

Occurrence of a New Generation of Disinfection Byproducts[†]

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A survey of disinfection byproduct (DBP) occurrence in the United States was conducted at 12 drinking water treatment plants. In addition to currently regulated DBPs, more than 50 DBPs that rated a high priority for potential toxicity were studied. These priority DBPs included iodinated trihalomethanes (THMs), other halomethanes, a nonregulated haloacid, haloacetoneitriles, haloaldehydes, halogenated furanones, haloamides, and nonhalogenated carbonyls. The purpose of this study was to obtain quantitative occurrence information for new DBPs (beyond those currently regulated and/or studied) for prioritizing future health effects studies. An effort was made to select plants treating water that was high in total organic carbon and/or bromide to enable the detection of priority DBPs that contained bromine and/or iodine. THMs and haloacetic acids (HAAs) represented the two major classes of halogenated DBPs formed on a weight basis. Haloacetaldehydes represented the third major class formed in many of the waters. In addition to obtaining quantitative occurrence data, important new information was discovered or confirmed at full-scale plants on the formation and control of DBPs with alternative disinfectants to chlorine. Although the use of alternative disinfectants (ozone, chlorine dioxide, and chloramines) minimized the formation of the four regulated THMs, trihalogenated HAAs, and total organic halogen (TOX), several priority DBPs were formed at higher levels with the alternative disinfectants as compared with chlorine. For example, the highest levels of iodinated THMs—which are not part of the four regulated THMs—were found at a plant that used chloramination with no prechlorination. The highest concentration of dichloroacetaldehyde was at a plant that used chloramines and ozone; however, this disinfection scheme reduced the formation of trichloroacetaldehyde. Preozonation was found to increase

[†] This article is part of the Emerging Contaminants Special Issue.

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the formation of trihalonitromethanes. In addition to the chlorinated furanones that have been measured previously, brominated furanones—which have seldom been analyzed—were detected, especially in high-bromide waters. The presence of bromide resulted in a shift to the formation of other bromine-containing DBPs not normally measured (e.g., brominated ketones, acetaldehydes, nitromethanes, acetamides). Collectively, ~30 and 39% of the TOX and total organic bromine, respectively, were accounted for (on a median basis) by the sum of the measured halogenated DBPs. In addition, 28 new, previously unidentified DBPs were detected. These included brominated and iodinated haloacids, a brominated ketone, and chlorinated and iodinated aldehydes.

Introduction

Approximately 600–700 disinfection byproducts (DBPs) have been reported in the literature for the major disinfectants used (chlorine, ozone, chlorine dioxide, chloramines) as well as their combinations (1–3). Of these DBPs, only a small percentage has been quantified in drinking waters. DBP surveys in the United States in the 1980s and 1990s provided data for assessing a new maximum contaminant level (MCL) for trihalomethanes (THMs) as well as to develop regulations for other DBPs. In 1985, the U.S. Environmental Protection Agency (EPA) measured chlorination DBPs at 10 operating utilities, utilizing both target compound and broad-screen analyses (2). The halogenated compounds, cumulatively, accounted for between 30 and 60% of the total organic halogen (TOX) found in these samples. In 1988–1989, a study of 35 U.S. utilities was conducted, which analyzed for 19 halogenated DBPs and two aldehydes (3). On a weight basis, THMs were the largest class of DBPs detected; the second largest fraction was haloacetic acids (HAAs). In addition, Glaze and Weinberg studied the formation of ozonation DBPs at 10 North American utilities in 1990–1991 (4). This study demonstrated that aldehydes could be removed with biofiltration (5), and bromate formation could be minimized at a lower ozonation pH (6).

In 1997–1998, 296 U.S. utilities operating a total of 500 plants conducted a DBP survey under the Information Collection Rule (ICR) (7). This survey included measurements for the 4 regulated THMs, 6–9 HAAs (5 are regulated), 4 haloacetoneitriles, 2 haloaldehydes, trichloronitromethane (chloropicrin), trichloroacetaldehyde (chloral hydrate), cyanogen chloride, chlorite, chlorate, bromate, glyoxal, methyl glyoxal, and 11 other aldehydes. The ICR, which included the same DBPs from the earlier studies (3, 4), greatly expanded our knowledge on the occurrence of these DBPs.

Other DBPs of health concern have had less extensive monitoring. The chlorinated furanone 3-chloro-4-(dichloromethyl)-5-hydroxy-2-(5H)-furanone (MX) has been measured in a limited number of studies in the United States (8, 9) and elsewhere (10). For example, Kronberg and colleagues found from 15 to 67 ng/L of MX in chlorinated drinking water from three towns in Finland (10). MX, its geometric isomer (E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX), and their oxidized and reduced forms were found in U.S. waters (11), while MX and brominated analogues of MX (BMXs) have been identified in Japanese drinking waters (12).

