Formation and control of emerging C- and N-DBPs in drinking water

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A survey of 16 US drinking water treatment plants was conducted regarding the occurrence, formation, and control of emerging disinfection by-products (DBPs), with a focus on drinking waters that were impacted by treated wastewater and/or algae. The formation and control trends of certain emerging carbonaceous (haloacetaldehyde) and nitrogenous (haloacetanilide, halonitromethane, cyanogen halide, nitrinosamine) DBPs were different from those of the regulated trihalomethanes (THMs). This was due to differences in the sources of precursors (e.g., humic substances versus proteinaceous materials) plus differences in the effect of disinfection processes on these DBPs. For example, ozone increased the formation potential (FP) of chloropicrin (median = 226%), whereas biofiltration typically decreased the FP of the ozonated water (median = 48%), which—together with coagulation or softening—resulted (in general) in a net decrease (median = 33%) in FP through the ozone plants. Alternatively, coagulation with the polymer polyDADMAC (a source of N-nitrosodimethylamine [NDMA] precursor) increased the FP of NDMA (43–82%), whereas ozonation often destroyed NDMAFP (median to maximum = 10–87%). This article discusses how utilities can minimize and balance the formation of THMs and haloacetic acids with that of certain emerging DBPs.

KEYWORDS: chloropicrin, cyanogen halide, disinfection by-products, haloacetaldehydes, haloacetanilides, N-nitrosodimethylamine

Certain nitrogenous disinfection by-products (N-DBPs; e.g., haloacetanilides [HANs]) and certain nonregulated carbonaceous DBPs (C-DBPs; haloacetaldehydes) may be of higher health concern than the regulated C-DBPs (e.g., trihalomethanes [THMs], haloacetic acids; Muellner et al, 2007; Plewa & Wagner, 2009a). For example, the US Environmental Protection Agency’s (USEPA’s) Integrated Risk Information System database indicates that for eight nitrosamines, including N-nitrosodimethylamine (NDMA), drinking water concentrations in the low nanogram-per-litre level are associated with a 10–6 lifetime cancer risk. In contrast, comparable risk levels for drinking water concentrations for certain THMs and haloacetic acids are in the range of 0.6–4 µg/L.

Previous research has focused on natural organic matter (NOM) precursors (e.g., humic substances) for regulated C-DBPs (Reckhow et al, 1990). Recent research (Mitch et al, 2009) evaluated the formation of N-DBPs and certain other C-DBPs from waters impaired by algae or treated wastewater. Algal organic matter (AOM) includes macromolecules and cell fragments. Furthermore, the watershed for a drinking water treatment plant (DWTP) can contain upstream point-source discharges of treated wastewater. In addition to influent refractory substrates not assimilated by bacteria (e.g., NOM from the drinking water source), effluent organic matter (EfOM) from biological wastewater treatment plants (WWTPs) is composed of degradation products and soluble microbial products (Namkung & Rittmann, 1986). These soluble microbial products consist of macromolecules and cellular debris with a protein (nitrogen-enriched) and polysaccharide signature. Both AOM and EfOM are microbial in origin and are sources of organic nitrogen (Leenheer et al, 2007), including amino acids (Dotson & Westerhoff, 2009). In addition, there are anthropogenic chemicals (e.g., pharmaceuticals and personal care products) in WWTP discharges (Ternes, 1998).

AOM and EfOM are significant precursors for emerging N- and C-DBPs. For example, EfOM has been shown to be a source of precursors for HANs, haloacetaldehydes, and nitrosamines (Krasner et al, 2009). AOM and EfOM contain a greater amount of amino acids than NOM. Chlorination of amino acids can result in the formation of aldehydes and nitriles, with certain amino acids (e.g., aspartic acid) forming chloral hydrate (trichloroacetaldehyde) and dichloroacetanilide (Trehy et al, 1986). Other research showed that cyanogen chloride (CNCl) was sometimes formed in the presence of certain amino acids and hypochlorous acid but was always formed in the presence of the
Amino acids tested when both hypochlorous acid and the ammonium ion (i.e., chloramines) were present (Hirose et al, 1988).

Among the nitrosamines, NDMA has been shown to be a by-product of chloramine disinfection, particularly of waters affected by wastewater (Mitch et al, 2003). Certain pharmaceuticals and personal care products have been shown to react with chloramines to form NDMA and other nitrosamines (Shen & Andrews, 2011). In addition, NDMA formed from a fungicide (tolylfluamide) transformation product in ozonated drinking water (Schmidt et al, 2008). Moreover, some polymers used during water treatment (e.g., polydiallyldimethylammonium chloride [polyDADMAC]) contribute to NDMA precursor material (Kohut & Andrews, 2003).

This study surveyed the formation of N-DBPs and selected C-DBPs at 16 DWTPs, most of which were impacted by either wastewater or algal sources in their watersheds, where the EfOM and AOM were anticipated to promote the formation of emerging N- and C-DBPs. First, DBP formation potential (FP) results across the different treatment facilities and their unit processes are presented to evaluate the net reactivity of EfOM- and AOM-impacted waters, and then the lower, actual C- and N-DBP levels formed at the actual full-scale facilities are presented and discussed.

