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# Occurrence of Disinfection Byproducts in United States Wastewater Treatment Plant Effluents

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Effluents from wastewater treatment plants (WWTPs) contain disinfection byproducts (DBPs) of health concern when the water is utilized downstream as a potable water supply. The pattern of DBP formation was strongly affected by whether or not the WWTP achieved good nitrification. Chlorine addition to poorly nitrified effluents formed low levels of halogenated DBPs, except for (in some cases) dihalogenated acetic acids, but often substantial amounts of N-nitrosodimethylamine (NDMA). Chlorination of well-nitrified effluent typically resulted in substantial formation of halogenated DBPs but much less NDMA. For example, on a median basis after chlorine addition, the well-nitrified effluents had 57  $\mu\text{g/L}$  of trihalomethanes [THMs] and 3 ng/L of NDMA, while the poorly nitrified effluents had 2  $\mu\text{g/L}$  of THMs and 11 ng/L of NDMA. DBPs with amino acid precursors (haloacetonitriles, haloacetaldehydes) formed at substantial levels after chlorination of well-nitrified effluent. The formation of halogenated DBPs but not that of NDMA correlated with the formation of THMs in WWTP effluents disinfected with free chlorine. However, THM formation did not correlate with the formation of other DBPs in effluents disinfected with chloramines. Because of the relatively high levels of bromide in treated wastewater, bromine incorporation was observed in various classes of DBPs.

## Introduction

In recent years, greater portions of treated wastewater are included in drinking water supplies through reclamation,

recycling, and reuse (intentional and incidental) (1, 2). Wastewater treatment plants (WWTPs) are sources of disinfection byproducts (DBPs) when chlorine or chloramine disinfection is practiced (2). While DBPs generally are not regulated in WWTP effluents, some trihalomethanes (THMs) (e.g., chloroform) are designated in National Pollutant Discharge Elimination System (NPDES) discharge permits. This study focuses on the presence of reclaimed wastewater in source water for potable water treatment plants. Although losses of DBPs may occur between the point of wastewater discharge and point of potable water intake (3), the DBP levels found in this study represent a maximum to be expected.

WWTPs generally add chlorine or apply ultraviolet (UV) light for final disinfection prior to discharge. Research on DBP formation in treated wastewater has included broad screening analyses (e.g., gas chromatography/mass spectrometry [GC/MS]) to identify unknown DBPs (4), target-compound analyses for specific known DBPs (1, 2), and bulk parameters (e.g., total organic halogen [TOX]) (5). The types and amounts of DBPs that can be formed from wastewater effluent organic matter (EfOM) depend in part on the level of wastewater treatment and especially on ammonia ( $\text{NH}_3$ ) and dissolved organic nitrogen (DON) concentrations (2, 6). A well-nitrified WWTP effluent with a low ammonia concentration ( $<0.5 \text{ mg/L as N}$ ) produced large amounts of THMs, whereas poorly nitrified effluents (e.g.,  $\text{NH}_3\text{-N} > 5 \text{ mg/L}$ ) generally inhibited the production of THMs (7). Chlorination (oxidation) of amino acids can result in the formation of aldehydes and nitriles, with subsequent or concomitant chlorine substitution to form chloral hydrate (trichloroacetaldehyde) and dichloroacetonitrile, respectively (8). Trehy and colleagues (8) found that chlorinated wastewater from an extended aeration treatment plant produced 32–80  $\mu\text{g/L}$  of chloroform, 7–14  $\mu\text{g/L}$  of dichloroacetonitrile, and 20–38  $\mu\text{g/L}$  of chloral hydrate. The chlorination of uracil can form 5-chlorouracil (9), with a higher chlorine dose destroying the aromatic ring and forming chloral hydrate and haloacetic acids (HAAs) (7).

In a study of DBP formation in reclaimed water (1), THM levels in chlorinated reclaimed water were 35–86  $\mu\text{g/L}$  and HAAs were 99–262  $\mu\text{g/L}$ . Samples collected upstream of the chlorine addition point had 0.7–3.2  $\mu\text{g/L}$  of THMs and 1–6  $\mu\text{g/L}$  of HAAs, most likely because THMs and HAAs were present in the drinking water source, which serves as the “carrier” water for sewage. Because THMs and trihalogenated HAAs (TXAAs) are not readily biodegradable (3), they may persist in the treated wastewater before chlorine addition (10, 11).