Trihalonitromethanes with bromine have been identified in bench-scale chlorination studies (13), and bromopicrin

was detected in pilot-plant studies after ozone treatment (14). In addition to trihalonitromethanes, mono- and dihalogenated nitromethanes were identified in pilot-scale studies of chlorine and chloramines, with and without preozonation (15, 16). Brominated trihaloacetaldehydes have been found in chlorinated fulvic acid solutions containing bromide (17), and iodinated THMs have been reported in chlorinated and chloraminated drinking water (18–21). Iodinated THM formation in bench- and plant-scale studies was favored by chloramination, especially if the ammonia was added first.

Because many of the non-ICR DBPs have only been studied at bench scale or in limited full-scale surveys, there is significant uncertainty over the identity and levels of DBPs that people are exposed to in their drinking water. Moreover, only a limited number of DBPs have been studied for adverse health effects because such studies are extremely expensive.

To focus this research, an expert toxicology review of the ~500 DBPs reported in the literature (as of 1998) was conducted (22) with an in-depth mechanism-based structural activity relationship analysis—supplemented by an extensive literature search for genotoxicity and other data—used to rank the carcinogenic potential of these DBPs. Approximately 50 DBPs that received the highest ranking for potential toxicity, and that were not already included in the ICR, were selected for a new U.S. occurrence study (23). Highest in this ranking were the bromonitromethanes, which recently have been shown to be more cytotoxic and genotoxic than their chlorinated analogues or their halomethane counterparts (16, 24). Using *in vitro* mammalian cell assays, the bromonitromethanes were more cytotoxic and genotoxic than most of the regulated HAAs (16, 25).

The priority DBPs in this study included mono-, di-, tri-, and/or tetra-substituted species of halomethanes (including iodinated species), haloacetonitriles, haloketones, haloacetaldehydes, halonitromethanes, haloamides, and halogenated furanones (Table 1). Because most of the priority DBPs were from chlorine or chloramine disinfection, a few additional ozone and chlorine dioxide DBPs (e.g., carbonyls) that were not ranked as a high priority were also included for completeness (i.e., to provide more information on those alternative disinfectants). In addition, methyl *tert*-butyl ether (MTBE) and methyl bromide (bromomethane), which are volatile organic compounds (VOCs) but not DBPs, were included in the list of target analytes because they are important source water pollutants, and their measurement would provide valuable occurrence information. Carbon tetrachloride and methylethyl ketone, which are also VOCs, are possible DBPs. Regulated and some ICR DBPs were also included in this study for comparison purposes (Table 2). In addition, routine water quality measurements, such as total organic carbon (TOC), ultraviolet absorbance (UVA) at 254 nm, bromide, and TOX, were determined.

The objectives of this new nationwide occurrence study included the development of quantitative analytical methods for measuring the priority DBPs; the occurrence levels of these DBPs—together with those in the ICR—in drinking waters across the United States (including waters treated with chlorine, chloramines, ozone, and/or chlorine dioxide); the effect of source water and treatment conditions on their formation; the fate and transport of these DBPs in the distribution system; and the identification of new, previously unreported DBPs. Because chemical standards were often not commercially available, several of the DBP standards had to be synthesized for the methods development and quantitation effort. This paper presents an overview of the U.S. occurrence of a new generation of DBPs of health and regulatory concern as well as water quality and treatment/disinfection parameters that affect the formation and control of these DBPs.

Experimental Methods

Chemical Standards. A number of the priority DBPs were synthesized for this study (Supporting Information) (22, 26). Since the project began, some of the standards have become commercially available (Orchid Helix, New Westminster, BC, Canada). Other synthesized standards used to confirm broadscreen identifications were provided by CanSyn Chem Corp. (Toronto, ON, Canada). All other chemicals and reagents were purchased at the highest level of purity from Acros Organics (Pittsburgh, PA), Aldrich Chemical Co. (Milwaukee, WI), ChemService (West Chester, PA), Fluka Chemical Co. (Ronkonkoma, NY), Mallinckrodt (Phillipsburg, NJ), Sigma Chemical Company (St. Louis, MO), Supelco (Bellefonte, PA), TCI America (Portland, OR), or Ultra Scientific (North Kingston, RI) (23, 26).