METHODS

Survey. A survey of 16 full-scale US DWTPs was conducted in 2006–07. Eleven DWTPs were sampled twice, once each year, and five were sampled once in year 2. Seven of the sites were sampled during an algal bloom event in each year, as determined by monitoring algae cell counts. In terms of the effluent-impacted sites, they were sampled in the summer when river flow was low because some streams can be more effluent-impacted at this time of year. Primidone and carbamazepine, anticonvulsants that are conservative in rivers, were used as indicators of the relative contribution of wastewater to drinking water sources (Guo & Krasner, 2009). In three watersheds, a DWTP that was not algae- or wastewater-impacted was sampled to provide a reference. DWTPs were sampled that used a range of treatment processes (coagulation, lime softening, ultrafiltration, filtration with granular activated carbon [GAC]) and disinfectants (chlorine, chloramine dioxide, chloramines, ozone, ultraviolet [UV] irradiation) (Table 1). The sample sites were located in various geographical regions of the United States.

Grab samples were collected from source waters (rivers or reservoirs upstream of plant intakes), plant influents, locations in the DWTPs that were before and after selected treatment/oxidation processes that could affect DBP formation (e.g., coagulation/sedimentation, lime softening, filtration, ozonation, chlorination), and plant effluents. Samples were evaluated for various water quality parameters, simple NOM characterization, algal counts, wastewater indicators, DBPFPs, and actual DBP formation (they were taken at the same time). Samples for dissolved organic carbon and nitrogen (DOC and DON), UV absorbance (UVA) at 254 nm, and DBPFPs were filtered through 0.45 µm filters. Chlorinated or chloraminated plant effluent samples for DBPs were not filtered in the laboratory; however, they did undergo full-scale filtration. Chlorine and chloramine residuals were quenched (with sufficient reagent to dechlorinate typical disinfectant residual levels with a safety factor) and DBP samples were preserved (e.g., at an acidic pH level with acid or buffer) as per each of the published methods. Samples were all analyzed within their published hold times (e.g., two weeks for DBPs).

Analytical methods. All samples were analyzed with quality assurance/quality control programs to ensure accurate and precise data free of bias. This included the analysis of blanks, replicate samples, spiked samples, and calibration curves. Precision was generally within 20%, and accuracy was typically within 80 and 120%.

The samples were analyzed for DOC, DON, UVA, bromide, free and combined amino acids, DBPs (i.e., four THMs, three HANs, four halonitromethanes [HNMs], seven haloacetaldehydes, two cyanoaneg halides [CNXs], and eight nitrosamines), and DBPFPs. Selected samples were analyzed for algal counts, wastewater tracers/indicators, and/or aldehydes (formaldehyde, acetaldehyde).

A low-level DON method used dialysis pretreatment to remove dissolved inorganic nitrogen (Lee & Westerhoff, 2005). Free and total amino acids and amino sugars were separated by high-performance liquid chromatography and detected with fluorescence using a proprietary amino acid analysis method; total amino acids were determined after using one of two hydrolysis methods (Dotson & Westerhoff, 2009). Three wastewater tracers (primidone, carbamazepine, caffeine) were concentrated with solid-phase extraction (SPE), and the sample extracts were analyzed by liquid chromatography/tandem mass spectrometry (MS) under electrospray positive ionization mode (Vanderford et al, 2003).

The four regulated THMs, the three dihalogenated HANs, and chloropiricin (trichloronitromethane) were measured using a liquid/liquid extraction (LLE) and gas chromatograph (GC)/electron capture detection (ECD) method (USEPA, 1995). The minimum reporting level (MRL) was 0.5 µg/L for each THM and 0.25 µg/L for each HAN or chloropicrin. The three dihalogenated HNMs, the three dihalogenated haloacetaldehydes, and the four trihalogenated haloacetaldehydes were measured using an SPE and GC/MS technique (Chinn et al, 2007), with

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Operations at surveyed DWTPs</th>
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<tbody>
<tr>
<td>Parameter</td>
<td>Count</td>
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<tr>
<td>Cationic polymer dose—mg/L</td>
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<tr>
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<tr>
<td>Ozonation pH</td>
<td>8</td>
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<tr>
<td>Filter empty bed contact time—min</td>
<td>4</td>
</tr>
</tbody>
</table>

* Number of sample events with this information, which used this process or chemical
* Other coagulants used: 24–45 mg/L of alum, 24–33 mg/L of ferric sulfate, 8 mg/L of aluminum chloride
* Dose of polymer solution, which was typically ~ 20% active ingredient
* All ozone plants
CNXFP samples were prechlorinated for 3 h ($Cl_2 = 3 \times DOC$) and then postchloraminated for 21 h ($Cl_2/NH_3-N = 4.5:1$, weight basis). In one set of tests, CNXFP of blends of river water and treated wastewater (i.e., 0, 25, 50, 75, and 100% treated wastewater, volume basis) from one of the watersheds in this study was determined using $^{15}$N-labeled ammonia. In previous research with amino acids, $^{15}$N-labeling indicated that inorganic chloramines and/or certain amino acids were the source of the nitrogen in CNCl (Hirose et al, 1988).