Three other classes of DBPs were in relatively high concentrations in chlorinated reclaimed water: aldehydes (21–114  $\mu\text{g/L}$ ), chloral hydrate (44–76  $\mu\text{g/L}$ ), and haloacetonitriles (HANs) (14–33  $\mu\text{g/L}$ ). In addition to halogenated byproducts, nonhalogenated DBPs such as nitrosamines (e.g., N-nitrosodimethylamine [NDMA]) have been found in treated wastewater, where their precursors are secondary amines (12, 13). In one study, chlorination of secondary wastewater effluent typically resulted in the formation of 20–100 ng/L of NDMA (13). Nitrification of wastewater to completely remove ammonia prior to chlorine addition reduced NDMA formation by approximately an order of magnitude (12).

The objective of this study was to determine the occurrence of DBPs at WWTPs, with a focus on emerging DBPs of health concern (14–18). Most WWTP studies have examined only selected halogenated DBPs or nitrosamines. Thus, in

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this research, a combination of DBPs was studied, including emerging carbonaceous, nitrogenous, halogenated, and nonhalogenated species. Moreover, because nitrification has a profound impact on effluent water quality in general (6), the impact of well-nitrified versus poorly nitrified EfOM on DBP occurrence was examined.

## Experimental Methods

**Survey.** A survey was conducted in different seasons at 23 WWTPs in the United States; they were geographically diverse and employed a range of treatment processes (6). For WWTPs that used chlorine disinfection, the secondary effluent was sampled prior to chlorination to determine background levels of DBPs. WWTP discharges, after chlorination (and dechlorination when practiced), were sampled. At selected WWTPs, samples were collected after chlorination and before dechlorination. Although sulfur-reducing agents (commonly used for dechlorination) can destroy some DBPs (19), DBP levels did not differ before and after dechlorination.

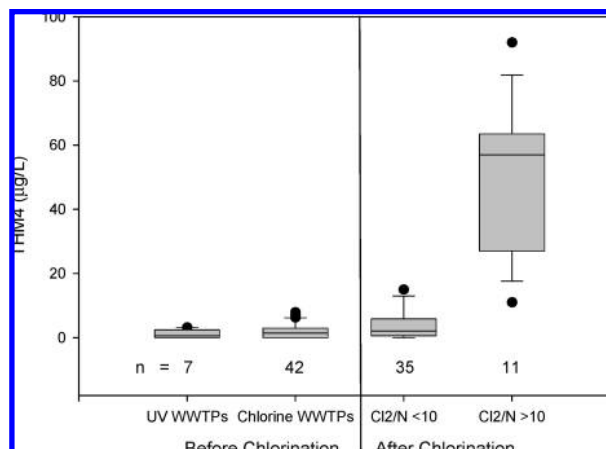
**Analytical Parameters.** Samples were analyzed for dissolved organic carbon (DOC), DON, ultraviolet absorbance (UVA) at 254 nm, bromide, total iodine, and ammonia. Details on the analytical methods for these parameters are presented in the Supporting Information. Information on the levels of DBP precursors in this study are provided in the Supporting Information.

DBPs regulated in drinking water (i.e., THMs and HAAs) and emerging DBPs that are likely associated with elevated DON and dissolved inorganic nitrogen precursors in treated wastewater (8, 13) were measured using GC and GC/MS methods (20) before and after full-scale chlorination to differentiate their presence in wastewater from their formation during chlorination. The emerging DBPs included six iodine-containing THMs that are not part of the four species regulated in drinking water, HANs, haloacetaldehydes, halonitromethanes, and nitrosamines. In addition to chloral hydrate, dihalogenated and/or brominated analogues of chloral hydrate were measured (20). Besides chloropicrin (trichloronitromethane), dihalogenated nitromethanes were measured (20). Selected samples were analyzed for TOX (21) (those results are discussed in the Supporting Information). Details of the analytical methods for the DBPs are discussed in the Supporting Information.

## Results and Discussion

**Disinfection and Oxidation Practices.** At the WWTPs in this study, a disinfectant was usually not applied until after final sedimentation or filtration. Then, chlorine (gas or hypochlorite solution) or UV disinfection typically was utilized. At two WWTPs, ammonia was added along with the chlorine (to well-nitrified EfOMs) to form chloramines instead of free chlorine. In one instance, a WWTP indicated that they periodically added chlorine to the aeration basins in addition to the plant effluent for controlling filamentous bacteria and sludge bulking. Some WWTPs dechlorinated the effluent (e.g., with sodium bisulfite) prior to discharge.