Analytical Methods. A brief description of the analytical methods follows; more extensive details can be found in the Supporting Information. Most of the halogenated DBPs—THMs, tribromochloromethane, haloacetonitriles, haloacetones, di- and trihalogenated acetaldehydes, halonitromethanes, tetrabromochloroethane, and benzyl chloride—were analyzed for and quantified using a liquid/liquid extraction (LLE)-gas chromatography (GC)/electron capture detection (ECD) method (23, 26). A purge-and-trap-GC/mass spectrometry (MS) method was used to analyze for VOCs and certain volatile chemicals that have been reported as possible DBPs (mono- and dihalogenated methanes, carbon tetrachloride, methylethyl ketone) and to provide MS confirmation of other volatile DBPs (23, 26). A solid-phase extraction (SPE) method was used to provide MS confirmation of semivolatile DBPs (23, 26). A solid-phase microextraction (SPME)-GC/ECD method was used in lieu of the LLE method in the last sampling quarter of the study (27).

Nonhalogenated carbonyl compounds and chloroacetaldehyde were derivatized with pentafluoro-benzylhydroxylamine (PFBHA), and the oxime products were extracted and analyzed by GC/ECD (23). A LLE-GC/ECD method was used for quantifying bromochloromethyl acetate (23). Another LLE-GC/ECD method was used for quantifying the haloacetamides (23). The halogenated furanones were extracted from water, derivatized with boron trifluoride in methanol, back extracted, and analyzed by GC/ECD (23, 28).

The ICR HAAs were measured using acidic and salted LLE, derivatization with acidic methanol, and GC/ECD analysis (29). Another haloacid, 3,3-dichloropropenoic acid, was analyzed by a similar method, substituting diazomethane for acidic methanol in the derivatization step (30). TOC measurements were made with the UV-persulfate oxidation method (31). The UVA measurements were made at 254 nm with filtered samples at ambient pH, using a UV-visible spectrophotometer. Bromide was measured by ion chromatography (IC) (31). TOX was analyzed using the adsorption-pyrolysis titrimetric method (31). During the last sampling quarter of the study, selected samples were also analyzed for total organic bromine (TOBr) and total organic chlorine (TOCl). The off-gas from the TOX combustion furnace was collected in water, and the concentrations of the bromide and chloride ions were determined by IC (32).

Finally, selected samples were comprehensively (broad-screen) analyzed for DBPs (to enable the detection of DBPs that were not among the ICR compounds and the group of >50 priority DBPs quantified). GC with high- and low-resolution electron ionization (EI) and chemical ionization (CI) MS was used primarily to identify the DBPs (23, 33). When possible, tentative identifications were confirmed through the analysis of authentic chemical standards, purchased commercially or synthesized.

Sampling Survey. A survey of 12 U.S. full-scale treatment plants was conducted in the years 2000–2002. Each plant

TABLE 1. Priority DBPs Selected for Nationwide Occurrence Study

halomethanes		
chloromethane bromomethane (methyl bromide) ^a bromochloromethane dibromomethane	dichloriodomethane bromochloriodomethane dibromiodomethane ^b chlorodiodomethane ^b	bromodiodomethane ^b triiodomethane (iodoform) ^b carbon tetrachloride tribromochloromethane
haloacids		
3,3-dichloropropenoic acid		
haloacetonitriles		
chloroacetonitrile bromoacetonitrile	bromodichloroacetonitrile dibromochloroacetonitrile	tribromoacetonitrile
haloacetates		
bromochloromethyl acetate		
haloketones		
chloropropanone 1,3-dichloropropanone 1,1-dibromopropanone 1,1,3-trichloropropanone	1-bromo-1,1-dichloropropanone 1,1,3,3-tetrachloropropanone 1,1,1,3-tetrachloropropanone	1,1,3,3-tetrabromopropanone ^b 1,1,1,3,3-pentachloropropanone ^c hexachloropropanone ^c
haloaldehydes		
chloroacetaldehyde dichloroacetaldehyde	bromochloroacetaldehyde ^b	tribromoacetaldehyde ^b
halonitromethanes		
chloronitromethane ^b bromonitromethane dichloronitromethane ^b	bromochloronitromethane ^b dibromonitromethane bromodichloronitromethane ^b	dibromochloronitromethane ^b tribromonitromethane (bromopicrin) ^b
haloamides		
monochloroacetamide ^b monobromoacetamide ^b	dichloroacetamide dibromoacetamide ^b	trichloroacetamide ^b
halogenated furanones		
3-chloro-4-(dichloromethyl)-5-hydroxy-2(5 <i>H</i>)-furanone (MX) 3-chloro-4-(dichloromethyl)-2-(5 <i>H</i>)-furanone (red-MX) (<i>E</i>)-2-chloro-3-(dichloromethyl)butenedioic acid (ox-MX) (<i>E</i>)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX) (<i>Z</i>)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (ZMX) ^g 2,3-dichloro-4-oxobutenoic acid (mucochloric acid) (MCA) (ring and open forms)	3-chloro-4-(bromochloromethyl)-5-hydroxy-2(5 <i>H</i>)-furanone (BMX-1) 3-chloro-4-(dibromomethyl)-5-hydroxy-2(5 <i>H</i>)-furanone (BMX-2) 3-bromo-4-(dibromomethyl)-5-hydroxy-2(5 <i>H</i>)-furanone (BMX-3) (<i>E</i>)-2-chloro-3-(bromochloromethyl)-4-oxobutenoic acid (BEMX-1) ^b (<i>E</i>)-2-chloro-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-2) ^b (<i>E</i>)-2-bromo-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-3) ^b	
VOCs^d and miscellaneous DBPs		
1,1,1,2-tetrabromo-2-chloroethane ^a 1,1,2,2-tetrabromo-2-chloroethane ^b	methyl- <i>tert</i> -butyl ether ^a	benzyl chloride
carbonyls		
2-hexenal 5-keto-1-hexanal ^f	cyanoformaldehyde methylethyl ketone ^f	6-hydroxy-2-hexanone ^f dimethylglyoxal

