

Supporting Information

The Occurrence of Disinfection Byproducts in USA Wastewater Treatment Plant Effluents

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Analytical Methods

DOC, DON, and UVA measurements were performed on samples that had been filtered (using 0.45- μ m membrane filters [e.g., polyethersulfone] prewashed with organic-free water). Analyses for DOC, UVA, bromide, and ammonia were carried out according to *Standard Methods* (1). The DON method employed a prolonged (48-hr) dialysis pretreatment to separate dissolved inorganic nitrogen from total dissolved nitrogen, so as to reduce analytical error (2). Dialysis pretreatment used cellulose ester dialysis tubes with a nominal molecular weight cutoff of 100 Da. DON by this method was comparable to total Kjeldahl nitrogen (TKN) minus the ammonia concentration for well nitrified effluents. Total iodine, the sum of organic iodine and inorganic iodide, was measured with inductively coupled plasma (ICP)/MS. Organic iodine can include iodine-containing X-ray contrast agents, which would typically be present at ng/L levels. It is the inorganic iodide that can act as a DBP precursor.

THMs, HANs, and chloropicrin were measured using USEPA Method 551.1 (3). The MRL for each THM was 0.5 μ g/L, and the MRL for each HAN or chloropicrin was 0.25 μ g/L. HAAs were measured using USEPA Method 552.2 (4). The MRL for each HAA was 1.0 μ g/L, except for monochloro- and tribromoacetic acid, which each had an MRL of 2.0 μ g/L. Haloacetaldehydes, dihalogenated halonitromethanes, and iodinated THMs were analyzed for using either a liquid/liquid extraction–GC/electron capture detection or a solid-phase extraction (SPE)–GC/MS method (5). For the latter two methods, the MRL for individual species was typically \sim 1 μ g/L; for some DBPs during certain analytical runs, the MRLs were \sim 2–5 μ g/L. Nitrosamine samples were concentrated using SPE with Ambersorb (6) and were analyzed using chemical ionization GC/MS (7). The MRL for each nitrosamine was 2 ng/L.

DBP Precursors: EfOM, Bromide, and Iodide

The impact of WWTP processes on organic DBP precursors (DOC, DON, UVA) in this study has been discussed elsewhere (8). The range (and median) levels of DOC for WWTPs with no nitrification and good nitrification were 7.9–16.5 (12.1) and 4.8–15.5 (7.0) mg/L, respectively, whereas DON was 0.53–2.40 (1.10) and 0.15–1.25 (0.52) mg/L as N, respectively. The specific UVA (SUVA) (i.e., UVA [in m^{-1}]/DOC) was 0.98–1.86 (1.50) and 1.22–2.74 (2.08) L/mg-m. On a central tendency basis (e.g., based on median data), good nitrification resulted in less DOC and DON, but higher SUVA than no nitrification; the higher SUVA infers that biological treatment preferentially removed the portions of the DOC that absorbed UV weakly (8) and/or added organic matter with a higher degree of humification during nitrification.

The observed bromide levels at the WWTPs were higher than those typically observed for drinking water sources. The 25th percentile, median, and maximum levels of bromide were 0.12, 0.19, and 0.42 mg/L, respectively, for the WWTPs that did not use RO. In a survey of U.S. drinking waters, bromide (seasonal averages) in randomly selected sources that supplied large utilities ranged from 0.004 to 0.43 mg/L (median = 0.057 mg/L) (9). Likewise, the concentration of total iodine at the WWTP effluents without activated carbon or RO (14–91 [median = 49] $\mu\text{g/L}$) was higher than at the drinking water plants surveyed in this study (ND to 22 $\mu\text{g/L}$, median = 6 $\mu\text{g/L}$). Bromide and iodide are not expected to be removed during biological wastewater treatment. The drinking-water treatment plants were in the same communities as the WWTPs.

Finally, the effluent pH was 6.2–8.1 (7.1) and 6.4–7.7 (7.0), respectively, and temperature was 15.0–27.0 (22.3) and 5.7–31.5 (22.0)°C, respectively, for no nitrification and good nitrification.

Bromine Incorporation into DBPs

The bromine incorporation factor (BIF) was determined for the different DBPs, where BIF equals the molar sum of bromine incorporated into a class of DBPs divided by the molar sum of that DBP class (*10-11*). For the THMs, BIF values can theoretically range from 0 (all chloroform) to 3 (all bromoform). A BIF of 1.0 corresponds to water in which the “average” THM species is bromodichloromethane. For the HANs, BIF values can range from 0 (all dichloroacetonitrile) to 2 (all dibromoacetonitrile).

Previous research in drinking water has shown that bromine incorporation into TXAAs was similar to that of the THMs (*12*). Likewise, occurrence data for TXAAs, as well as for trihalogenated acetaldehydes, showed similar bromine incorporation as that of the THMs for the WWTP effluents disinfected with free chlorine (Figure 5). However, the slopes of the regression lines (for the BIFs for TXAAs or trihalogenated acetaldehydes versus the BIFs for the THMs) were less than 1.0 (i.e., 0.91 and 0.69, respectively), which indicates that there was less bromine incorporation into TXAAs or trihalogenated acetaldehydes than into THMs on a central tendency basis. There may have been less bromine incorporation in the TXAAs or trihalogenated acetaldehydes for two reasons. Because of the presence of the functional group (e.g., carboxylic acid) in the TXAAs or trihalogenated acetaldehydes, there may have been steric interference in incorporating too many bromine atoms. Alternatively, brominated species may have formed but degraded to some extent (*13-14*). SI Figure 6 shows the relationship of the BIFs for the

dihalogenated DBPs. The slope of the regression line for the BIFs for the dihalogenated HANs versus the BIFs for the DXAAs was greater than 1.0 (i.e., 1.71), which indicates that there was more bromine incorporation into HANs than into DXAAs on a central tendency basis. Obolensky and Singer (15) also saw more bromine incorporation into HANs when data from U.S. drinking waters were examined. The rank order of genotoxic potency of the dihalogenated HANs (14) was dibromo- > bromochloro- > dichloroacetonitrile. For other classes of DBPs, the bromine-containing DBPs were typically more toxic than the fully chlorinated species (16-17). Thus, samples with higher BIF values may be of more health concern, as they represent waters with higher degrees of bromine incorporation for a wide range of DBPs.