WWTPs with partial or poor nitrification (i.e.,  $\text{NH}_3\text{-N} \geq 2.0$  mg/L) had chlorine doses (for those that used chlorine) of 0.6 to 22 mg/L as  $\text{Cl}_2$  (median and 75th percentile doses of 2.7 and 8.0 mg/L as  $\text{Cl}_2$ , respectively). (All data are provided in Figure 1 of the Supporting Information.) The  $\text{Cl}_2/\text{N}$  ratios for these WWTPs ranged from 0.06 to 3.1 mg/mg (median and 75th percentile ratios of 0.3 and 0.5 mg/mg, respectively). In order to achieve breakpoint chlorination, a chlorine dose of 7.6 mg/L as  $\text{Cl}_2$  is *theoretically* required for each 1.0 mg/L of  $\text{NH}_3\text{-N}$ . However, in actual WWTP practice, a higher chlorine dose (e.g., 10 mg/L for each 1.0 mg/L of  $\text{NH}_3\text{-N}$ ) is required (22). Therefore, the presence of a high amount of ammonia in many of the secondary- and tertiary-treated wastewaters resulted in the formation of combined chlorine (chloramines) when chlorine was added.



**FIGURE 1. Occurrence of THMs at participating WWTPs (top and bottom of box = 75th and 25th percentiles, respectively; top and bottom of whiskers = 90th and 10th percentiles, respectively; line across inside of box = median [50th percentile]; points beyond whiskers = outliers;  $n$  = number of samples). Reproduced from ref 2. Copyright 2008 AWWA Research Foundation.**

WWTPs with good nitrification (i.e.,  $\text{NH}_3\text{-N} < 2.0$  mg/L) had chlorine doses (for those that used chlorine) of 0.3 to 14 mg/L as  $\text{Cl}_2$  (median and 75th percentile doses of 2.4 and 5.1 mg/L as  $\text{Cl}_2$ , respectively; Figure 1 of the Supporting Information). The  $\text{Cl}_2/\text{N}$  ratios for these WWTPs ranged from 0.4 to >400 mg/mg (median and 75th percentile ratios of 30 and >100 mg/mg, respectively). Therefore, the majority of these WWTPs clearly achieved breakpoint chlorination and produced a free chlorine residual.

For WWTPs in which the chlorine dose was reported (not every WWTP provided their operational data to the research team), the data were segmented into two groups: WWTPs that did not achieve breakpoint chlorination (i.e.,  $\text{Cl}_2/\text{N} < 10$  mg/mg) and those that did (i.e.,  $\text{Cl}_2/\text{N} > 10$  mg/mg). WWTPs that did not achieve breakpoint chlorination had ammonia–nitrogen concentrations of 0.5 to 44 mg/L (25th percentile and median levels of 2.6 and 11 mg/L, respectively) and  $\text{Cl}_2/\text{N}$  ratios of 0.06 to 9.1 mg/mg (median and 75th percentile ratios of 0.4 and 0.6 mg/mg, respectively). In addition to all of the poorly nitrified EfOMs, some (but not many) of the well-nitrified EfOMs were in this group. WWTPs that did achieve breakpoint chlorination had ammonia–nitrogen concentrations from not detected (ND, <0.03) to 0.2 mg/L and had  $\text{Cl}_2/\text{N}$  ratios from 25 to >400 mg/mg.

**Background Levels of Halogenated DBPs.** Low  $\mu\text{g/L}$  levels (ND to 7.9  $\mu\text{g/L}$ ; median = 1.3  $\mu\text{g/L}$ ) of THMs (the sum of four species [THM4]) were usually detected before chlorine was added (Figure 1). In addition, HAAs (the sum of nine species [HAA9]) often were present (ND to 35  $\mu\text{g/L}$ ; median = 6.2  $\mu\text{g/L}$ ) (Figures 2,3 of the Supporting Information). Before chlorination, typically neither chloropicrin nor the HANs were detected. The THMs and HAAs were most likely in the influents of the WWTPs, with their source due (in large part) to chlorinated drinking water. The relative absence of THMs compared to HAAs may have been due (in part) to the volatilization of the THMs in the aeration basins. Henry's constants ( $H_c$ ) for THMs (i.e.,  $4.4 \times 10^{-4}$  to  $7.8 \times 10^{-3}$  atm  $\text{m}^3/\text{mol}$ ) indicate that this class of DBPs are more volatile than the HAAs ( $H_c = 8.4 \times 10^{-10}$  to  $3.5 \times 10^{-7}$  atm  $\text{m}^3/\text{mol}$ ) (3). Moreover, THMs can undergo dehalogenation during anoxic treatment (23). In addition, the amount of dihalogenated HAAs (DXAAs) before chlorination was typically low compared to that of the TXAAs. This may have been due to aerobic biodegradation in the biological treatment processes at the WWTPs. DXAAs showed more than a 50% loss in EfOM in bioreactors under aerobic conditions, whereas TXAAs were