^a Not a DBP but included because it is an important source water contaminant. ^b DBP not originally prioritized (identified in drinking water after initial prioritization) but included due to similarity to other priority compounds. ^c Not analyzed; not stable in water. ^d Carbon tetrachloride, which is also a VOC, listed under halomethanes as a possible DBP. ^e Not analyzed; standard not available. ^f DBP not given a high priority but included for completeness sake to provide more representation to ozone DBPs for occurrence. ^g Isomer of EMX.

was sampled four to five times to obtain information on seasonal effects. Samples were collected in the fall (October–December) of 2000; the winter (plus early spring) (January–April), summer (July–September), and fall of 2001; and the winter (plus early spring) of 2002. Most of the halogenated DBPs were measured each quarter, whereas some analytical fractions (i.e., certain carbonyls, haloacetamides, halogenated furanones, 3,3-dichloropropenoic acid, and TOX) were monitored for at half of the utilities each quarter (i.e., the latter parameters were measured at each utility up to 2–3 times over the course of the study). Qualitative, broadscreen analyses were also conducted at half of the utilities each quarter, with each plant sampled at least once over the course of the study.

Two plants that treat water from the same watershed but use different treatment/disinfection scenarios were sampled together (Table 3). An effort was made to select plants treating water that was high in TOC and/or bromide to enable the detection of priority DBPs that contained bromine and/or iodine (iodide levels were not measured, but in one study of waters impacted by saltwater intrusion or connate water they were 8–25% of the bromide levels on a weight basis (34)). All of the plants treated surface-water supplies except for two plants (7 and 8), which treated a colored groundwater. This study was not an occurrence survey per se, rather it was a targeted survey of waters with “challenged” conditions. The treatment technologies encompassed by the plants included coagulation, lime softening, membrane softening,

TABLE 2. ICR and Regulated DBPs Included for Comparison

halomethanes	
chloroform	dibromochloromethane
bromodichloromethane	bromoform
haloacetonitriles	
dichloroacetonitrile	dibromoacetonitrile
bromochloroacetonitrile	trichloroacetonitrile
haloacetic acids	
monochloroacetic acid	trichloroacetic acid
monobromoacetic acid	bromodichloroacetic acid
dichloroacetic acid	dibromochloroacetic acid
bromochloroacetic acid	tribromoacetic acid
dibromoacetic acid	
halonitromethanes	
trichloronitromethane (chloropicrin)	
haloketones	
1,1-dichloropropanone	1,1,1-trichloropropanone
haloaldehydes	
chloral hydrate	
oxyhalides	
bromate	chlorate
chlorite	

biological filtration, chlorination, ozonation, chlorine dioxide disinfection, and chloramination. Most of the plants that used biological filtration had granular activated carbon (GAC) filters or contactors. In addition, some plants added powdered activated carbon (PAC).

Results and Discussion

Overview. The concentrations of selected DBPs and their precursors are presented in Table 4. On a median basis, the raw-water levels of TOC (5.8 mg/L) and bromide (0.12 mg/L) for the surveyed plants were much higher than those of the plants studied in the ICR (median TOC and bromide were 2.4 and 0.04 mg/L, respectively). The raw-water specific UVA (SUVA), which is an indicator of the humic content of the water and provides an indication of the reactivity of TOC to form DBPs (e.g., THMs, TOX), was (on a median basis) 2.9 L/mg·m for the surveyed plants. The median value corresponds to a source water of intermediate humic content.