RESULTS

Organic matter. Table 2 summarizes the concentration of organic matter and DBP precursors (surrogate parameters) in the source waters and plant influents. (Most plants were sampled at two locations: the source water upstream of the plant intake and at the plant influent; both represented raw water before treatment.) Plant influents and filter effluents had mean DOCs of 3.33 and 2.2 mg/L, respectively, and mean DONs of 0.29 and 0.20 mg-N/L, respectively. In another study, the mean DON concentration for 28 DWTPs in the United States was 0.19 mg-N/L for raw waters (Lee et al, 2006). DON was higher on a central tendency basis because wastewater- or algae-impacted source waters were targeted in the study reported here. Biologically derived organic matter (bacteria at WWTPs or algae in surface waters) contains proteins and other organic nitrogen–based compounds. The mean DOC-to-DON ratio (12.6 mg C/mg N) of the surveyed waters confirms that these sources were influenced by elevated levels of DON compared with the previous study (Lee et al, 2006), in which the average DOC-to-DON ratio was 18 mg C/mg N.

For the waters sampled in this study, the amino acids with the highest concentration (on a median basis) in the hydrolyzed samples were glycine, serine, threonine, alanine, and glutamic acid (Dotson & Westerhoff, 2009). On average, total amino acids and amino sugars together accounted for 15% (median = 9.6%) of the DON present in plant influents. Therefore, other nitrogenous organic compounds or undetected amino acids were also present.

Other indicators. There was a wide range of algal counts (e.g., 300–22,700/mL) at the participating utilities that were algae-
impacted. Excluding three waters that were not believed to be effluent-impacted, primidone was 2.5–37 ng/L (median = 7.5 ng/L), carbamazepine ranged from not detected (ND) to 156 ng/L (median = 18 ng/L), and caffeine was ND–687 ng/L (median = 112 ng/L). In a previous study, primidone concentrations in WWTP effluents (four of which were in the watersheds in the current study) typically ranged from 100 to 200 ng/L (Krasner et al, 2006a). On the basis of primidone, for which there was an extensive database, the estimated range of wastewater contribution to the drinking water supplies during the sampling was on the order of a few percent to ~20–30%, which met the goal of examining drinking waters with a range of effects.

DBPFPs. As expected, there was much more THMFP in the source waters and plant influents because of chlorination (range = 57–492 µg/L, median = 158 µg/L) than chloramination (range = 4.0–42 µg/L, median = 12 µg/L). Because the waters also contained bromide, the FP was affected by the formation of bromine-containing DBPs that weighed more than the chlorine-containing analogues. However, in FP tests, chlorine tends to outcompete bromine because of the relatively high chlorine-to-bromine ratios (Symons et al, 1993). For example, in one plant influent with high levels of precursors (THMFP attributable to chlorination was 303 µg/L [2.4 µmol/L]), including 0.1 mg/L of bromide, 76 or 82% of the THMFP was resulting from chloroform on a weight or molar basis, respectively. Likewise, in the THMFP test with chloramines (26 µg/L [0.2 µmol/L]), 73 or 80% of the THMFP was due to chloroform on a weight or molar basis, respectively.

The formation of the trihalogenated acetaldehydes (e.g., chloral hydrate) resulting from chlorination (range = 7.4–85 µg/L, median = 30 µg/L) was substantially higher than that caused by chloramination (range = ND–5.9 µg/L, median =1.3 µg/L). On a median basis, dihalogenated acetaldehyde (e.g., dichloroacetaldehyde) formation resulting from chlorination and chloramination was similar (medians = 2.1 and 2.5 µg/L, respectively). However, the maximum dihalogenated acetaldehyde FP resulting from chloramination (11 µg/L) was higher than chlorination (7.1 µg/L). For the DWTP that had a dihalogenated acetaldehyde FP resulting from chloramination of 11 µg/L, its dihalogenated acetaldehyde FP caused by chlorination was only 2.8 µg/L.

For the dihalogenated HANs, the amount of FP was typically similar with either test (chlorine or chloramine FP) for the source waters and plant influents. The range (and median) was 0.9–12 (3.4) µg/L and 0.7–7.5 (3.2) µg/L, respectively. There was a good linear relationship between dihalogenated HANFP caused by chlorination and DOC ($R^2 = 0.76$) or UVA ($R^2 = 0.73$), but there was a poor relationship with DON ($R^2 = 0.24$). Also, there was no correlation between dihalogenated HAN yield (i.e., FP/DOC) and specific UVA. Trehy and Bieber (1981) found that certain amino acids (e.g., aspartic acid, tryptophan, kynurenine—which is a tryptophan degradation product) and humic acid could react with chlorine to form dihalogenated HANs, whereas other amino acids (e.g., glycine, alanine, serine) did not. Two of the latter amino acids were those with the highest concentration in this study. Thus, DON may not be a good surrogate for certain N-DBPFPs because of differences in the reactivity of certain portions of the DON to form N-DBPs.