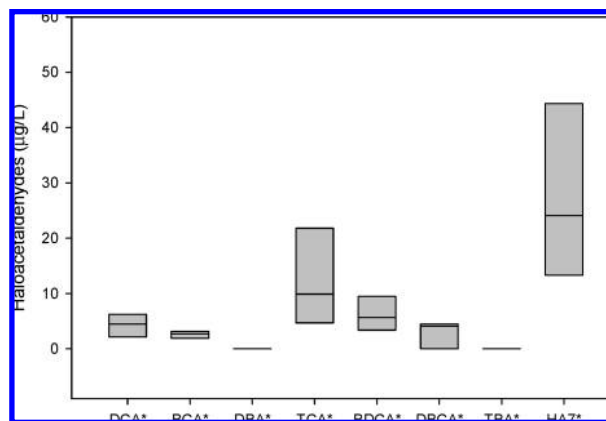
relatively stable (3). Moreover, calculated bioindices (these were computed from EPIWIN software following the group contribution method for predicting probability and rate of aerobic biodegradation) of DXAAs were 0.54–0.62, which were substantially higher than those for TXAAs (i.e., 0.09–0.22) (3). Figure 1 and Figures 2 and 3 of the Supporting Information show the background occurrence (before chlorine addition) of the THMs and HAAs separately for the WWTPs dosed with UV or chlorine.

**Formation of Halogenated DBPs at WWTPs Using Chloramines.** After chlorination (and dechlorination), relatively low levels of halogenated DBPs were detected at most of the WWTPs (e.g., median and 75th percentile values: 4.9 and 15  $\mu\text{g/L}$  of THMs, 5.2 and 13  $\mu\text{g/L}$  of DXAAs, 12 and 22  $\mu\text{g/L}$  of TXAAs, respectively) in spite of relatively high levels of DBP precursors in the EfOM, e.g., WWTPs with no nitrification had median formation potentials (FPs) of 259  $\mu\text{g/L}$  for THMs, 155  $\mu\text{g/L}$  for DXAAs, and 131  $\mu\text{g/L}$  for TXAAs (6). A good relationship was found between THM or HAA FP and UVA at 254  $\text{cm}^{-1}$  of the EfOM, which suggested that humic substances were an important source of THM and HAA precursors (2). The presence of chloramines during the disinfection process at many of the WWTPs probably reduced the formation of most of the halogenated DBPs because chloramines are much less reactive with humic substances to form THMs and HAAs than free chlorine (24).

WWTP effluents disinfected with combined chlorine typically had low levels of THMs (median and 90th percentile increases of 0.6 and 4.1  $\mu\text{g/L}$ , respectively) or HAAs (median and 90th percentile increases of 0 and 8.6  $\mu\text{g/L}$  of TXAAs, respectively; median and 90th percentile increases of 2.7 and 14  $\mu\text{g/L}$  of DXAAs, respectively) formed over the background concentrations (Figure 1 and Figures 2,3 of the Supporting Information). For the WWTPs at which THMs or HAAs were quantitatively detected in the background samples, the increases in formation over the background concentrations (i.e., increase/background) were relatively low for THMs (median and 90th percentile increases of 0 and 2.1x, respectively) and TXAAs (median and 90th percentile increases of 0 and 2.8x, respectively). However, some WWTPs showed a substantial increase in the formation of DXAAs (median and 90th percentile increases of 1.0x and 4.9x, respectively). In drinking water, chloramines generally minimize the formation of THMs and TXAAs more than for DXAAs (25, 26). Hong and colleagues (26) found that the direct reaction of monochloramine with dissolved organic matter in drinking water was the major pathway for HAA formation during chloramination. These researchers found that at least 80% of the HAAs formed from chloramines were DXAAs, whereas the formation of TXAAs was usually negligible. Disinfection of treated wastewater with combined chlorine had a similar impact as humic substances and other HAA precursors in EfOM will be impacted by the same mechanism.