Figure 1 shows the occurrence (using box-and-whisker plots) of the target DBPs and TOX in the finished waters of the 12 plants over the five quarters, and the Supporting Information includes additional data for the 12 plants. As has been observed before (3, 7), THMs and HAAs were the two major classes of halogenated DBPs. Although the surveyed plants treated waters relatively high in DBP precursors, the use of alternative disinfectants at most of the plants allowed them to minimize the formation of the sum of the four regulated THMs (THM4) in the plant effluents (median value of 31 $\mu\text{g/L}$). The median concentration of THM4 in finished waters in the ICR—which included many low-TOC groundwater systems—was 23 $\mu\text{g/L}$. In the ICR, when segmented by source of supply, the median THM4 value for distribution systems was 39 $\mu\text{g/L}$ for surface-water systems and 7.8 $\mu\text{g/L}$ for groundwater systems. The sum of the nine HAAs in the surveyed plants was (on a median basis) 34 $\mu\text{g/L}$, whereas the median value in the ICR was 20 $\mu\text{g/L}$. (ICR HAA data segmented by source of supply were not available for comparison.)

In the ICR (7) and other studies (3), chloral hydrate was the only haloacetaldehyde measured (median and 75th

percentile values of 1.7 and 4.0 $\mu\text{g/L}$, respectively, in the ICR). The occurrence of chloral hydrate in the surveyed plants (Table 4) was similar to that found in the ICR. With the addition of mono- and dihalogenated as well as bromine-containing species the haloacetaldehydes represented the third largest class of halogenated DBPs formed (on a weight basis—albeit, at much lower concentrations than that of the THMs or HAAs) in many of the waters in this study (Figure 1, Supporting Information).

In the plant effluents, the TOX was (on a median basis) 178 $\mu\text{g/L}$ as Cl^- . In the ICR, the median value for surface-water plants was 122 $\mu\text{g/L}$. On a median basis, THM4, HAAs, and haloacetaldehydes accounted for 14, 12, and 2% of the TOX, respectively, in the surveyed plants (Figure 2, Supporting Information). Collectively, ~30% of the TOX was accounted for (on a median basis) by the sum of the halogenated DBPs (halo-DBPs) (i.e., ~70% remains unknown). For individual plants, the percentage of TOX accounted for by the halo-DBPs ranged from 10 to 66% (Figure 2), which is similar to that reported in other studies (2).

For seven plants sampled in the last quarter of the study, the effluent TOBr was (on a median basis) 79 $\mu\text{g/L}$ as Br^- , which is equivalent to 35 $\mu\text{g/L}$ as Cl^- . The percentage of TOBr accounted for by the halo-DBPs ranged from 6 to 58%, with a median value of 39% (Figure 3). This compares favorably to the range of values observed in a bench-scale study of disinfection of Suwannee river fulvic acid (35). In that study, bromine-containing DBPs represented >60, 26, 14, and 8.2% of the TOBr in the samples treated with chlorine, chlorine dioxide, chloramines, and ozone, respectively.

In the plant effluents, the TOCl was (on a median basis) 161 $\mu\text{g/L}$ as Cl^- . On a median basis, more of the TOX (as Cl^-) was due to TOCl than as TOBr. The percentage of TOCl accounted for by the halo-DBPs ranged from 12 to 33%, with a median value of 24% (Figure 3, Supporting Information). Zhang and colleagues found that the chlorine-containing ICR DBPs represented ~50, 31, 17, and 0% of the TOCl in the Suwannee river fulvic acid samples treated with chlorine, chlorine dioxide, chloramines, and ozone, respectively (35). The percentage of TOX, TOBr, or TOCl that was accounted for in chlorinated waters tended to be higher than in samples treated with alternative disinfectants (35).

In the drinking water plant effluents, bromide utilization in the halo-DBPs ranged from 1 to 41% of the raw-water bromide, with a median value of 22%. Amy and colleagues found that when bromide is oxidized during disinfection to hypobromous acid, it is an efficient halogen substitution agent, and as much as 50% or more of the bromide was incorporated into THMs in formation potential tests (36). In our full-scale study, in which chlorination doses were not as high and reaction times not as long as in formation potential tests, somewhat less bromide utilization was observed and was found to be incorporated into a wide range of DBPs, not just THMs.

