs for DXAAs and DHNMs in the nationwide occurrence study. In most cases, there was low occurrence of the DHNMs, where only one species was detected. The comparison was re-conducted, where only samples that had two or three of the DHNMs detected were examined. Because of the limited number of data points, it is difficult to make much of these data. Nonetheless, the general trend was with increasing bromine incorporation into a regulated DBP subclass (DXAAs), there was somewhat similar bromine incorporation into this emerging DBP subclass of health concern.

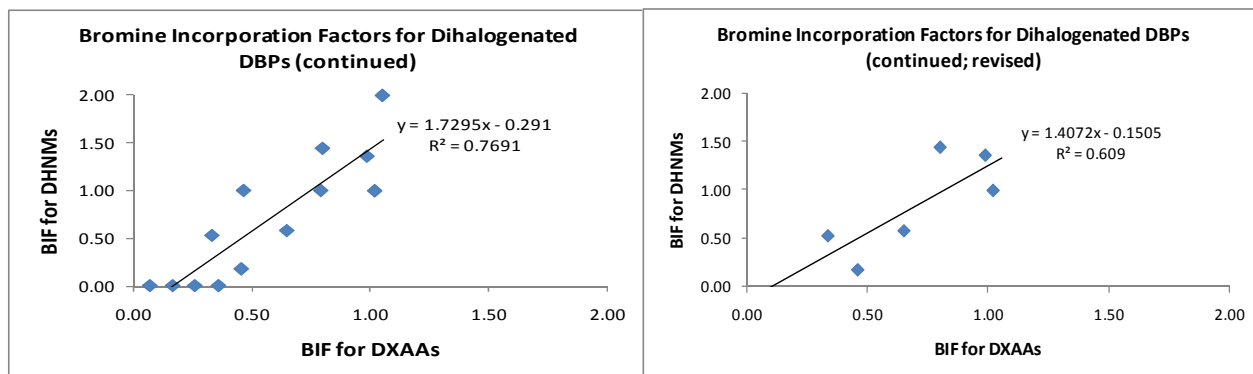


Figure 4. Comparison of BIFs for DXAAs and DHNMs in U.S. nationwide DBP occurrence study: (a [left]) all data; (b [right]) including only samples where two or three of the DHNMs were detected

Table 1 shows the relative preponderance of mono-, di-, and trihalogenated species in the nationwide occurrence study. The TXAA/DXAA molar ratio was 0.7, whereas it was 1.0 and 2.1 for the 75th percentile and maximum values, respectively. Alternatively, the THNM/DHNM molar ratios were significantly higher (interquartile range = 25th to 75th percentile = 2.4 to 6.3). In terms of the HAs, only two of the three DHAs and only two of the four THAs were analyzed for at that time. So a comparison was made between the chloro-only species for that class of

DBPs. The median and 75th percentile molar ratio of chloral hydrate/dichloroacetaldehyde was 1.0 and 2.5, respectively, which was somewhat similar to the ratios for the HAAs.

Table 1. Relative preponderance of mono-, di-, and trihalogenated DBP species in U.S. nationwide DBP occurrence study

DBP Subclass Ratio (Molar Basis)	Minimum	25th Percentile	Median	75th Percentile	Maximum
TXAAs/DXAAs	0	0.2	0.7	1.0	2.1
THNMs/DHNMs	0	2.4	4.7	6.3	30
Chloral hydrate/ dichloroacetaldehyde	0	0.6	1.0	2.5	14
Trichloroacetamide/ dichloroacetamide	0.04	0.08	0.48	0.6	0.9
DXAAs/MXAAs	5.9	7.0	11	17	25
DHANs/MHANs	8.2	16	21	54	62
Dichloroacetamide/ monochloroacetamide	0.9	2.4	3.9	4.4	4.8

Table 2 shows an example from plant 10 in the nationwide DBP occurrence study. When this plant used chlorine only (September 5, 2001), TXAAs were the predominant HAA species. Likewise, when the plant pre-chlorinated and post-chloraminated (January 10 and April 9, 2001), TXAAs were still dominant, but less so. Alternatively, when chloramines only were used (November 26, 2001 and February 25, 2002), DXAAs were the dominant HAA species. Moreover, for the HAs, the dominant species when chlorine only was used was chloral hydrate, which had the same molar ratio of trihalogenated to dihalogenated species as that of the HAAs (i.e., 2.7). With the use of chloramines, the dominant HA species was dichloroacetaldehyde. Thus, the use of chloramines at plant 10 tended to impact the distribution of tri- and dihalogenated HAAs and HAs to a similar extent.