In addition to HANs, another important class of nitriles in water is CNXs. All but one of the source waters and plant influents had measurable amounts of CNXFP. The range (when detected) was 2.7–34 µg/L (median = 11 µg/L). Figure 1 shows the results of a set of tests in which blends of river water and treated wastewater were evaluated for CNXFP. As the wastewater blend increased, the CNXFP increased (from 1.1 to 107 µg/L), whereas the percent of nitrogen derived from the ($^{15}$N-labeled) ammonia decreased. This meant that with treated wastewater, the DON produced more CNCl compared with the inorganic nitrogen contributed by monochloramine.

In terms of chloropicrin, the amount of FP was typically similar with either test (chlorine or chloramine FP) for the source waters and plant influents (range [and median] was ND–5.9 [0.9] and ND–3.4 [0.9] µg/L, respectively). In source waters and plant influents, dihalogenated HNMFP caused by chlorination was ND–3.6 µg/L (median <1.0 µg/L). Dihalogenated HNMFP caused by chloramination was not determined.

All but one of the source waters and plant influents had measurable amounts of NDMAFP. The 25th percentile, median, 75th percentile, 90th percentile, and maximum were 12, 22, 52, 83, and 261 ng/L, respectively. The NDMAFP results—for source waters and plant influents with primidone data in this study—were segmented into three groups: the low-primidone (i.e., ND–3.9 ng/L, middle-primidone (i.e., 4–8 ng/L), and high-primidone (i.e., 9–37 ng/L) tertiles (Guo & Krasner, 2009). In the low-primidone group (e.g., less than a few percent wastewater-impacted), NDMAFP ranged from 10 to 76 ng/L (median = 20 ng/L), whereas in the

![FIGURE 1](image.png)
middle- and high-primidone tertiles (e.g., of the order of ~5–30% wastewater-impacted), NDMAFP was 11–96 ng/L (median = 28 ng/L) and 22–261 ng/L (median = 53 ng/L), respectively. On a median basis, the presence of NDMAFP was higher in the more effluent-impacted waters, although it was not statistically significant across all sites.

**Impact of treatment processes on NOM and DBPFP.** For the DWTPs in this study, water treatment removed on average 30, 30, 25, and 65% of the DOC, DON, free amino acids, and combined amino acids (Dotson & Westerhoff, 2009). Because all of the surveyed DWTPs applied disinfectants/oxidants (i.e., chlorine, chloramines, chlorine dioxide, ozone) to the raw or settled waters (Dotson & Westerhoff, 2009), amino acids were most likely transformed in addition to being physically removed during the treatment process (Lee & Westerhoff, 2009).

For DWTPs that applied chlorine and/or chloramines to treated rather than raw water, the impact of various unit processes (coagulation, lime softening, ozonation, filtration) on amino rather than raw water, the impact of various unit processes (coagulation, lime softening, ozonation, filtration) on amino acids and DBPFP was evaluated. For example, the removal of DOC, UVA, DON, and DBPFP was examined at a lime-softening plant with intermediate ozonation and biological filtration using a GAC filter (example operating conditions: 167 mg/L of lime-softening pH = 10.7, 0.6 mg/L of polyDADMAC solution, 1.9 mg/L of ozone, ozonation pH = 8.3, GAC empty bed contact time = 5.4 min). Figure 2 shows the “sequential” impact of the unit processes at this plant (process effluent compared with process influent, not the raw water) on the precursors for various DBPs in this study. Table 3 summarizes the removal of DBP precursors through the different unit processes for DWTPs that applied chlorine or chloramines to treated rather than raw water.

**Impact of coagulation or softening.** For the three DWTPs over the two sampling events (count = 6) that did not apply chlorine or chloramines until after the coagulation process, the removal efficiency for the surrogate parameters was UVA > DOC > DON. The same was true for the DWTP using lime softening. For coagulation or lime softening, removal of FP for THMs and trihaloacetaldehydes caused by chlorination was bracketed by the removal efficiencies for DOC and UVA, whereas the removal of FP for dihaloacetaldehydes was (in general) not as good as the bulk DOC removal (Figure 3). In addition, the removal of chloropicrin and CNXFP was typically in between the removal of DOC and UVA (Figures 4 and 5). These results suggest that precursors for most of these DBPs were likely aromatic (i.e., humic substances). However, Dotson and Westerhoff (2009) found that water treatment removed (on average) 30, 30, 25, and 65% of the DOC, DON, free amino acids, and total amino acids, respectively.