SI Figure 7 gives an example of BIFs for drinking water, using data from a recent survey (18). This is similar to what was observed at the WWTPs (Figure 5). Although the level of bromide at the WWTPs was typically higher than what was in the drinking water (SI Figure 8), bromine incorporation is also impacted by the bromide-to-DOC ratio (11). For the WWTP effluents disinfected with free chlorine, the inter-quartile range (25th to 75th percentile) of the ratios was 0.015 to 0.039 mg/mg, and for the drinking waters in the latter survey (18) the interquartile range was 0.009 to 0.019 mg/mg (SI Figure 8). Although the ratios were lower in the drinking waters, there was overlap between the inter-quartile ranges.

Relationships between DBPs

In drinking water, the concentration of THMs has typically been around ten times higher than that of the HANs (19). In a recent survey of drinking water treatment plant effluents (18), their weight ratio (25th to 75th percentile) ranged from 6.7 to 13 $\mu\text{g THMs}/\mu\text{g HANs}$ (median = 7.3 $\mu\text{g THMs}/\mu\text{g HANs}$). However, at the WWTPs that achieved breakpoint chlorination, their

ratio for the inter-quartile range (25th to 75th percentile) was 3.1 to 4.4 $\mu\text{g THMs}/\mu\text{g HANs}$ (median = 3.4 $\mu\text{g THMs}/\mu\text{g HANs}$). In terms of their ratio of THMs to haloacetaldehydes in drinking water, the inter-quartile ratio (and median) was 3.7 to 7.0 (4.8) $\mu\text{g THMs}/\mu\text{g haloacetaldehydes}$, whereas at the WWTPs that chlorinated in the presence of free chlorine, their ratios were 1.6 to 2.1 (1.9) $\mu\text{g THMs}/\mu\text{g haloacetaldehydes}$.

SI Figures 9-15 examine correlations between the concentrations of the various DBPs and that of the THMs in EfOM. For the WWTP effluents disinfected with free chlorine, the relationship between DXAAs or TXAAs to that of THMs was fair ($R^2 = 0.52\text{-}0.58$). However, there was a set of data that was a substantial outlier (62 $\mu\text{g/L}$ of THMs, 3 $\mu\text{g/L}$ of DXAA, 10 $\mu\text{g/L}$ of TXAAs). When that set of outliers was removed, the relationships substantially improved ($R^2 = 0.76\text{-}0.84$). In addition, the relationships between the haloacetaldehydes ($R^2 = 0.79\text{-}0.93$) or HANs ($R^2 = 0.69$) and that of the THMs in the effluents disinfected with free chlorine were good. However, there was no relationship between the formation of NDMA and that of THMs in the effluents disinfected with free chlorine ($R^2 = 0.21$). For the WWTP effluents disinfected with chloramines, there were no relationships between the formation of the halogenated DBPs or NDMA with that of THMs. Only one pattern emerged from these data. At a water recycling plant that used flocculation, filtration and chlorination to treat a poorly nitrified EfOM, they produced substantially more NDMA, dihalogenated HANs, and DHAs than the other WWTPs, and this plant produced some of the highest levels of DXAAs. Results from various studies have shown that NDMA and certain dihalogenated DBPs (DXAAs, HANs, DHAs) can be preferentially formed by chloramines. At this particular plant, there was something about the EfOM and/or treatment/disinfection process that maximized the formation of a wide range of chloramine DBPs.

Total Organic Halogen (TOX)

At selected sites, TOX was measured (*I*), which represents the sum of all of the adsorbable halogenated organic chemicals in a sample. As an example, a WWTP with parallel treatment trains was sampled for TOX before and after chlorination. Train A achieved nitrification and partial denitrification, whereas train B was poorly nitrified. At train A, ammonia was added with the chlorine to form chloramines. TOX at the WWTP before chlorine addition was 97 $\mu\text{g/L}$ as Cl^- . Because the DBPs in this study include bromine- and chlorine-substituted species, the results were converted to a molar basis and expressed as the amount of halogen (X). Before chlorine addition, a small amount of THMs were detected and none of the other target DBPs in the study were detected (SI Figure 16). The THMs accounted for only 1 percent of the TOX (on a molar basis). This is because wastewater can include synthetic organic contaminants that are halogenated (e.g., solvents, pesticides), which are not DBPs. After chlorination at trains A and B, the level of DBPs and TOX went up (to 110 and 140 $\mu\text{g TOX/L}$ as Cl^- , respectively), but most of the TOX was still unaccounted for by the target DBPs (SI Figure 16). After chlorination, the target DBPs detected accounted for 4 and 14 percent of the TOX (on a molar basis) at trains A and B, respectively.

At the example WWTP, after chlorination, the amount of TOX increased by $110 - 97 = 13$ $\mu\text{g/L}$ as Cl^- at train A (and by $140 - 97 = 43$ $\mu\text{g/L}$ as Cl^- at train B). These increases in TOX levels were most likely due to the formation of DBPs. For example, after chlorination, the amount of THMs increased by $1.5 - 1.0 = 0.5$ $\mu\text{g/L}$ and HAAs were now present at 5.2 $\mu\text{g/L}$ (HAAs were not detected before chlorination) at train A. In this example, 2 and 25 percent of the additional TOX produced after chlorination at train A was accounted for (on a molar basis) by THMs and HAAs, respectively, which were formed after chlorination. However, 73 percent

of the additional TOX produced was not accounted for by the target DBPs in this study. A higher percentage of the TOX produced at train B was accounted for by THMs (7 percent) and HAAs (36 percent) that were formed after chlorination, with 57 percent unaccounted. At both trains, because of the presence of ammonia, the addition of chlorine formed chloramines. These results are consistent with research in drinking water, where chloramination forms very little TOX and that a very high percentage of the TOX formed during chloramination is not accounted for by THMs, HAAs, and other typically measured DBPs (20).