Table 2. Relative preponderance of di- and trihalogenated HAA and HA species at plant 10 in U.S. nationwide DBP occurrence study

DBP Subclass Ratio (Molar Basis)	1/10/2001 [*]	4/9/2001 [*]	9/5/2001 [†]	11/26/2001 [‡]	2/25/2002 [‡]
TXAAs/DXAAs	1.5	1.2	2.7	0.4	0.7
Chloral hydrate/ dichloroacetaldehyde	0.5	0	2.7	0.3	0.3

^{*}Pre-chlorination, post-chloramination

[†]Chlorine only

[‡]Chloramines only

In terms of the monohalogenated DBPs their relative formation was quite low. For example, the median molar ratio for DXAAs/MXAAs in the nationwide DBP occurrence study was 11, whereas for DHANs and monohalogenated acetonitriles (MHANs) it was 21. Likewise, Cowman and Singer (1996) found the mole fraction of MXAA to be low. Among the bromo- and chloro- substituted HAAs, Plewa and colleagues (2002) found monobromoacetic acid to be

the most toxic; monochloroacetic acid was the second most genotoxic. Thus, one needs to consider both the relative toxicity and concentration of individual DBP species.

Figure 5 shows the relative formation and speciation of haloacetamides and HAAs at plant 12 from the nationwide DBP occurrence study, which treated a water high in bromide (0.33 mg/L). Although not all of the bromine- and chlorine-containing haloacetamide species were analyzed, it does appear that the relative concentrations of the haloacetamides compared well to the HAAs (i.e., similar degree of halogen incorporation), where the haloacetamides were in a concentration range of ~10 times less than the HAAs. The dichloro species of each DBP class were formed at higher concentrations than the trichloro species, where the presence of an elevated level of bromide resulted in a shift in speciation of the dihalogenated species to the more bromine-substituted compounds. Thus, it is likely that brominated analogues of trichloroacetamide, as well as bromochloroacetamide, were also formed in this water. Using the BIFs for other DBP classes in which all of the species were measured, one could predict what the concentrations were for the haloacetamides not measured. This is important from an exposure assessment perspective, as haloacetamides are a new family of DBPs of health concern (Plewa et al., 2008a).

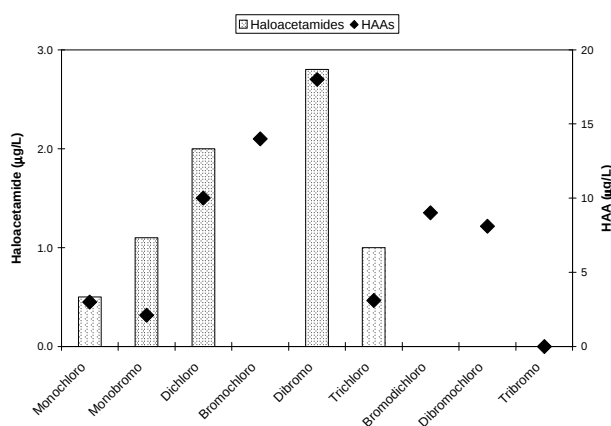


Figure 5. Relative formation and speciation of haloacetamides and HAAs in plant 12 effluent (February 2002) in U.S. nationwide DBP occurrence study (haloacetamides not measured in this study included bromochloro, bromodichloro, dibromochloro, and tribromo species)

Source: Krasner et al., 2006. Copyright 2006 American Chemical Society

Table 3 shows the impact of bromide on the formation of di- and trihalogenated HAs and HAAs in the effluent of plant 2 in the nationwide DBP occurrence study. When the bromide level was the highest (0.40 mg/L), there was a significant formation of bromochloro- and tribromoacetaldehyde. When the bromide concentration was lower (0.12-0.14 mg/L), both brominated species were formed at lower levels and the formation of the chlorinated species (dichloroacetaldehyde and chloral hydrate) were typically the major HAs produced. Likewise, when the bromide level was the highest, the formation of the bromine-containing DXAAs and TXAAs were much higher in concentration. Since this study was conducted, standards have been made available for the other bromine-containing DHAs and THAs, and new occurrence data are available for this emerging DBP class of health concern (see below).