For the WWTP effluents disinfected with combined chlorine, the concentration of HANs after chlorine addition was ND to 12  $\mu\text{g/L}$  (median and 75th percentile levels of 0.3 and 0.8  $\mu\text{g/L}$ , respectively), and chloropicrin was present from ND to 0.6  $\mu\text{g/L}$ . However, most of the HANs and all of the chloropicrin were present before chlorine addition at these WWTPs (after chlorine addition, the median and 90th percentile increases in HANs were 0.3 and 2.8  $\mu\text{g/L}$ , respectively). Other DBPs were measured at selected WWTPs, and low levels were detected: ND to 6.4  $\mu\text{g/L}$  of dihalogenated acetaldehydes (DHAs) and ND to 2.0  $\mu\text{g/L}$  of trihalogenated acetaldehydes (THAs) (Figure 4 of the Supporting Information), whereas dihalogenated nitromethanes were not detected.

**Formation of Halogenated DBPs at WWTPs Using Free Chlorine.** For the WWTP effluents disinfected with free chlorine, THMs concentrations were 11 to 92  $\mu\text{g/L}$  (median



**FIGURE 2. Speciation of haloacetaldehydes (HAs) at participating WWTPs after chlorination, where  $\text{Cl}_2/\text{N} > 10 \text{ mg/mg}$ ;  $n = 7$  (count too low to determine 10th and 90th percentile values; therefore, no whiskers or outliers in these plots). \*Key to acronyms: B = bromo-, C = chloro-, A = acetaldehyde, D = di-, T = tri-, and 7 = sum of seven species (e.g., TBA = tribromoacetaldehyde).**

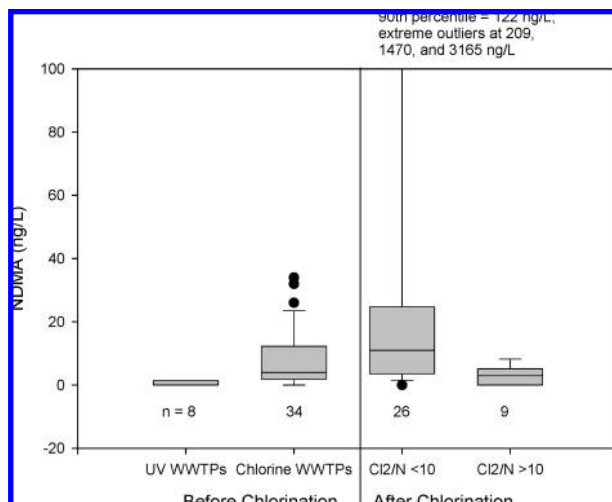
= 57  $\mu\text{g/L}$ ; Figure 1). The sum of the nine HAAs was 13 to 136  $\mu\text{g/L}$  (median = 70  $\mu\text{g/L}$ ; Figures 2,3 of the Supporting Information). HAN levels were 0.9 to 30  $\mu\text{g/L}$  (median = 16  $\mu\text{g/L}$ ), and DHAs and THAs were present at 2.1 to 12  $\mu\text{g/L}$  (median = 7.2  $\mu\text{g/L}$ ) and 3.8 to 49  $\mu\text{g/L}$  (median = 16  $\mu\text{g/L}$ ), respectively (Figure 4 of the Supporting Information). Chloropicrin and dihalogenated nitromethanes were ND to 0.7  $\mu\text{g/L}$  and ND to 0.5  $\mu\text{g/L}$ , respectively. An iodinated THM (i.e., dichloriodomethane) was detected in one chlorinated effluent (at 1.6  $\mu\text{g/L}$ ) (where its minimum reporting level [MRL] was typically 1.0  $\mu\text{g/L}$ ). For WWTPs with good nitrification, median FPs were 231  $\mu\text{g/L}$  for THMs, 117  $\mu\text{g/L}$  for DXAAs, 113  $\mu\text{g/L}$  for TXAAs, 13  $\mu\text{g/L}$  for HANs, 4.0  $\mu\text{g/L}$  for DHAs, and 50  $\mu\text{g/L}$  for THAs (6). As expected, full-scale formation was less than that formed in the FP tests. However, the trend for the concentrations was (in general) the same: THMs ~ HAAs > THAs ~ HANs > DHAs.