Impact of UV and RO on Nitrosamines

At the WWTPs in this study that used UV for disinfection, the UV wavelength and dose (for those WWTPs that reported that information to the project team) were 254 or 265 nm and 35-100 mJ/cm², respectively. At these WWTPs, the levels of nitrosamines (e.g., NDMA, NMOR) before and after UV disinfection were the same (SI Figure 17). Although UV may destroy some of the NDMA present, its efficiency is somewhat low at germicidal UV dosages. However, at a water recycling plant that used UV (low-pressure, high-output lamps; dose ~300-400 mJ/cm²) with hydrogen peroxide (3 mg/L) as an advanced oxidation process to treat reverse osmosis (RO) product water, the nitrosamines were well removed (e.g, the concentration of NDMA was lowered from 28-39 to 2-4 ng/L). This difference in nitrosamine destruction may have been due to the use of low-pressure UV (no photolysis) and low-pressure, high-output UV (photolysis) and/or the use of a very high UV dose rather than the presence or absence of hydrogen peroxide. (UV irradiation has been shown to remove NDMA from water to very low levels. NDMA absorbs UV light in a strong band centered at 228 nm and a weak band centered at 340 nm. Initial absorption of light at 228 nm results in cleavage of the N-N bond.) (21)

However, one cannot discount hydroxyl radical oxidation. (UV/oxidation typically combines UV light with an oxidant, such as hydrogen peroxide. The process involves the generation of highly reactive hydroxyl radicals in sufficient quantity to affect water purification through a destruction process acting at near ambient or room temperatures.) (21) Nonetheless, in other studies, UV treatment has been found to be very effective at removing nitrosamines, even without hydrogen peroxide. In addition, the difference in nitrosamine destruction may have been due to matrix effects (i.e., UV treatment of secondary or tertiary effluent versus UV treatment of RO product water at the water recycling plant). At this water recycling plant, RO treatment did not significantly remove NDMA (the concentration of NDMA in the RO feed was 47-48 ng/L and it was 28-39 ng/L in the product water), but NMOR was well rejected (the concentration of NMOR in the RO feed was 12-42 ng/L and it was ND to 3 ng/L in the product water). At this WWTP, UV/hydrogen peroxide was used to ensure that NDMA levels were significantly minimized in the WWTP effluent.

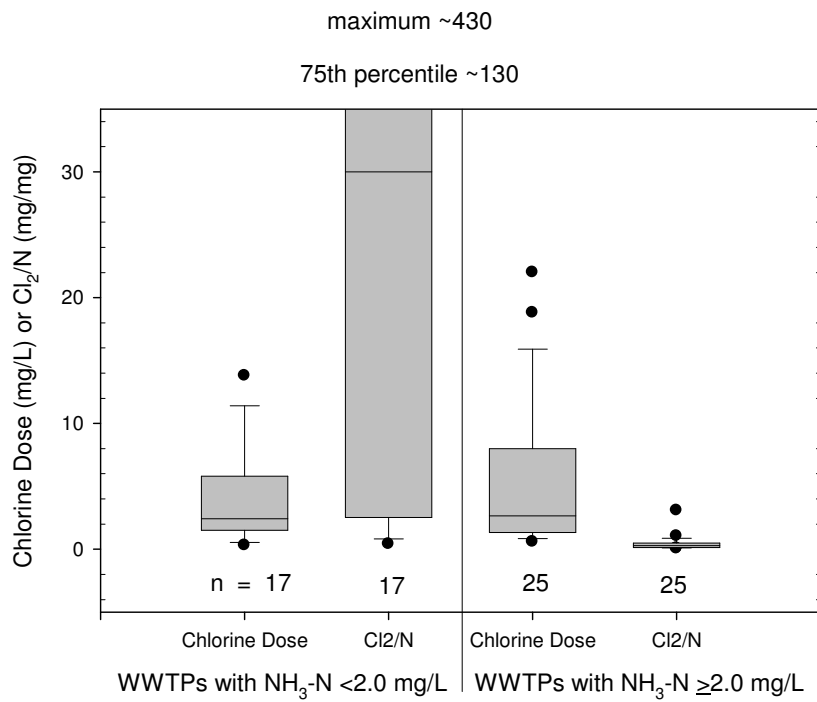
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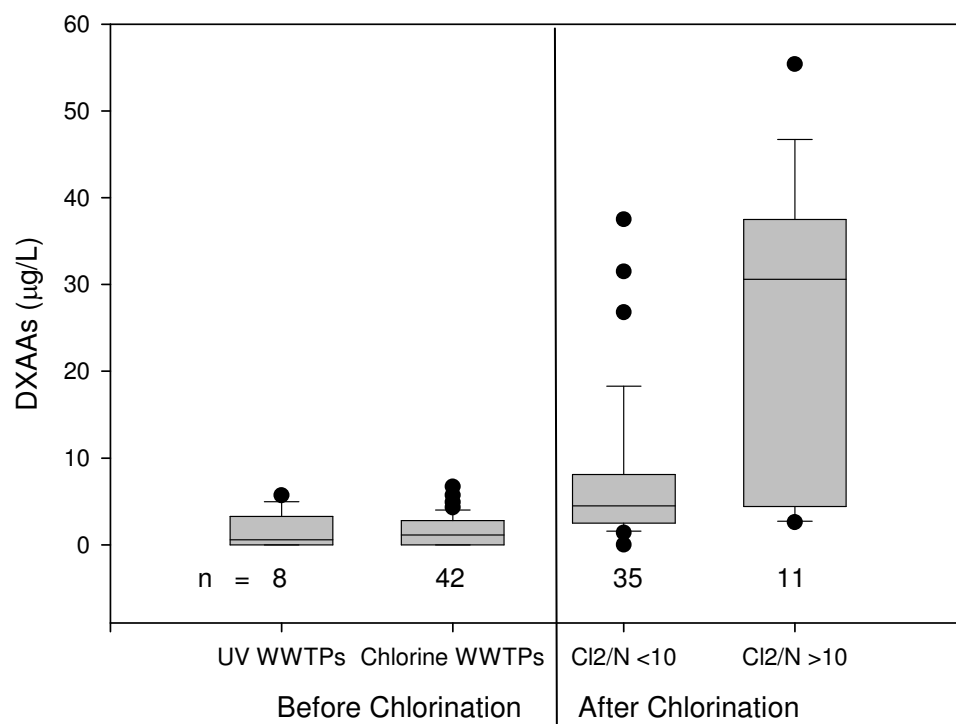
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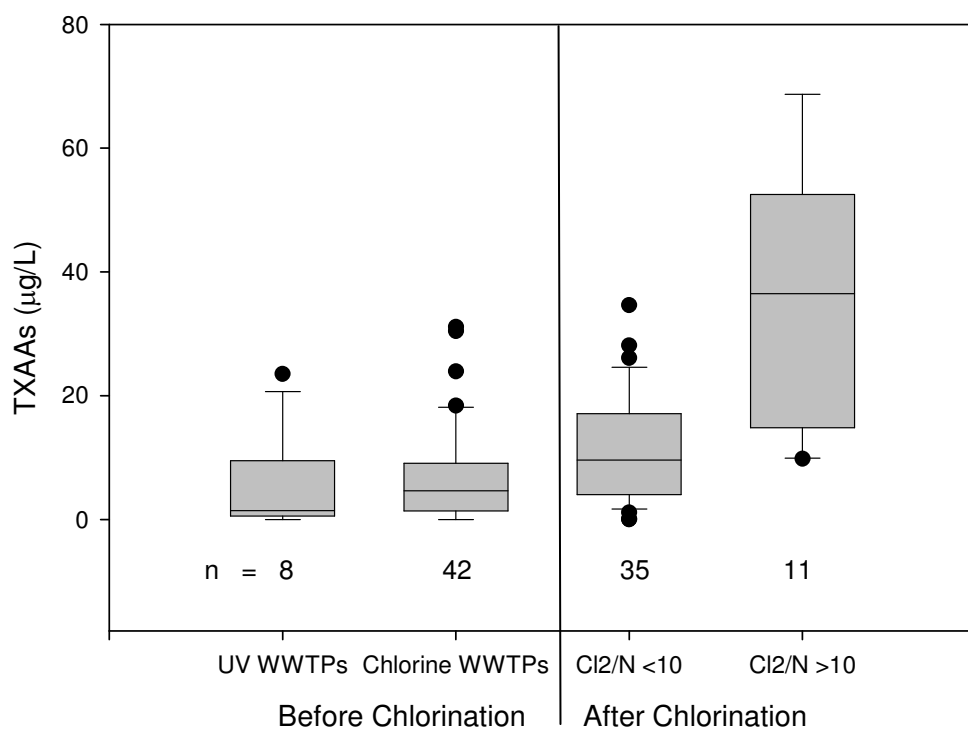
SI Figure 1. Chlorination conditions used at participating WWTPs