Table 3. Formation of di- and trihalogenated HAs and HAAs in plant 2 effluent in U.S. nationwide DBP occurrence study*

Analyte (µg/L)	1/23/2001	7/17/2001	3/19/2002
Bromide	400	140	120
DXAAs:			
Dichloroacetic acid	14	12	19
Bromochloroacetic acid	18	11	6.1
Dibromoacetic acid	18	6.2	3.4
TXAAs:			
Trichloroacetic acid	8.6	9.0	13
Bromodichloroacetic acid	15	7.8	9.2
Dibromochloroacetic acid	15	3.6	2.4
Tribromoacetic acid	3.6	ND [†]	ND
Selected DHAs:			
Dichloroacetaldehyde	2	1	2
Bromochloroacetaldehyde	3.8	1	0.5
Selected THAs:			
Chloral hydrate	1.3	2	3
Tribromoacetaldehyde	3	0.2	0.1

*DHAs and THAs not measured in this study included dibromo, bromodichloro, and dibromochloro species

[†]ND = Not detected

Wastewater DBP Study

Figure 6 shows a comparison of BIFs for trihalogenated DBPs at well nitrified WWTPs in the U.S. When all of the data were examined for the THMs and TXAAs, the R^2 of the linear regression was 0.61. There was a significant outlier for a data point with a BIF of 0.65 for the THMs and a BIF of 0 for the TXAAs. When that outlier was removed, the R^2 increased to 0.96. Moreover, the slope was close to 1.0 (i.e., 0.91). With the measurement of all four THAs, a comparison of the BIFs for THMs and THAs could be made. The R^2 of the linear regression was good (i.e., 0.87), but the slope was less than 1.0 (i.e., 0.69). Again, there may have been less apparent bromine incorporation in the THAs because of steric hindrance and/or the instability of the THAs. Xie and Reckhow (1996) found that the brominated THAs could undergo base-catalyzed hydrolysis. Also, these researchers found that these DBPs could be degraded in the presence of sulfite. Many WWTPs in the U.S. that chlorinate use a sulfur-reducing agent to dechlorinate before discharging the treated wastewater.

Figure 7 shows a comparison of BIFs for dihalogenated DBPs at well nitrified WWTPs in the U.S. When all of the data were examined for the DHANs and DXAAs, the R^2 of the linear regression was 0.74. There were two significant outliers for data sets with very low levels of DCAA (i.e., 2.6-3.0 µg/L), where the other DXAAs were not detected at or above their MRLs (1.0 µg/L each). When those outliers were removed, the R^2 increased to 0.96. Nonetheless, the slope was less than 1.0 (i.e., 0.56). This slope is similar to the one observed in the nationwide DBP occurrence study conducted at DWTPs (Figure 2). With the measurement of all three DHAs, a comparison of the BIFs for DXAAs and DHAs could be made. When all of the data

were examined for the DHANs and DXAAs, the R^2 of the linear regression was 0.46. There were two significant outliers for data sets with very low levels of DCAA (i.e., 3.0 $\mu\text{g/L}$) or dichloroacetaldehyde (i.e., 2.1 $\mu\text{g/L}$), where the other DXAAs or DHAs were not detected at or above their MRLs. When those outliers were removed, the R^2 increased somewhat to 0.60. The slope was less than 1.0 (i.e., 0.72), but was higher than the slope when DXAAs were compared to DHANs. Thus, among the dihalogenated DBPs, bromine incorporation into DHANs appears to be somewhat higher than for DXAAs or DHAs.