These precursor control processes removed DOC but not bromide. For example, for the softening plant, which had 0.1 mg/L of bromide, 52% (or 54%) and 46% (or 48%) of the THMs were removed (on a weight or molar basis, respectively) in the FP tests conducted with chlorine and chloramines, respectively. In comparison, there was a reduction in chloroform formation of 61 and 50% in these two FP tests, respectively, or a reduction in bromodichloromethane of 34 and 42% in the FP tests, respectively. There was less reduction in bromodichloromethane FP because DOC was removed but not bromide.

In general, the removal of FP for dihalogenated HANs caused by chlorination was similar to that for the removal of DON (Figure 4). Although total amino acids were better removed than the bulk DON, not all amino acids are precursors for this DBP class. In six waters, the removal of dihalogenated HANFP resulting from chloramination was higher than chlorination.

At most of the DWTPs, the level of NDMAFP was higher after coagulation or lime softening (i.e., “negative” removals) (Figure 5), which was most likely due to the use of certain polymers (Kohut & Andrews, 2003). (A negative percent removal represented an increase in DBP formation.) When the coagulation DWTPs were segmented by polyDADMAC use or not, NDMAFP was found to change by −43 to −82% (i.e., increased by 43 to 82%) at the polyDADMAC plants and by −18 to 18% at the DWTP that did not use a cationic polymer. The latter DWTP represented no change, as the coefficient of variation of NDMA measurements was ~20%.

**Impact of ozonation.** In terms of ozonation, UVA was well-removed (median = 48%), whereas the removal efficiencies for DON and DOC were low (medians = −3 to 4%). Likewise, the removal of FP for THMs, dihalogenated HANs, and dihaloge-
nated acetaldehydes during ozonation were low to moderate (medians = 16–33%). In three waters, ozonation significantly destroyed or transformed NDMAFP (median to maximum of all waters = 10–87%), which is consistent with other research that showed that ozone can destroy or transform NDMA precursors (Shah et al, 2012; Lee et al, 2007). Alternatively, ozonation always increased the FP of chloropicrin (median resulting from chlorination or chloramination equal to –226 or –133%, respectively). In addition, ozonation tended to increase the FP of trihalogenated acetaldehydes (minimum to 75th percentile = –49 to –1%) and sometimes increased the FP of CNXs (minimum to median: to –178 to –4%). This is consistent with previous research that showed that preozonation increased chloral hydrate (McKnight & Reckhow, 1992) or chloropicrin (Hoigné & Bader, 1988) formation during subsequent chlorination and CNCl formation during subsequent chloramination (Pedersen et al, 1999). In two cases, this phenomenon may be due to the intermediate formation of aldehydes. Acetaldehyde can react with chlorine to form chloral hydrate (McKnight & Reckhow, 1992), whereas formaldehyde can react with chloramines to form CNCl (Pedersen et al, 1999). (See later discussion of aldehyde data.)

**Impact of filtration.** In terms of filtration at ozone plants, which had biofiltration in four of the five sample events, the removal of DOC, UVA, and DON was low (medians = 11–18%). Likewise, the removal of FP for THMs, dihalogenated HANs, dihalogenated acetaldehydes, and CNXs was low.

### TABLE 3
Removal of DBP precursors (FP—Cl₂ and/or NH₂Cl*) through different unit processes for surveyed DWTPs that applied chlorine and/or chloramines to the treated (not the raw) water†

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<th>Statistic</th>
<th>DOC</th>
<th>UVA</th>
<th>DON</th>
<th>THMs</th>
<th>Dihalogenated HANs</th>
<th>Dihaloacetaldehydes</th>
<th>Trihaloacetaldehydes</th>
<th>Chloropicrin</th>
<th>NDMA</th>
<th>CNX</th>
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<td>19</td>
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<td>4</td>
<td>3</td>
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<td>Overall (coagulation or lime softening, ozonation, and filtration) at ozonation plants</td>
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</table>

Cl₂—chlorine, DOC—dissolved organic carbon, DON—dissolved organic nitrogen, DWTPs—drinking water treatment plants, FP—formation potential, HANs—haloacetonitriles, N—number of samples, N/A—not applicable, NH₂Cl—chloramines

*FP conducted in the presence of Cl₂ or NH₂Cl
†Not including data in which one of the results (before or after the unit process) was a nondetect
‡Number of samples with these data
§Not including extreme outlier
**Filtration at ozone plants that had biofiltration in four of the five sample events

In terms of the ozone plants, the median overall removal attributable to coagulation or softening, ozonation, and filtration of DOC, UVA, and DON was 55, 82, and 33%, respectively. The median overall removal of FP resulting from chlorination for THMs, dihalogenated HANs, trihalogenated acetaldehydes, and chloropicrin was 62, 53, 71, and 33%, respectively, whereas the median overall removal of FP because of chloramination for NDMA and CNXs was 80 and 50%, respectively.

As discussed earlier, formaldehyde and acetaldehyde can react with chlorine or chloramines to form some of the DBPs discussed in this study, including trihalogenated acetaldehydes. Aldehydes can be removed in biologically active filters (e.g., Weinberg et al., 1993). At the DWTPs that did not have (or were believed to not have) biologically active filters (e.g., chlorine or chloramines were applied upstream of the filters with a significant dose), there was the presence of a moderate amount of aldehydes in the filter effluents (e.g., median for formaldehyde = 22 µg/L). Alternatively, at DWTPs in which the filters were believed to be biologically active (e.g., chlorine or chloramines were applied downstream of the filters or only a small dose was applied upstream), low levels (if any) of the aldehydes were detected.