Occurrence of Different Classes of DBPs

THMs. The concentration of the iodinated THMs was typically low compared to THM4 (Figure 1; Table 4). The ratio of the iodo-THMs to THM4 was 2% on a median basis, with 75th percentile and maximum values of 7 and 81%, respectively. The highest formation of iodo-THMs was at plant 12 in November 2001 (iodo-THMs at 81% of the THM4), which added chlorine and ammonia simultaneously to form chloramines in a water with a moderate amount of bromide (0.15 $\mu\text{g/L}$ in November 2001) (Figure 4). There was no measurable free chlorine in this sample. As has been observed in previous research (19, 21), the formation of iodo-THMs was favored by chloramination, especially if the ammonia was added first. Overall, dichloroiodomethane was the most common iodo-THM observed and was even found in waters

TABLE 3. Treatment/Disinfection Processes at Surveyed Plants

plant no. ^a	EPA region ^b	treatment ^c	disinfectants
1	9	flocculation, coagulation, sedimentation, biological filtration	ozone, chlorine, chloramines
2	9	coagulation, flocculation, sedimentation, filtration	chlorine, chloramines
3	3	flocculation, coagulation, sedimentation, filtration, biological filtration	chlorine, chloramines
4	3	flocculation, coagulation, sedimentation, filtration	chlorine
5	4	flocculation, coagulation, sedimentation or solids contact-upflow clarification, biological filtration	ozone, chlorine
6	4	coagulation, clarification, filtration	chlorine dioxide, chlorine, chloramines
7	4	lime softening, filtration	chloramines, ozone
8	4	lime softening, filtration or membrane softening	chlorine, chloramines
9	7	lime softening, coagulation, sedimentation, PAC, filtration	chlorine, chloramines
10	5	PAC, flocculation, coagulation, sedimentation, filtration or biological filtration	chlorine, chloramines, or chlorine only
11	6	upflow-solids contact, flocculation/clarification, filtration	chlorine dioxide, chlorine, chloramines
12	6	coagulation, filtration	(chlorine dioxide), chloramines

^a The following pairs of plants treated water from the same or similar watersheds: plants 1 and 2; 3 and 4; 5 and 6; 7 and 8; 9 and 10; and 11 and 12. ^b The 12 plants in this survey were located in six of the nine regions defined by the USEPA. The states included in each of these six regions are as follows: EPA Region 9—Arizona, California, Hawaii, Nevada; EPA Region 3—Delaware, Maryland, Pennsylvania, Virginia, West Virginia, Washington D.C.; EPA Region 4—Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee; EPA Region 7—Iowa, Kansas, Missouri, Nebraska; EPA Region 5—Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin; EPA Region 6—Arkansas, Louisiana, New Mexico, Oklahoma, Texas. ^c Some plants had parallel trains with different treatment processes.

TABLE 4. Concentration of Selected DBPs and Their Precursors in U.S. Occurrence Study in Waters Exhibiting High-Precursors Loadings^a

parameter	unit	location	minimum	median	75th percentile	maximum
TOC	mg/L	raw water	3.0	5.8		13
SUVA	L/mg-m	raw water	1.9	2.9		3.9
bromide	mg/L	raw water	0.02	0.12		0.40
THM4	µg/L	plant effluent	4	31	45	164
sum of 6 iodinated THMs	µg/L	plant effluent	ND ^b	0.4	2	19
sum of 9 HAAs	µg/L	plant effluent	5	34	56	130
3,3-dichloropropenoic acid	µg/L	plant effluent	ND ^b (<0.1)	ND ^b	0.7	4.7
sum of haloacetaldehydes	µg/L	plant effluent	0.2	4	7	20
chloral hydrate	µg/L	plant effluent	ND ^b	1	3	16
dichloroacetaldehyde	µg/L	plant effluent	ND ^b	1	2	14
sum of haloacetonitriles	µg/L	plant effluent	ND ^b	3	4	14
dichloroacetonitrile	µg/L	plant effluent	ND ^b	1	2	12
sum of haloacetamides	µg/L	plant effluent	ND ^b	1.4	2.5	7.4
2,2-dichloroacetamide	µg/L	plant effluent	ND ^b	1.3	2.0	5.6
sum of haloketones	µg/L	plant effluent	ND ^b	2	4	9
1,1,1-trichloropropanone	µg/L	plant effluent	ND ^b	0.8	3	7
1-bromo-1,1-dichloropropanone	µg/L	plant effluent	ND ^b	0.2	<1	<3
sum of halonitromethanes	µg/L	plant effluent	ND ^b	1	3	10
chloropicrin	µg/L	plant effluent	ND ^b	0.2	0.4	2.0
bromopicrin	µg/L	plant effluent	ND ^b	ND ^b	ND ^b	5
sum of halogenated furanones	ng/L	plant effluent	ND ^b	310	610	2,380
MX	ng/L	plant effluent	ND ^b (<20)	20	60	310
BMX-1	ng/L	plant effluent	ND ^b (<20)	ND ^b	80	170
BEMX-1	ng/L	plant effluent	ND ^b (<20)	ND ^b	ND ^b	720
BMX-2	ng/L	plant effluent	ND ^b (<20)	ND ^b	ND ^b	30
BEMX-2	ng/L	plant effluent	ND ^b (<20)	ND ^b	30	810
BMX-3	ng/L	plant effluent	ND ^b (<20)	ND ^b	ND ^b	40
BEMX-3	ng/L	plant effluent	ND ^b (<20)	ND ^b	180	410
TOX	µg/L as Cl ⁻	plant effluent	21	178	206	284
TOCl	µg/L as Cl ⁻	plant effluent	87	161	194	206
TOBr	µg/L as Br ⁻	plant effluent	36	79	80	229
TOBr	µg/L as Cl ⁻	plant effluent	16	35	36	102
cyanoformaldehyde	µg/L	plant effluent	ND ^b	ND ^b	ND ^b	0.3
5-keto-1-hexanal	µg/L	plant effluent	ND ^b	ND ^b	ND ^b	ND ^b
6-hydroxy-2-hexanone	µg/L	plant effluent	ND ^b	ND ^b	ND ^b	ND ^b
dimethylglyoxal	µg/L	plant effluent	ND ^b	0.1	1.4	3.5
trans-2-hexenal	µg/L	plant effluent	ND ^b	ND ^b	ND ^b	0.7
methyl ethyl ketone	µg/L	plant effluent	ND ^b	ND ^b	ND ^b	5