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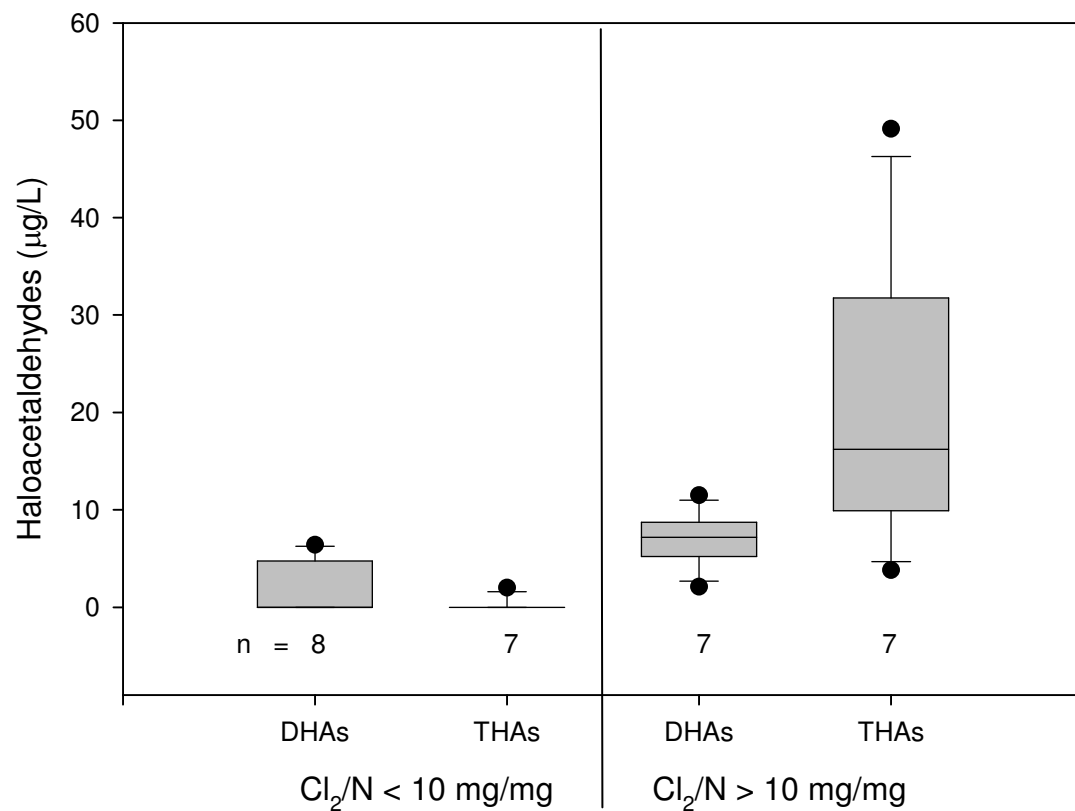
SI Figure 2. Occurrence of dihalogenated HAAs (DXAAs) at participating WWTPs

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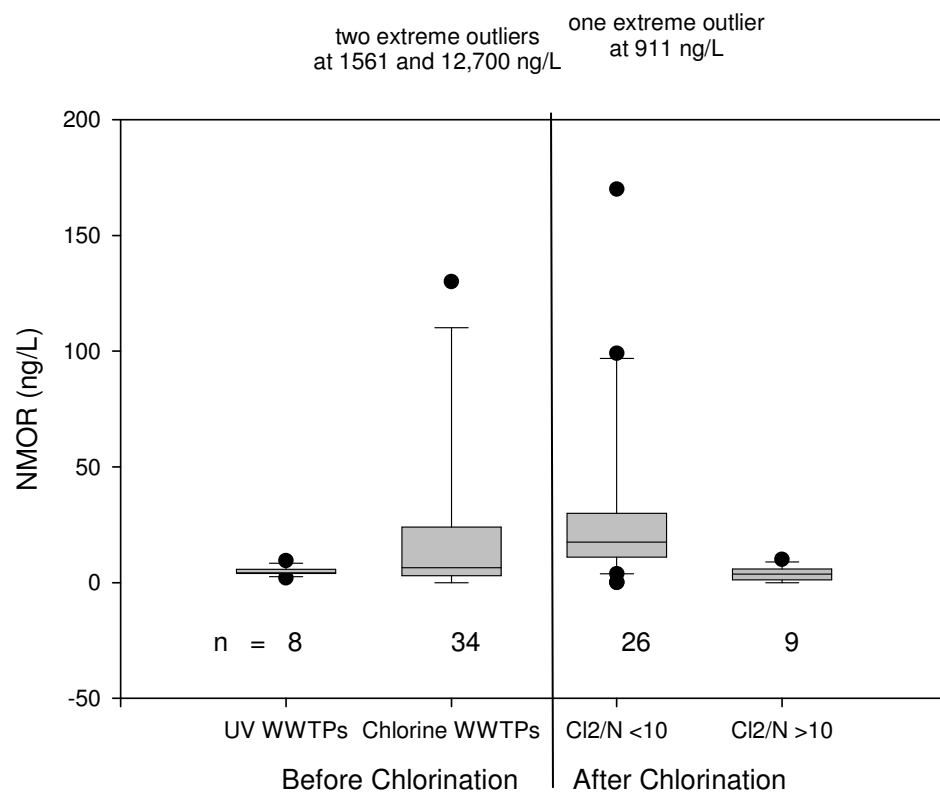
SI Figure 3. Occurrence of trihalogenated HAAs (TXAAs) at participating WWTPs