**Overall impact of treatment/ozonation.** The overall impact of treatment/ozonation is shown in Figure 3. The figure illustrates the relationship between the removal of precursors for THMs and haloacetaldehydes (in the presence of chlorine) to the removal of DOC or UVA during coagulation or lime softening. The data points represent the removal efficiency of various parameters at different treatment plants. The line of perfect correlation indicates the ideal scenario where both DOC and UVA removal closely follow the same trend. However, the actual data points deviate from this line, indicating the complexity and variability in the treatment process.

**FIGURE 3** Relationship of the removal of precursors for THMs and haloacetaldehydes (in the presence of chlorine) to the removal of DOC or UVA during coagulation or lime softening.

- **UVA** removal
- **THMFP** removal
- **Dihaloacetaldehyde FP** removal
- **Trihaloacetaldehyde FP** removal

DBPFP—disinfection by-product formation potential, DOC—dissolved organic carbon, THMFP—trihalomethane formation potential, UVA—ultraviolet absorbance
part) to differences in bromine incorporation during chlorination versus chloramination. In terms of chloropicrin, the amount of FP was similar with either test (conducted with chlorine or chloramines) for the plant influent and softened water. However, ozonation resulted in a larger increase in chloropicrin FP from chlorination than it did from chloramination.

During this sampling event, dihalogenated HNMs were not detected in FP tests. However, in another sample event for the same plant they were detected; tests were only conducted with chlorine for the dihalogenated HNMs. Lime softening did not remove their FP, ozonation increased their FP (from 1.7 to 6.9 µg/L), and biofiltration brought them down somewhat (to 4.9 µg/L).

**Ambient formation and occurrence of DBPs.** Full-scale DBP formation is impacted by the level of DBPFPP as well as the bromide-to-DOC ratio, type of treatment, concentration of chlorine, and the chlorine contact time. This section presents actual DBP levels formed at the full-scale facilities.

**Chlorination DBPs.** Table 4 shows the occurrence of THMs, HANs, haloacetaldehydes, and HNMs in the full-scale plant effluents. These were not segmented by chlorine or chloramine usage because most of the formation of these DBPs at DWTPs that postchloraminated was during prechlorination. A DWTP with ozone and chloramines and no free chlorine contact time produced the lowest levels of these DBPs (4.3–8.8 µg/L of THMs; not detected and 0.7 µg/L of dihalogenated HANs; not detected for the haloacetaldehydes and HNMs).

In other research, the concentration of THMs was typically around 10 times higher than that of the dihalogenated HANs (Krasner et al, 1989; Oliver, 1983). In this survey, the median ratio (i.e., 7.3 µg THM/µg HAN) was somewhat lower, suggesting that HAN precursors were more prevalent in the effluent- and algae-impacted waters in this study. Two of the DWTPs with relatively high ratios (i.e., 15 and 21 µg THM/µg HAN) in 2006 were not significantly algae-impacted (counts = 300 and 25/mL, respectively). In 2007, one of the previously mentioned DWTPs had similar algal counts and a similar THM-to-dihalogenated-HAN ratio, whereas the other DWTP had more algal counts (i.e., 2,000/mL) and a lower THM-to-dihalogenated-HAN ratio (i.e., 6.9 µg THM/µg HAN).

In terms of the emerging DBPs, trihalogenated acetaldehydes were present in the highest concentration (e.g., 75th percentile = 5.9 µg/L and maximum = 19 µg/L). Dihalogenated acetaldehydes were detected in seven waters at concentrations of 3.0 µg/L or higher (75th percentile and maximum values were 3.1 and 11 µg/L, respectively). The DWTP with the highest level of trihalogenated acetaldehydes (i.e., 19 µg/L) also had the second highest level of dihalogenated HANs (i.e., 9.5 µg/L) and the highest algal count (i.e., 22,700/mL). However, the levels of DOC and DON
in that plant influent (i.e., 3.3 mg/L and 0.19 mg-N/L, respectively), were not that high (i.e., ~40th and ~15th percentiles, respectively). The formation of certain DBPs is likely due to the presence of specific components of the NOM as well as the operations at each DWTP.

The highest formation of dihalogenated acetaldehydes (i.e., 5.1–11 µg/L) occurred at three DWTPs that used ozone and chloramines, two of which did not use biological filtration. Alternatively, another DWTP with ozone, biological filtration, and chloramines did not produce dihalogenated acetaldehydes. In another US nationwide occurrence study, the highest formation of dihalogenated acetaldehydes was at a DWTP that used chloramines and ozone without biological filtration (Krasner et al, 2006b). In the latter study, it was hypothesized that acetaldehyde produced by ozone can react with chloramines to form dihalogenated acetaldehydes. At the two ozone/chloramine plants without biofiltration in this study that produced high levels of dihalogenated acetaldehydes, the highest levels of acetaldehyde in this study were detected (i.e., 8–12 µg/L), whereas at the ozone/chloramine plant with biofiltration and no dihalogenated acetaldehydes, acetaldehyde was not detected in one sample event and was detected at a low level (1.9 µg/L) during a second sampling.