^a Twelve plants, up to 5 seasons each. ^b ND = not detected.

that had average levels of bromide (which should also have had some iodide) (e.g., note plants 5 and 6 in the Supporting Information).

Haloacids. The one priority haloacid that was quantified in this study was 3,3-dichloropropenoic acid (Table 4). Its determination provides quantitative evidence that haloge-

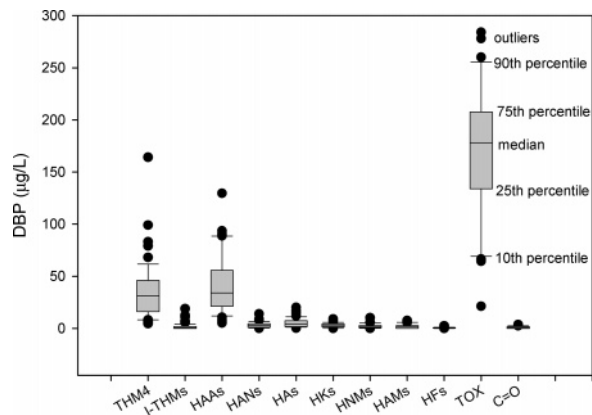


FIGURE 1. Concentration of DBPs in plant effluents in U.S. occurrence study in waters exhibiting high-precursors loadings (12 plants, up to 5 seasons each). I-THMs = iodinated THMs, HANs = haloacetonitriles, HAs = haloacetaldehydes, HKs = haloketones, HNMs = halonitromethanes, HAmS = haloacetamides, HFs = halogenated furanones, and C=O = carbonyls.

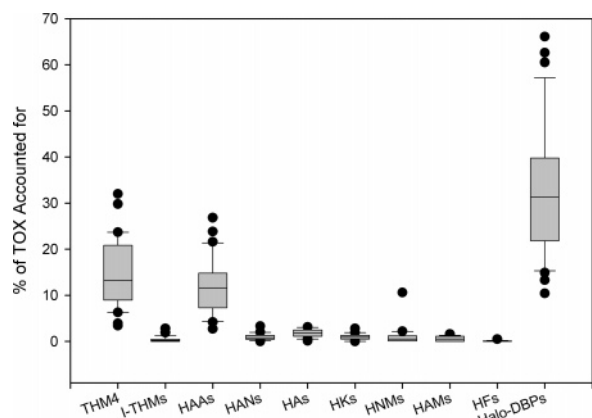


FIGURE 2. Percentage of TOX accounted for in plant effluents in U.S. occurrence study (12 plants, up to 3 seasons each). I-THMs = iodinated THMs, HANs = haloacetonitriles, HAs = haloacetaldehydes, HKs = haloketones, HNMs = halonitromethanes, HAmS = haloacetamides, and HFs = halogenated furanones.