The levels of THMs, HAAs, HANs, and THAs at the WWTPs that achieved breakpoint chlorination were similar to those historically detected at an extended aeration treatment plant (8) and at a set of five reclamation plants (1). The levels detected after chlorine addition were substantially higher than the background amounts. Median and 75th percentile increases in concentrations of THMs were 47 and 58  $\mu\text{g/L}$  (18x and 25x), respectively. For TXAAs, the increases were 36 and 49  $\mu\text{g/L}$  (13x and 22x), respectively. For DXAAs, the increases were 28 and 34  $\mu\text{g/L}$  (11x and 12x), respectively. For HANs, the increases were 16 and 19  $\mu\text{g/L}$  (>1x), respectively.

This is the first account of the presence of analogs of chloral hydrate in treated wastewater (Figure 2). Some of the other haloacetaldehydes are more toxic than chloral hydrate (16). At WWTPs that achieved breakpoint chlorination, chloral hydrate accounted for 23–53% (median = 35%) of the percentage of the sum of seven haloacetaldehydes (on a weight basis). Disinfection in the presence of chloramines instead of free chlorine controlled the formation of THAs much more than that of DHAs (Figure 4 of the Supporting Information), similar to the relative efficacy of chloramines in controlling the formation of TXAAs better than that of the DXAAs.

The levels of DBPs formed at the WWTPs that achieved breakpoint chlorination were similar to what was formed in drinking water (20, 27), except for a higher formation of the HANs, a class of nitrogenous DBPs, and the haloacetaldehydes, a class of carbonaceous DBPs (see Supporting Information for further discussion). Trehy and colleagues





**FIGURE 3. Occurrence of NDMA at participating WWTPs. Reproduced from ref 2. Copyright 2008 AWWA Research Foundation.**

(8) studied chlorinated lake waters and chlorinated wastewater and found that chloroform formation was independent of the formation of dichloroacetonitrile and chloral hydrate, which suggests different precursors for these chlorination byproducts (i.e., humic substances versus amino acids or other nitrogenous substances, whereas treated wastewater would have relatively more nitrogenous substances). In terms of the drinking water treatment plants in the aforementioned survey (27), the concentration of DON in the plant influents (range [median] = 0.07–0.49 [0.30] mg/L as N) was substantially lower than that of the WWTPs in this study, which explains (in part) the difference in formation of DBPs with amino acid precursors (i.e., HANs, haloacetaldehydes).

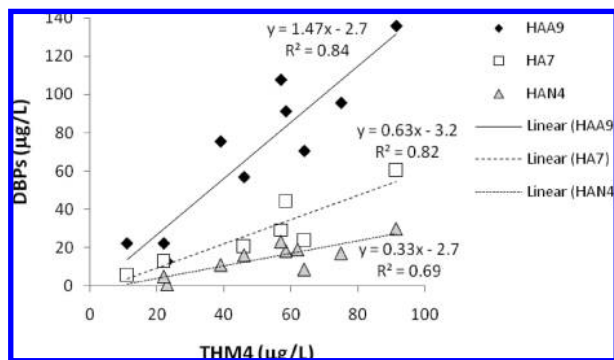
**Nitrosamines.** Two of the nitrosamines were detected frequently in the treated wastewater before chlorine addition (Figure 3 and Figure 5 of the Supporting Information). NDMA concentrations of ND to 34 ng/L (median and 75th percentile levels of 2.7 and 8.5 ng/L, respectively) and N-nitrosomorpholine (NMOR) ranged from ND to 12700 ng/L (median and 75th percentile values of 5.5 and 17 ng/L, respectively). At one WWTP, the concentrations of NMOR before chlorination was consistently very high and variable (i.e., 130, 1561, and 12700 ng/L for different sample observations). NDMA and NMOR may have been present in the influents to the WWTPs (e.g., NDMA and NMOR have been detected in toiletries and cosmetic products (28) and in the rubber and tire industry (29) and/or were formed at the WWTPs through a “nitrosation” pathway (12). In other studies, nitrosation was found to affect the formation of cyanide at WWTPs (30). NDMA and NMOR had higher levels (before chlorine or UV disinfection) at the chlorine WWTPs when compared to the UV ones, which suggests that some of the WWTPs may have applied some chlorine upstream of the plant effluent. For example, at one water recycling plant, chlorine was applied in two locations, where only the second location was for disinfection. During one sample event at the reclamation plant, pre- and postchlorine doses were 4 and 18 mg/L as  $\text{Cl}_2$ , respectively. Although most of the NDMA at this plant was formed during the disinfection process (e.g., 3165 ng/L was detected at the plant effluent), a substantial amount was formed during prechlorination (e.g., 215 ng/L was detected before the disinfection process). In terms of the other nitrosamines, they were seldom detected or (i.e., N-nitrosodiethylamine [NDEA], N-nitrosodipropylamine [NDPA], N-nitrosopiperidine, and N-nitrosodibutylamine) were usually present at low ng/L levels (typically  $\leq 4$  ng/L) in the treated water before chlorine addition.