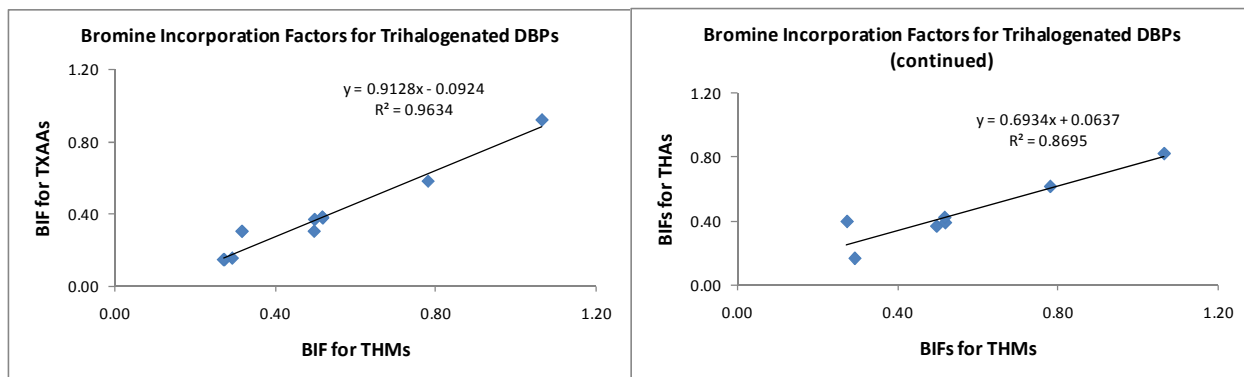


Figure 6. Comparison of BIFs for trihalogenated DBPs at well nitrified WWTPs in the U.S.: (a [left]) THMs and TXAAs; (b [right]) THMs and THAs

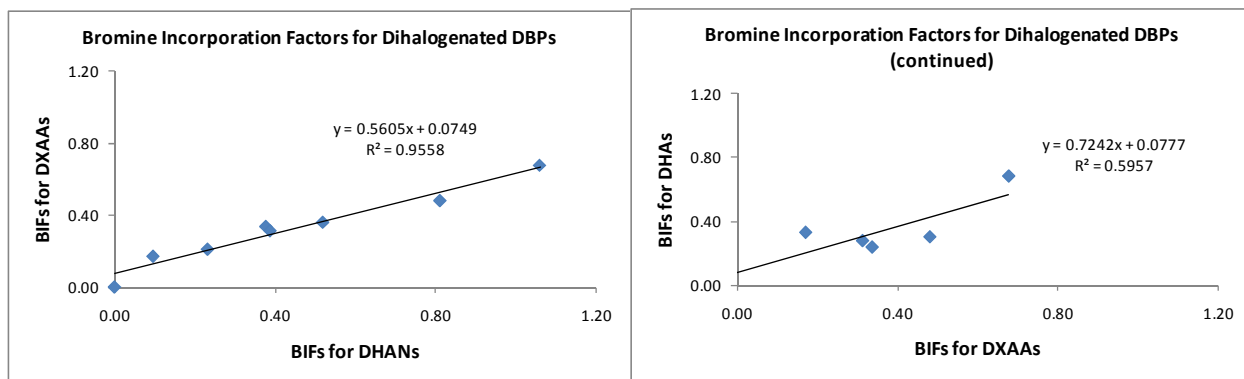


Figure 7. Comparison of BIFs for dihalogenated DBPs at well nitrified WWTPs in the U.S.: (a [left]) DHANs and DXAAs; (b [right]) DXAAs and DHAs

For these WWTPs, the TXAA/DXAA molar ratio was 0.9 to 4.6 (median = 1.2), the DXAA/MXAA molar ratio was 3.4 to 30 (median = 6.7), and the THA/DHA molar ratio was 1.2 to 3.2 (median = 2.0). These ratios were somewhat similar to what was observed at DWTPs in the nationwide DBP occurrence study (Table 1).

For the DWTPs in the wastewater DBP study, the R^2 for the regression between THMs and TXAAs was good (i.e., 0.93) and the slope was somewhat less than 1.0 (i.e., 0.80). In terms of the THAs, the database was small. Nonetheless, the R^2 for the regression between THMs and THAs was good (i.e., 0.88) and the slope was close to 1.0 (i.e., 0.93). When all of the data were examined for the DHANs and DXAAs, the R^2 of the linear regression was 0.48. There were three significant outliers for data sets with very low levels of DCAA (i.e., 2.4-3.8 $\mu\text{g/L}$) or dichloroacetonitrile (i.e., 2.0 $\mu\text{g/L}$), where the other DXAAs or DHANs were not detected at or

above their MRLs. When those outliers were removed, the R^2 increased to 0.86; the slope was somewhat less than 1.0 (i.e., 0.82).