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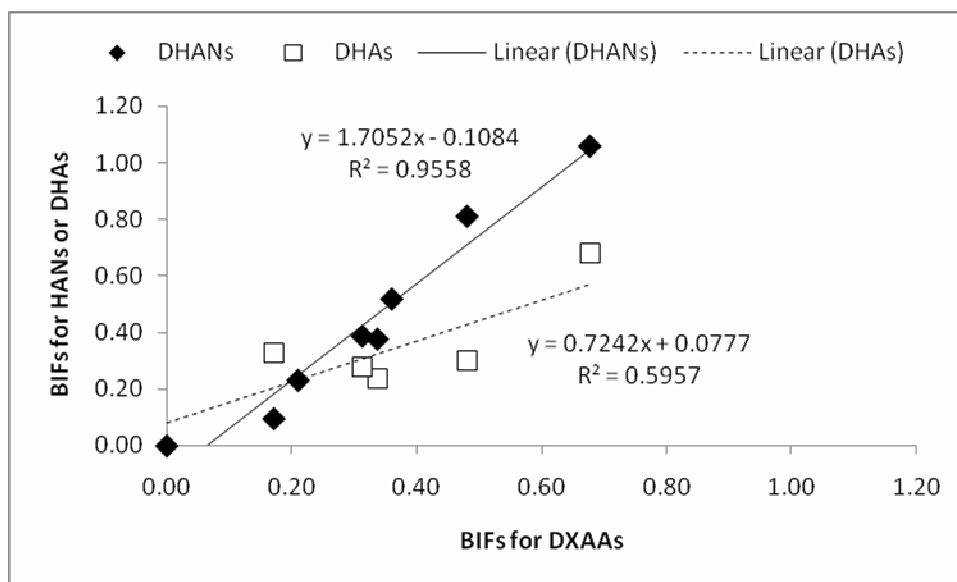
SI Figure 4. Occurrence of haloacetaldehydes at participating WWTPs after chlorination (25th percentile and median for DHAs for $Cl_2/N < 10$ mg/mg were both ND)

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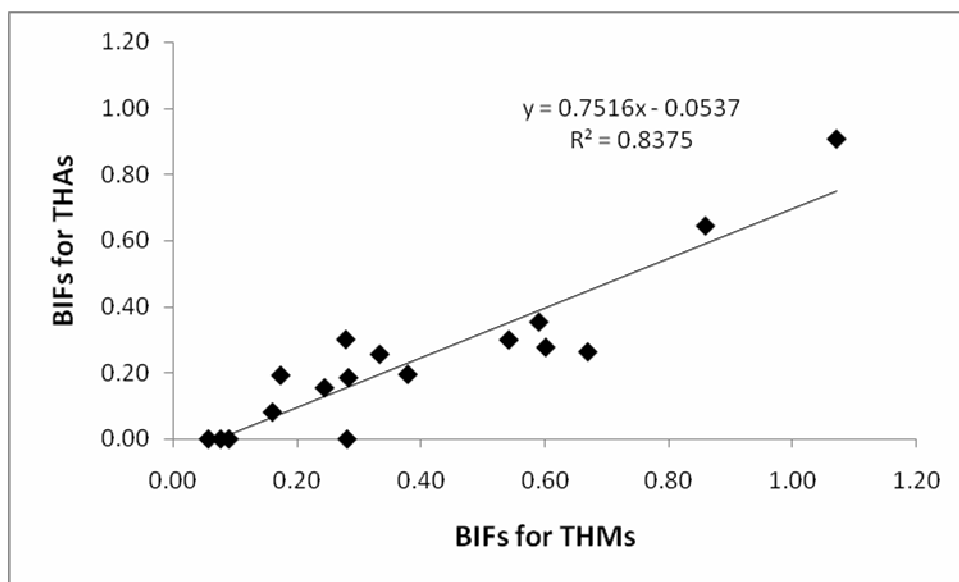


SI Figure 5. Occurrence of NMOR at participating WWTPs

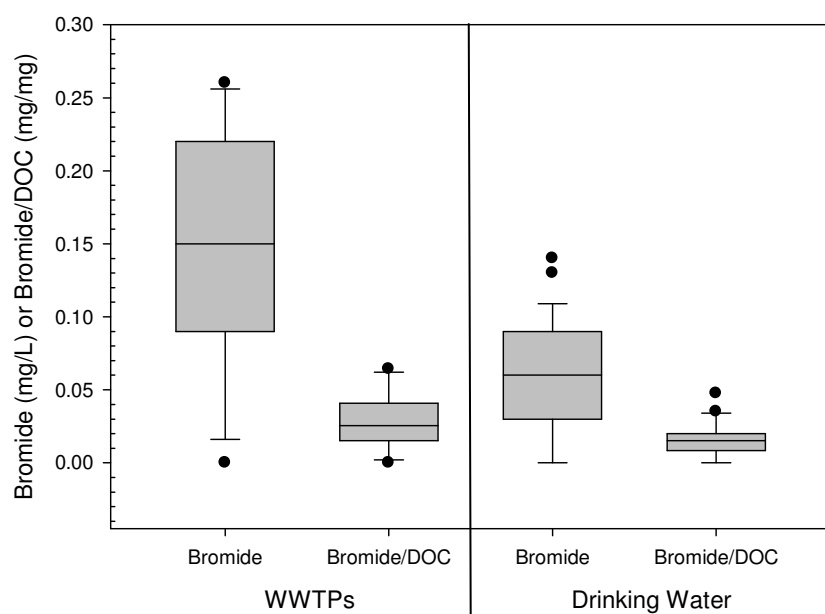
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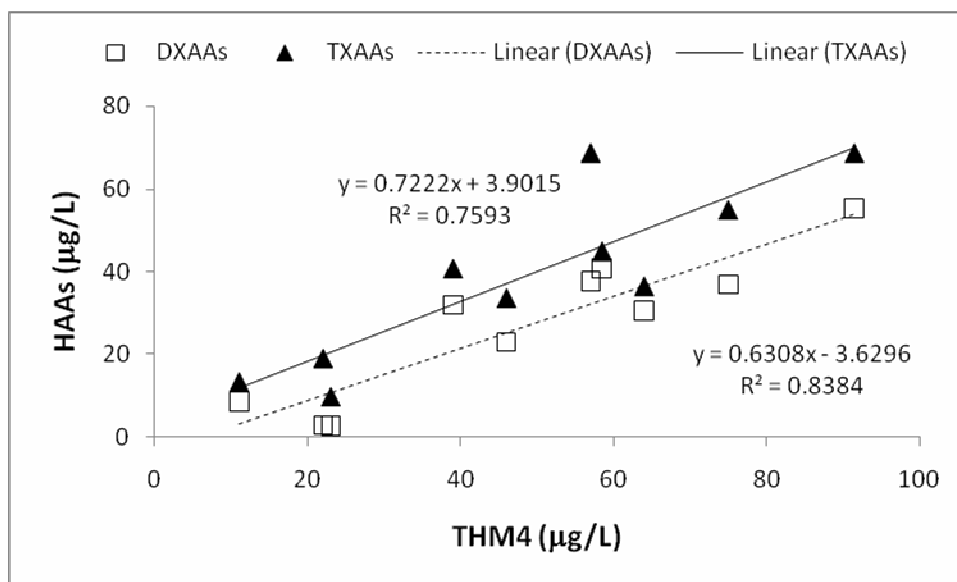
SI Figure 6. Comparison of BIFs for dihalogenated DBPs in WWTP effluents disinfected with free chlorine