After chlorination, NDMA sometimes increased when chloramines were the disinfectant (Figure 3). NDMA concentrations at the WWTPs with a  $\text{Cl}_2/\text{N}$  ratio  $<10$  mg/mg were from ND to 3165 ng/L (median and 75th percentile levels of 11 and 24 ng/L, respectively). In contrast, NDMA levels at the WWTPs with a  $\text{Cl}_2/\text{N}$  ratio  $>10$  mg/mg were lower, from ND to 8.2 ng/L (median = 3.0 ng/L). The WWTP effluents disinfected with free chlorine typically had low levels of NDMA over the background concentrations (median, 75th percentile, and maximum increases of 1.0, 1.8, and 5.8 ng/L, respectively). In contrast, for the WWTP effluents disinfected with chloramines, the median, 75th percentile, 90th percentile, and maximum increases in NDMA over the background concentrations were 0, 4.0, 132, and 3,163 ng/L, respectively. For the WWTPs at which NDMA was quantitatively detected in the background samples, the increases in formation over the background concentrations were relatively low for WWTP effluents disinfected with free chlorine (median and maximum increases of 0.2x and 0.7x, respectively), whereas there was sometimes a substantial increase in NDMA formation in the WWTP effluents disinfected with chloramines (median, 75th, and 90th percentile increases of 0, 0.4x and 313x, respectively). This is consistent with other research that demonstrated that NDMA is preferentially formed in the presence of chloramines (i.e.,  $\text{Cl}_2/\text{N}$  ratio  $<10$  mg/mg) (12). For WWTPs with no nitrification, the median NDMA FP was 878 ng/L (6). The NDMA FP samples were held for 3 days as NDMA formation is relatively slow (31). Thus, instantaneous NDMA formation was usually substantially less than its FP. However, the NDMA FP of the aforementioned reclamation plant with high NDMA formation (i.e., 1470–3165 ng/L) was relatively consistent with its FP (i.e., 1288–1510 ng/L). Note that FP tests were run under controlled and well-mixed conditions, whereas full-scale operations can have mixing deficiencies that may affect NDMA formation. For example, poor mixing can lead to localized formation of dichloramine, which can increase NDMA formation (32).

NMOR concentrations after disinfection were not substantially different than those before chlorine addition (Figure 5 of the Supporting Information). For the WWTP effluents disinfected with free chlorine, low levels of NMOR (median and maximum increases of 0.1 and 1.2 ng/L, respectively) were formed over the background concentrations. For the WWTP effluents disinfected with chloramines, the median, 75th percentile, 90th percentile, and maximum increases in NMOR over the background concentrations were 0.6, 1.2, 5.6, and 40 ng/L, respectively. The increases in formation over the background concentrations were found to be relatively low for WWTP effluents disinfected with either free chlorine (median and maximum increases of 0 and 0.5x, respectively) or with chloramines (median, 90th percentile, and maximum increases of 0, 0.4x and 1.3x, respectively). Other nitrosamines showed some increases in the presence of chloramines (not chlorine), albeit infrequently in the concentrations of NDEA (to 3–30 ng/L); however the median and 75th percentile values were ND and 1.3 ng/L, respectively, N-nitrosopyrrolidine (NPYR) (to 8–22 ng/L at the WWTP with the highest NDMA formation), and NDPA (to 3.4 and 4.1 ng/L at two WWTPs). The impact of UV and RO on the nitrosamines is discussed in the Supporting Information.

As an example of one poorly nitrifying WWTP, NDMA and NMOR were present before chlorination at levels of 8.5 and 72 ng/L, respectively. After chlorine addition ( $\text{Cl}_2/\text{N}$  = 0.3 mg/mg), the concentration of NDMA increased dramatically (to 209 ng/L), but NMOR had a small increase (to 99 ng/L). Thus, NDMA was a chloramine DBP, whereas NMOR was not a DBP per se.