For these DWTPs, the TXAA/DXAA molar ratio was 0.3 to 2.0 (median = 0.7), the DXAA/MXAA molar ratio was 7 to 29, and the THA/DHA molar ratio for one sample with a detectable amount of DHAs was 5.

N-DBP Study

When all of the data in the N-DBP study were examined for the THMs and THAs, the R^2 of the linear regression was 0.58. There were two significant outliers for data sets with very low levels of chloral hydrate (i.e., 1.3-2.4 $\mu\text{g/L}$), where the other THAs were not detected at or above their MRLs. When those two outliers were removed, the R^2 increased to 0.84; the slope was somewhat less than 1.0 (i.e., 0.75). This is consistent with results from the wastewater DBP study.

Barcelona Study

In four of the five samples from Barcelona (Spain), bromoform was the dominant THM. Figure 8 shows a comparison of BIFs for THMs and TXAAs. Results were available from two laboratories, one in the U.S.A. and the other in Europe. The major difference was the reporting of higher values for the brominated TXAAs from the European laboratory. Both laboratories had slopes less than 1.0 for the regression between the TXAAs and THMs, especially the U.S. laboratory. Compared to the occurrence of other brominated DBPs from this sample event, some of the brominated TXAA results from the U.S. laboratory looked low. In fact, one use of calculating BIFs can be a quality control check on data, in helping to identify random or systematic errors. Based on the good R^2 values for the regression lines (i.e., 0.89-0.90), there appears to have been a systematic error.

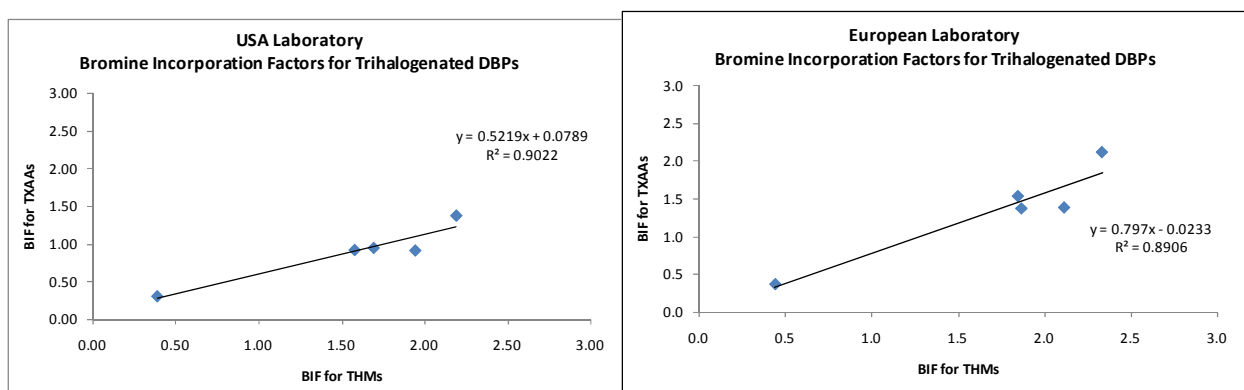


Figure 8. Comparison of BIFs for THMs and TXAAs in Barcelona (Spain): (a [left]) results from U.S. laboratory; (b [right]) results from European laboratory

Figure 9 shows some additional comparisons of BIFs for the samples from Barcelona. The R^2 for the regression between the THMs and THAs was fair (i.e., 0.56) and the slope was somewhat less than 1.0 (0.79). Alternatively, the R^2 for the regression between the DHANs and DXAAs was excellent (i.e., 0.98) and the slope was close to 1.0 (0.94). This data set provided an

opportunity to examine much higher BIF values than in the U.S. databases. In general, there were similar trends.