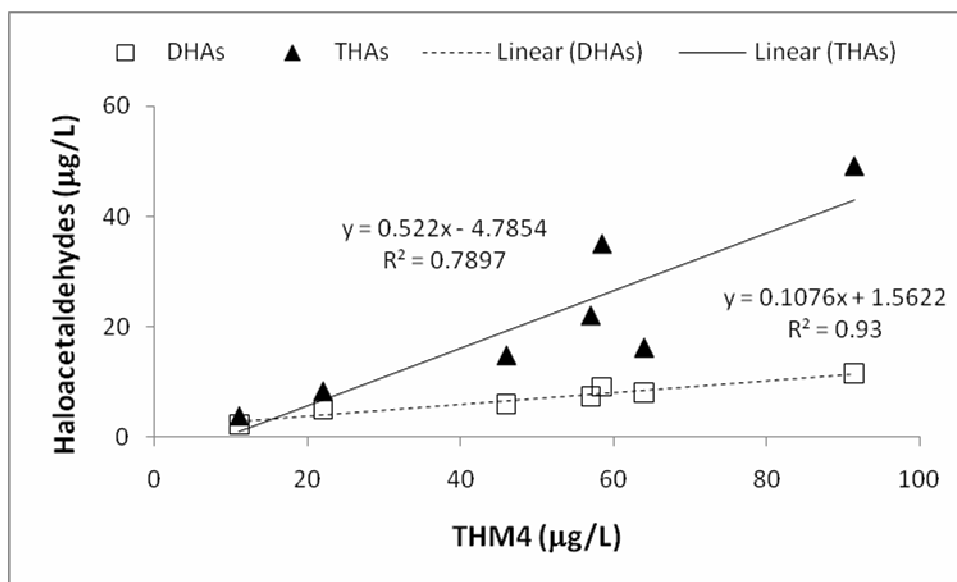
SI Figure 7. Comparison of BIFs for trihalogenated DBPs in drinking water treatment plant effluents from a recent survey (excluding two outliers where the bromine-containing THAs were below their MRLs such that the BIFs could not be accurately determined)



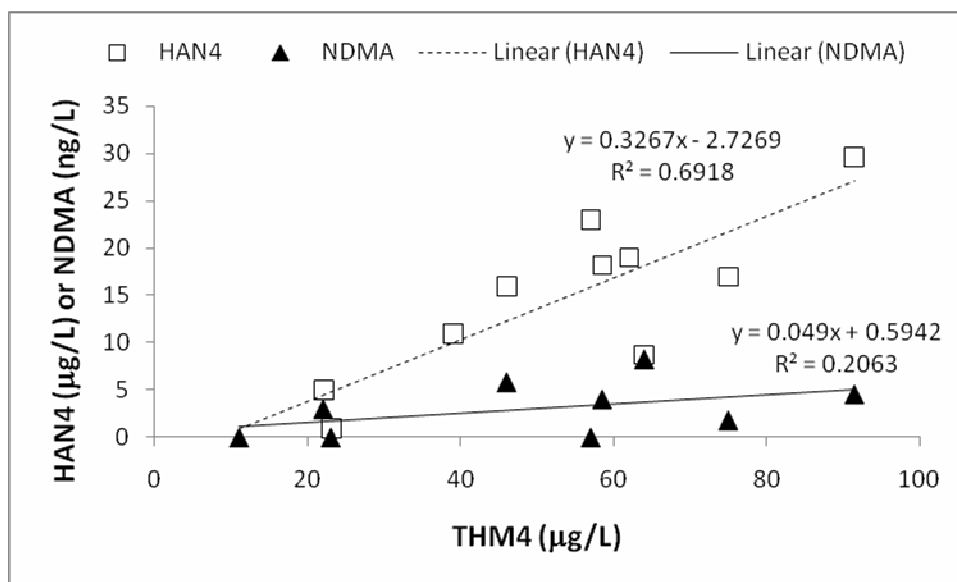
SI Figure 8. Comparison of bromide and bromide/DOC ratios for WWTP effluents disinfected with free chlorine and for drinking water from a recent survey