**Implications for Downstream Users.** Because of the toxicity associated with emerging DBPs (e.g., nitrosamines),

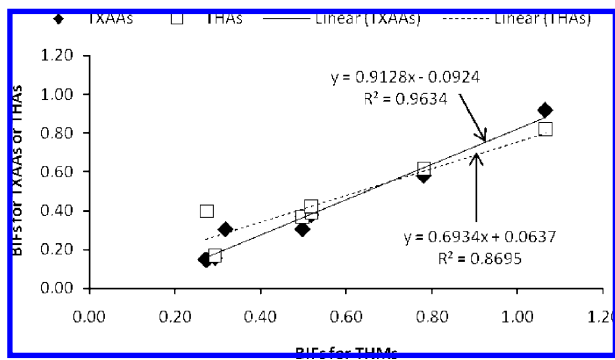


**FIGURE 4.** Relationship between HAA, haloacetaldehyde (HA), and HAN formation and that of THMs for WWTP effluents disinfected with free chlorine (excluding one set of HAA outliers) (number by each DBP class refers to the number of bromine- and chlorine-containing species that were measured).

it is important to monitor for DBPs beyond THMs. The formation of halogenated DBPs (i.e., HAAs, haloacetaldehydes, and HANs) but not that of NDMA was found to correlate ( $r^2 = 0.84$ ,  $0.82$ , and  $0.69$ , respectively) with the formation of THMs in WWTP effluents disinfected with free chlorine (Figure 4). Although correlations between THMs and emerging DBPs in drinking water have been evaluated, correlations had not been previously done in treated wastewater. Alternatively, THM formation did not correlate with the formation of other DBPs in effluents disinfected with chloramines (for additional discussion of DBP relationships, see the Supporting Information). Because many WWTPs only monitor for THMs, it is important to know when THMs can be used as a surrogate for other DBPs and when it cannot.

Because of the presence of DON and bromide in EfOM, various nitrogenous and bromine-containing DBPs of health concern may be formed. Because nitrogenous DBPs are in general of higher health concern than carbonaceous DBPs (15, 16), understanding the relative formation of nitrogenous DBPs in EfOM is important. Because of the relatively high levels of bromide (25th percentile, median, and maximum levels were  $0.12$ ,  $0.19$ , and  $0.42$  mg/L) in EfOM (from natural and anthropogenic sources, where most WWTP processes remove organic matter but not bromide), substantial amounts of bromine can be incorporated into the various classes of DBPs formed (i.e., THMs, HAAs, HANs, and haloacetaldehydes). There was a good correlation between the bromine incorporation factor (BIF) values of TXAAs and those of THMs or between the BIFs of trihalogenated acetaldehydes and those of THMs ( $r^2 = 0.96$  and  $0.87$ , respectively) (Figure 5). (For additional discussion of bromine incorporation, see the Supporting Information.) Because bromine-containing DBPs are of higher health concern than corresponding chlorine-containing species (16), understanding bromine incorporation in wastewater DBPs is important.

Disinfection and oxidation practices at WWTPs had a profound impact on the types and levels of DBPs formed. WWTPs that did not achieve breakpoint chlorination ( $\text{Cl}_2/\text{N} < 10$  mg/mg) tended to form low concentrations of the halogenated DBPs, but produced a substantial amount of NDMA. Alternatively, WWTPs that achieved breakpoint chlorination ( $\text{Cl}_2/\text{N} > 10$  mg/mg) typically formed considerable amounts of THMs, HAAs, haloacetaldehydes (which were the third largest fraction on a weight basis), and HANs but very little NDMA. Although previous research had examined the impact of nitrification on THM or NDMA formation (7, 12), this study was the first to examine a wide range of halogenated



**FIGURE 5.** Comparison of BIFs for trihalogenated DBPs (THAs = trihalogenated acetaldehydes) in WWTP effluents disinfected with free chlorine (excluding an outlier where the bromine-containing TXAAs were below their MRLs such that the BIF could not be accurately determined).

DBPs and nitrosamines together at a diverse group of WWTPs and reclamation plants (with a wide range of biological, chemical, and physical processes). Moreover, this study established that nitrification was not the only important issue, but that the  $\text{Cl}_2/\text{N}$  ratio was a controlling parameter. Finally, NMOR was found at many WWTPs but did not appear to be a DBP per se as it was present at substantial levels before chlorine addition.

This study found that WWTP discharges can be a source of a wide range of halogenated and nonhalogenated DBPs of health concern (e.g., bromine-containing and/or nitrogenous), which is important for growing water reclamation programs in arid portions of the United States and elsewhere.

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## Supporting Information Available

Information on analytical methods; DBP precursors in the EfOM; discussions of bromine incorporation into DBPs, the relationship between DBPs, and TOX formation; and the impact of UV and RO on nitrosamines. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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