Increasing bromide/DOC will result in more bromine incorporation and more DBP formation, on both a weight and molar basis (Symons et al, 1993). Because bromide levels often increase during low-flow seasons (e.g., summer) and most of the plants in this study were sampled in the summer when the algal activity or wastewater impact was higher (except for five plants that were...
resampled in year 2 in the winter or spring), bromide-to-DOC ratios may have been relatively higher. Figure 7 shows the bromine incorporation factor for trihalogenated acetaldehydes and THMs, which is the molar sum of bromine incorporated into a class of DBPs divided by the molar concentration of that class of DBPs (Symons et al, 1993). For the trihalogenated acetaldehydes, bromine incorporation values ranged from 0 (e.g., all chloral hydrate) to 3 (e.g., all tribromoacetaldehyde). A bromine incorporation factor of 1.0 for trihalogenated acetaldehydes corresponds to a water in which the “average” species is bromodichloroacetaldehyde. In this comparison, there was a good correlation ($R^2 = 0.84$) in bromine incorporation factors for the THMs and trihalogenated acetaldehydes. However, the slope was less than 1.0 (i.e., 0.75). There may have been less apparent bromine

### TABLE 4 Occurrence of THMs, HANs, haloacetaldehydes, and halonitromethanes in plant effluents

<table>
<thead>
<tr>
<th>Statistic</th>
<th>THMs µg/L</th>
<th>Dihalogenated HANs µg/L</th>
<th>THMs/Dihalogenated HANs µg/µg</th>
<th>Dihaloacet-aldehydes µg/L</th>
<th>Trihaloacet-aldehydes µg/L</th>
<th>Dihalogenated Nitromethanes µg/L</th>
<th>Chloropicrin µg/L</th>
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</thead>
<tbody>
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<td>Minimum</td>
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<td>3.6</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<tr>
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<td>6.7</td>
<td>ND</td>
<td>ND</td>
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<tr>
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<td>5.9</td>
<td>13</td>
<td>ND</td>
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<tr>
<td>90th percentile</td>
<td>60</td>
<td>7.7</td>
<td>16</td>
<td>4.5</td>
<td>15</td>
<td>0.6</td>
<td>1.9</td>
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<tr>
<td>Maximum</td>
<td>167</td>
<td>9.9</td>
<td>93</td>
<td>11</td>
<td>19</td>
<td>2.0</td>
<td>7.6</td>
</tr>
</tbody>
</table>

HANs—haloacetonitriles, MRL—minimum reporting level, ND—not detected, THMs—trihalomethanes

*MRLs for each species in the DBP class


![FIGURE 7](image-url)  
**Bromine incorporation factor for trihalogenated disinfection by-products**

$y = 0.7516x - 0.0537$

$R^2 = 0.8375$

*Excluding two significant outliers for data sets with low levels of chloral hydrate (i.e., 1.3–2.4 µg/L), where the other trihalogenated acetaldehydes were not detected at or above their minimum reporting levels
incorporation in the trihalogenated acetaldehydes because of steric hindrance and/or the instability of these DBPs. Xie and Reckhow (1996) found that the bromine-containing trihalogenated acetaldehydes could undergo base-catalyzed hydrolysis. In most studies, chloral hydrate is the only haloacetaldehyde measured. This study demonstrated that bromine-containing and/or dihalogenated species are also important. (A similar analysis was not done for the dihalogenated acetaldehydes because their occurrence was too low to see the effect of bromine incorporation.)

Although most finished waters had low levels of chloropicrin (median and 90th percentile values were 0.5 and 1.9 µg/L, respectively), one DWTP had a relatively high amount of this HNMs (i.e., 7.6 µg/L). The latter DWTP also had the highest concentration of THMs (i.e., 167 µg/L). The dihalogenated HNMs were typically not detected (90th percentile and maximum values were 0.6 and 2.0 µg/L, respectively).

**Chloramination DBPs.** Table 5 shows the formation of CNXs at the DWTPs. Although there was CNXFP in almost all of the sites studied, CNX formation was typically only observed at the DWTPs that used chloramines (median = 2.6 µg/L), which is consistent with previous research (Krasner et al, 1989); also, CNXs are not stable in free chlorine. The highest CNX formation (i.e., 8.4 µg/L) was at the DWTP with the highest level of dihalogenated HANs (i.e., 9.9 µg/L) and one of the lowest THM-to-dihalogenated-HAN ratios (i.e., 3.8 µg/µg). Yet, the levels of DOC and DON (i.e., 2.2 mg/L and 0.12 mgN/L, respectively) were relatively low (i.e., ~ 15th and ~ 5th percentiles, respectively). This plant used prechlorination, coagulation, filtration, chloramination, and post-UV disinfection.