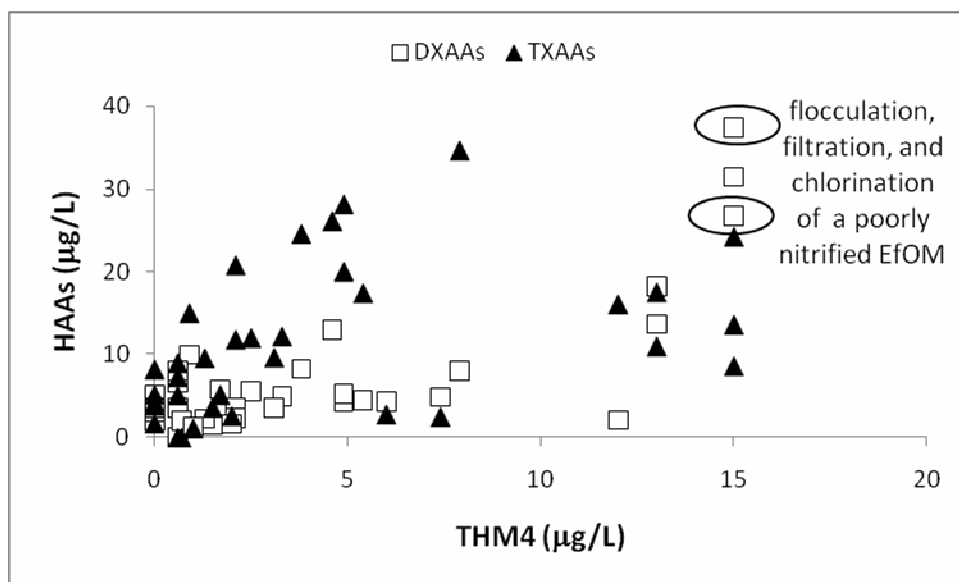
SI Figure 9. Relationship between HAA and THM formation for WWTP effluents disinfected with free chlorine (excluding one set of outliers)



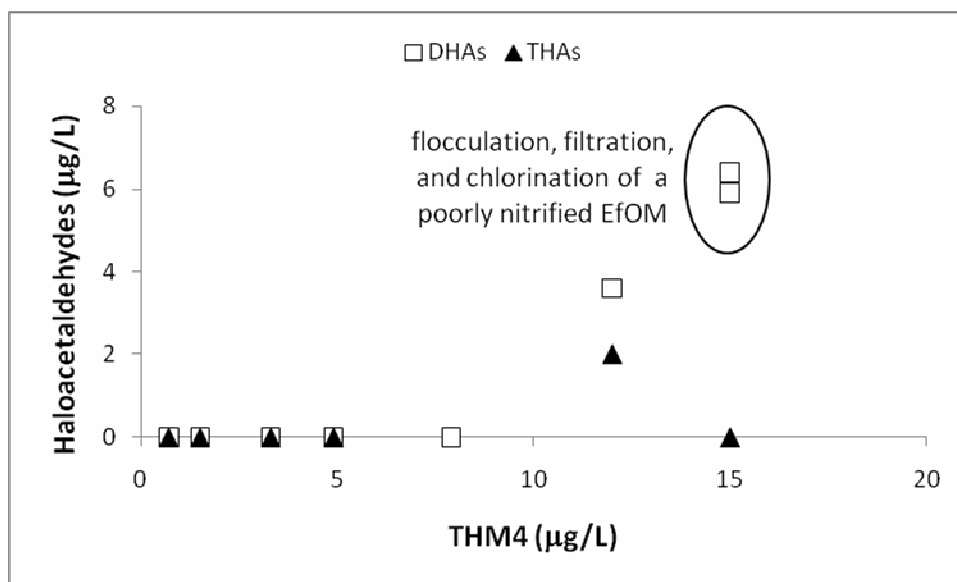
SI Figure 10. Relationship between haloacetaldehyde and THM formation for WWTP effluents disinfected with free chlorine



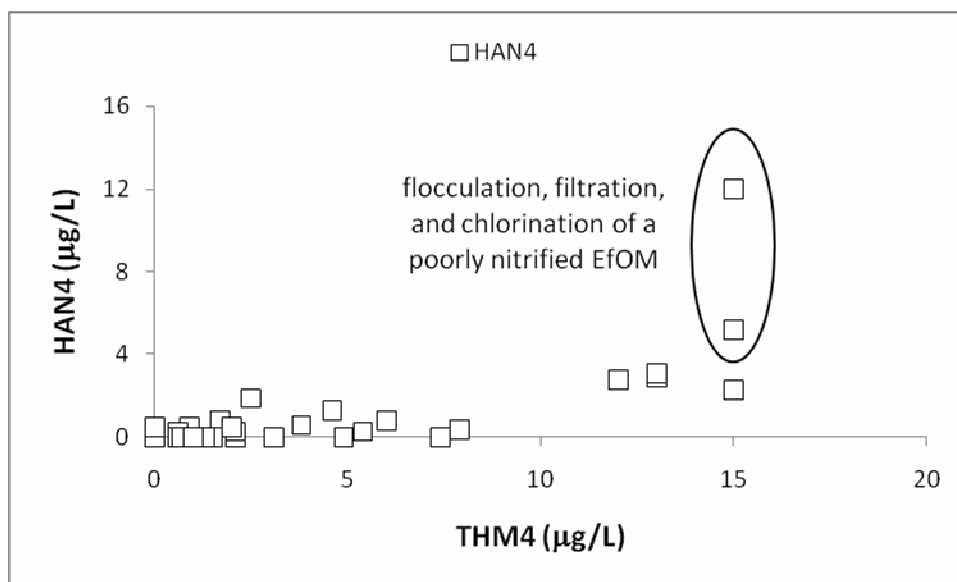
SI Figure 11. Relationship between nitrogenous DBPs and THM formation for WWTP effluents disinfected with free chlorine



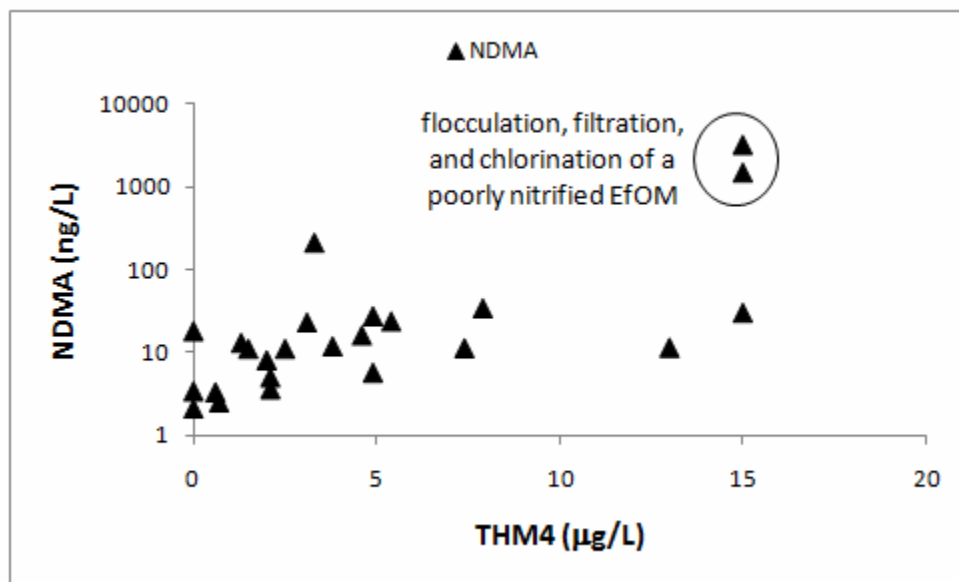
SI Figure 12. Relationship between HAA and THM formation for WWTP effluents disinfected with chloramines