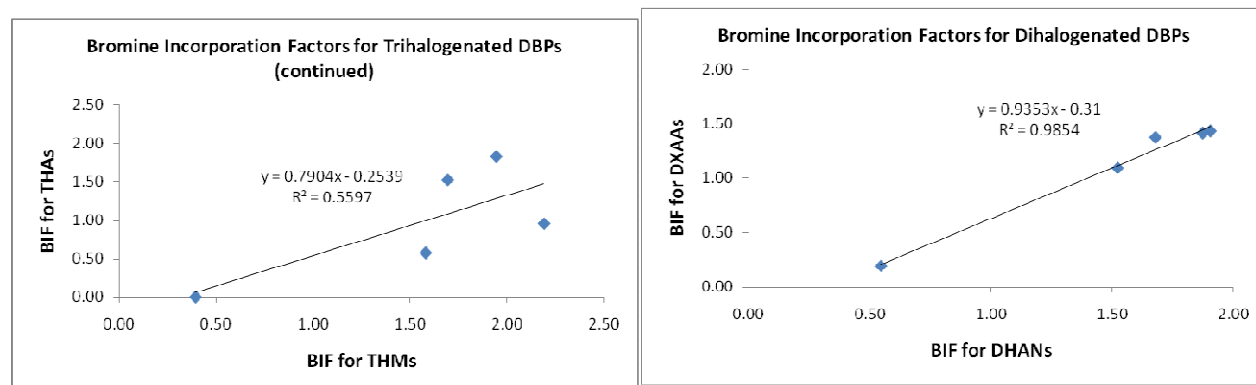


Figure 9. Comparison of BIFs for other DBPs in Barcelona (Spain): (a [left]) THMs and THAs; (b [right]) DHANs and DXAAs

For the Barcelona samples, the TXAA/DXAA molar ratio was 0.8 to 2.0 and the DXAA/MXAA molar ratio was 13 to 14. These ratios were similar to what was observed in the U.S. studies.

Chlorinated RO Concentrates

A large batch of RO concentrate from a U.S. source water was chlorinated every two weeks or so over a period of many months. Table 4 shows the BIFs for the chlorinated RO concentrates. Presuming that the DBP precursors were stable over the timeframe of this experiment and that each new chlorination was done consistently, one would expect similar BIFs over time. Indeed, most of these values were consistent for the different DBP subclasses. Among the trihalogenated species, there was more bromine incorporation into the THMs than into the THAs or THNMs, especially the latter DBP subclass. In fact, for a number of samples, a relatively large peak with a retention time that matched bromopicrin was observed (an electron capture detector was used with that gas chromatographic method) (Chinn et al., 2007). However, the occurrence of such a large bromopicrin peak was inconsistent with the very small occurrence of the mixed bromochloro THNMs or the very small occurrence of other fully brominated DBP species. Thus, the use of BIF data suggest that the bromopicrin results were false positives.

Among the dihalogenated DBPs, the DHANs and DHAs had similar BIF values, whereas most of the BIFs for the DHNMs were 0. That may have been due (in part) to the occurrence of a relatively low level of dichloronitromethane, where the other DHNMs were typically not detected at or above their MRLs.

As part of the study, chlorinated RO concentrates were kept at 4°C for up to approximately two weeks. At the end of each hold time, a stability study sample was run. Table 5 shows the BIFs for those samples. BIFs for the THMs were unchanged, whereas they were somewhat lower for the THAs and were 0 for the THNMs. In terms of the THAs, this was due to stability issues for this class of DBPs. For one sample, there was major degradation of the brominated THAs. The latter sample was accompanied by a large increase in the concentration

of dichloroacetaldehyde. Chinn and colleagues (2007) found that brominated THAs could, under certain conditions, degrade via a dehalogenation mechanism. In terms of the DHANs, the BIFs were relatively unchanged, whereas the BIF values for the DHAs were somewhat lower. Thus, selective degradation of certain species can result in a change in the BIF values.

Table 4. Bromine incorporation factors for DBPs detected in chlorinated RO concentrates

DBP Subclass	Minimum	10th Percentile	25th Percentile	Median	75th Percentile	90th Percentile	Maximum
Trihalogenated DBPs:							
THMs	0.35	0.36	0.38	0.41	0.42	0.44	0.45
THAs	0.12	0.14	0.16	0.18	0.18	0.19	0.20
THNMs	0.00	0.00	0.00	0.05	0.13	0.18	0.27
Dihalogenated DBPs:							
DHANs	0.31	0.33	0.34	0.36	0.39	0.41	0.44
DHAs	0.25	0.26	0.32	0.39	0.44	0.51	0.56
DHNMs	0.00	0.00	0.00	0.00	0.00	0.00	0.32
Monohalogenated DBPs:							
MHANs	0.39	0.41	0.42	0.44	0.46	0.49	0.50