At the three ozone/chloramine plants that did not use biological filtration, relatively high levels of formaldehyde were detected (18–50 µg/L). At two of these DWTPs, high levels of CNXs were formed (i.e., 4.6–8.1 µg/L), whereas CNXs were not detected at a third plant. CNCl can undergo base-catalyzed hydrolysis (Sclimenti et al, 1995). However, all three plants had similar finished water pH levels (i.e., 8.7–9.1). Differences in CNX occurrence may have been due in part to differences in retention time (e.g., in clearwells) at the three plants. Krasner and colleagues (1989) found that CNCl degraded over time at similar pH levels. At three ozone/chloramine plants that used biological filtration, CNXs were present at lower levels in general (i.e., 0.7, 1.9, and 4.1 µg/L).

Table 5 shows the occurrence of NDMA in the plant effluents. In the effluents that were chlorinated, NDMA was not detected, even though almost all had NDMAFP. In the effluents that were chloraminated, NDMA was typically < 2.0 ng/L. The 75th and 90th percentile NDMA occurrence in the chloraminated waters was 3.3 and 10 ng/L, respectively. Because all of the chloramine plants in this study used a strong preoxidant, this may explain in part the low occurrence of NDMA in the finished waters, even though all had NDMAFP (Shah et al, 2012). NDMA forms slowly because of chloramination (Charrois & Hruday, 2007), therefore it is probable that more NDMA formed in the distribution system.

Regardless of source water effects, effluent NDMA concentrations at chloramine plants generally increased with increasing usage of cationic polymer (polyDADMAC) (Figure 8). In other research, it was found that optimization of the polymer dose resulted in less NDMA formation (Wilczak et al, 2003). Figure 9 shows an example of the occurrence of NDMA and its FP at two DWTPs in the same watershed. Plant 1 treated water that was effluent-impacted (based on primidone, ~ 5–15%), whereas plant 2 took water upstream of WWTP discharges. Thus, plant 1 had much more NDMAFP in its plant influent. Nonetheless, plant 2 had much more NDMA in its finished water. Both plants practiced prechlorination, which would have destroyed/transformed NDMAFP from the source water.
Plant 2 used polyDADMAC (e.g., 1.2 mg/L dose of polymer solution), whereas plant 1 did not use any polymer. Thus, NDMA formation was the result of a complex interaction of source water precursors, polymer usage, and disinfection processes. This example demonstrates that it cannot be assumed a priori that wastewater-impacted waters will form more NDMA because polyDADMAC is another important source of precursors.

**SUMMARY**

This research has shown that the formation and control of certain emerging C- and N-DBPs may be different from that of the regulated THMs. This can be due to differences in the sources of precursors (e.g., humic substances versus proteinaceous materials) and/or differences in the effect of disinfection processes on these DBPs.

Utilities have installed and modified treatment practices to control the formation of regulated DBPs (e.g., THMs). To balance the control of regulated DBPs with that of emerging DBPs of health concern, utilities will need to optimize a series of unit processes to minimize the formation of a wide range of DBPs.

- Although chloramination minimizes the formation of THMs and trihalogenated acetaldehydes, it preferentially forms NDMA and CNXs. In samples affected by treated wastewater, the DON produced more CNCl compared with the inorganic nitrogen contributed by monochloramine.
- Although chlorination forms many halogenated DBPs and prechlorination may increase the formation of CNCl, prechlorination can destroy/transform NDMAFP.
- Ozone may destroy NDMAFP; however, preozonation may increase the formation of trihalogenated acetaldehydes and CNXs, and it increases the formation of HNMs.
- Coagulation or lime softening can remove the precursors for various halogenated DBPs, but the use of certain polymers may contribute NDMA precursor material.
- Biological filtration was able to remove aldehydes that were precursors to haloacetaldehydes and CNXs, and it was shown to reduce the FP of chloropicrin.
- NDMA formation was not observed at plants using free chlorine and was sometimes detected after chloramine application at plants with wastewater EfOM surrogates such as primidone or at plants using polyDADMAC polymers.
- Trends in DON removal, which occurred at 50–500 µg/L N, generally did not correlate strongly with reductions in specific N-DBFP or actual levels of N-DBP occurrence at full-scale WTPs. This implies that a very small fraction of DON was incorporated into N-DBPs, and that bulk DON measurements may not be as informative for N-DBP formation predictions as DOC measurements are for C-DBP formation.

The information in this study can be used by utilities to minimize and balance the formation of THMs and that of certain emerging DBPs of health concern. This is especially important for plants that use water affected by treated wastewater.
and/or algae, which are both sources of precursors for many of these emerging DBPs.

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PEER REVIEW

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FOOTNOTES

1AccQ-Tag™ method, Waters Corp., Milford, Mass.
2Ambersorb 572, Sigma Aldrich, St. Louis, Mo.

REFERENCES