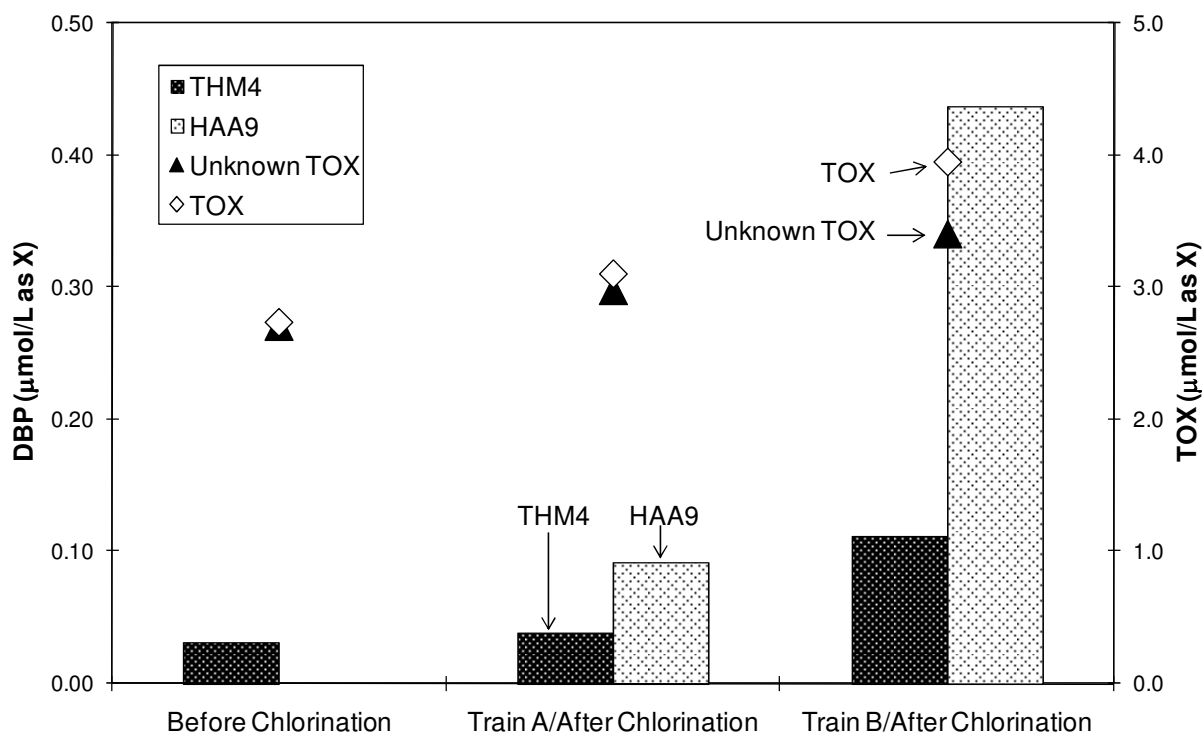
SI Figure 13. Relationship between haloacetaldehyde and THM formation for WWTP effluents disinfected with chloramines



SI Figure 14. Relationship between HAN and THM formation for WWTP effluents disinfected with chloramines

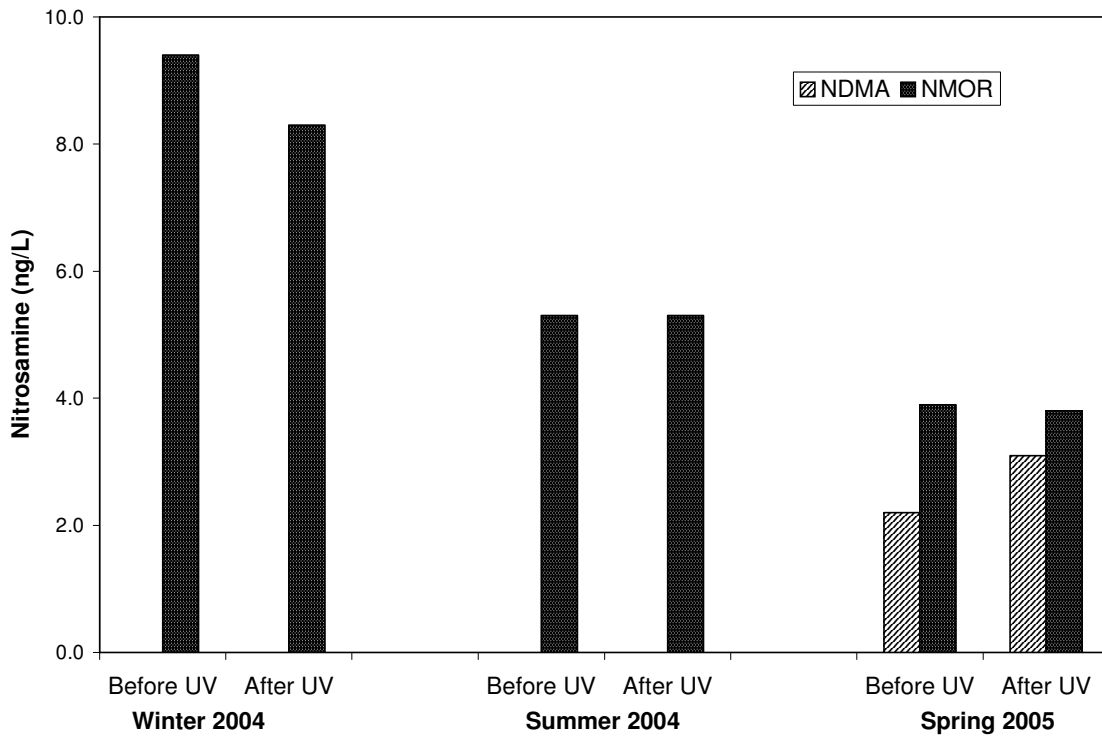


SI Figure 15. Relationship between NDMA and THM formation for WWTP effluents disinfected with chloramines



SI Figure 16. Amount of TOX accounted for by target DBPs at two parallel treatment trains of a participating WWTP

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SI Figure 17. Example of the impact of UV disinfection on nitrosamines at one WWTP

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