Table 5. Bromine incorporation factors for DBPs detected in stability study samples

DBP Subclass	Minimum	10th Percentile	25th Percentile	Median	75th Percentile	90th Percentile	Maximum
Trihalogenated DBPs:							
THMs	0.37	0.38	0.40	0.41	0.44	0.45	0.47
THAs	0.00	0.06	0.10	0.12	0.14	0.17	0.17
THNMs	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Dihalogenated DBPs:							
DHANs	0.33	0.35	0.35	0.37	0.42	0.51	0.64
DHAs	0.13	0.16	0.20	0.24	0.26	0.29	0.36
DHNMs	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Monohalogenated DBPs:							
MHANs	0.18	0.31	0.41	0.43	0.45	0.48	0.48

For the chlorinated RO concentrates, the THA/DHA molar ratio was 4.5 to 11 (median = 8.4), the THNM/DHNM molar ratio was 4.9 to 17 (median = 9.2), and the DHAN/MHAN molar ratio was 18 to 39 (median = 25) (Table 6). The ratios for the THNMs/DHNMs and the DHANs/MHANs were similar to what was observed in U.S. waters (Table 1), whereas the THA/DHA ratios were at the high-end of what has been observed in U.S. waters. This may reflect (in part) the use of chlorine only in the RO study, whereas chloramines were used by many plants in some of the U.S. occurrence studies. Because the RO process concentrated the TOC by two orders of magnitude, it presumably also resulted in concentrating DBP precursors by a similar amount. So chlorination of RO concentrates could serve as a tool to probe possible DBP occurrence in non-concentrated (ambient) samples.

For the stability study samples, some of the ratios changed somewhat (Table 7). This reflects differences in the amount of degradation between the two DBP subclasses.

Table 6. Preponderance of mono-, di-, and trihalogenated DBP species in chlorinated RO concentrates

Statistic	DHANs/MHANs	THAs/DHAs	THNMs/DHNMS
Minimum	18	4.5	4.9
25th percentile	21	7.3	7.8
Median	25	8.4	9.2
75th percentile	30	9.9	13
Maximum	39	11	17

Table 7. Preponderance of mono-, di-, and trihalogenated DBP species in stability study samples

Statistic	DHANs/MHANs	THAs/DHAs	THNMs/DHNMS
Minimum	1.8	2.5	5.1
25th percentile	18	5.2	13
Median	21	5.8	16
75th percentile	22	6.8	21
Maximum	35	12	48

CONCLUSIONS

- Among the trihalogenated DBP species, bromine incorporation into TXAAs, THAs, and THNMs was similar to or less than that of the THMs. When there was less apparent bromine incorporation into the non-THM DBPs, it may have been due to steric hindrance, relative instability of some brominated DBPs, and/or the presence of the DBPs at low levels relative to their MRLs.
- Among the dihalogenated DBP species, bromine incorporation into the DHANs was usually higher than that of the other DBP subclasses. However, even when there was lower bromine incorporation into other DBP subclasses, the trend was consistent (i.e., in most cases, the regression between DBP subclasses had a high R^2 ; the same was usually true for the trihalogenated DBPs).
- For DBPs in which standards were not available for all species (e.g., haloacetamides), it is possible to estimate the occurrence of the missing DBPs based on BIFs.
- The determination of BIFs can be used as a quality control tool in evaluating DBP data, in other words, to determine if the formation of brominated DBPs in different DBP subclasses are consistent or not.
- In epidemiology studies, finding an association between brominated DBP species (e.g., THMs and/or HAAs) and a particular adverse health effect may be due to the presence of other brominated DBPs of higher health concern (e.g., HANs, HNMs, HAs, haloacetamides).
- In addition to BIFs, the preponderance of mono-, di-, and trihalogenated DBP species should be examined. The relative degree of halogenation may be due to the nature of the organic matter, the disinfectant(s) applied, and/or the instability of certain species.
- For many DBP classes, there are nine bromo- and chloro-substituted DBP species. However, in many studies, as little as one DBP species (e.g., the trichlorinated species) in that class is measured, which can greatly underestimate actual DBP formation and exposure.

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