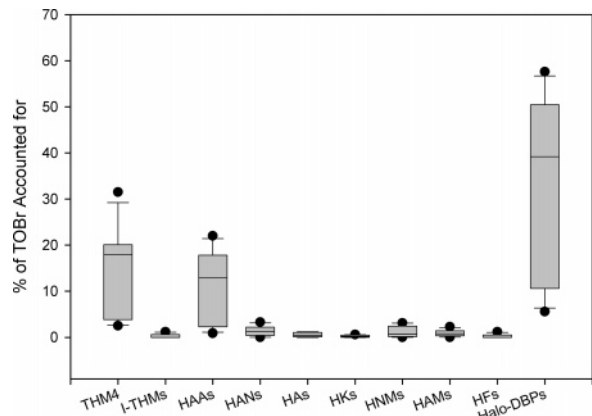


FIGURE 3. Percentage of TOBr accounted for in plant effluents in U.S. occurrence study (7 plants, 1 season each). I-THMs = iodinated THMs, HANs = haloacetonitriles, HAs = haloacetaldehydes, HKs = haloketones, HNMs = halonitromethanes, HAmS = haloacetamides, and HFs = halogenated furanones.

nated acids other than HAAs are DBPs. Also, it is significant to note that certain haloacids (dihalogenated HAAs [DXAAs]) were formed upon treatment with chlorine dioxide. Although some previously published studies (bench-, pilot-, and full-scale) have indicated that DXAAs and sometimes trihalo-

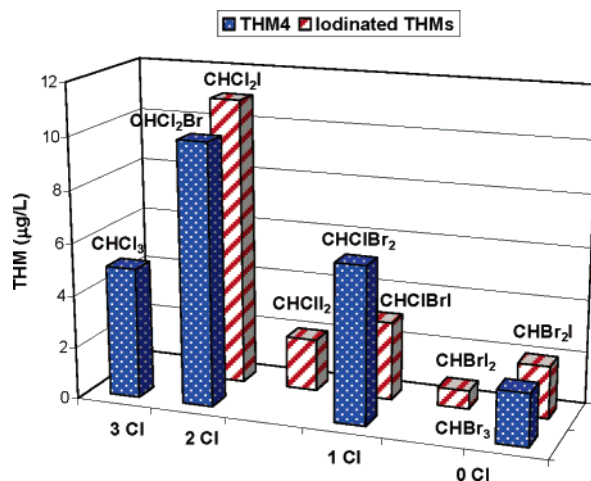


FIGURE 4. Effect of chloramination on iodo-THM formation at plant 12 effluent (11/15/01, bromide = 0.15 mg/L). The x-axis shows decreasing chlorine (Cl) and increasing bromine/iodine substitution.

genated HAAs can be formed by chlorine dioxide (35, 37–39), chlorite and chlorate are generally the only chlorine dioxide DBPs considered in most chlorine dioxide treatment studies. In our study, DXAAs were detected after pre-disinfection with chlorine dioxide—e.g., 16 µg/L at plant 6 in November 2000—but no trihalogenated HAAs were formed, and THM formation was quite low (2 µg/L) in this example (Figure 4, Supporting Information). After the addition of free chlorine, the levels of HAAs increased, including the formation of trihalogenated species. At plant 12, a significant level of total HAAs (32 µg/L) was produced during pretreatment with chlorine dioxide disinfection (this pre-disinfectant was only used at this plant during the February 2002 sampling), whereas very little THMs (3 µg/L) were formed. The majority of the HAAs produced were DXAAs (21 µg/L). In this high-bromide water (0.33 mg/L), all three DXAAs were formed, which included a significant amount of dibromoacetic acid.

Many brominated acids were identified in several finished waters that contained elevated levels of bromide in their source waters. A number of them were identified for the first time (Table 5), with carbon chain lengths of three and four being common as well as the presence of diacids and double bonds in their structures. Many of these products have also been recently identified in drinking waters from Israel containing elevated levels of bromide (~2 mg/L) that have been treated with chlorine or chlorine dioxide-chloramines (39). The most unusual bromo acids identified in this study included the bromo-oxo-acids (3,3-dibromo-4-oxopentanoic acid and 3-bromo-3-chloro-4-oxopentanoic acid), which were identified in finished drinking waters from plant 1 and 11. 3,3-Dibromo-4-oxopentanoic acid and its chlorinated analogue, 3,3-dichloro-4-oxopentanoic acid, have recently been identified, respectively, in drinking water from Israel treated with chlorine or chlorine dioxide-chloramines (39) and in pilot-plant water that was either chlorinated or ozonated-chlorinated (40). The only other previous report of halo-oxo-acids was the tentative identification of 2,3-dichloro-4-oxopentanoic acid and trichloro-4-oxopentanoic acid in a previous bench-scale study involving the reaction of humic acids with chlorine (cited in ref 1).

The EI mass spectrum for an unusual brominated oxo-acid identified is shown in Figure 5, Supporting Information. A discussion of how this new DBP was identified is provided in the Supporting Information.

Another significant finding in this study was the discovery of iodoacids for the first time: iodoacetic acid, bromiodoacetic acid, (*E*)-3-bromo-3-iodopropenoic acid, (*Z*)-3-bromo-3-iodopropenoic acid, and (*E*)-2-iodo-3-methylbutenedioic

TABLE 5. New DBPs Identified at Surveyed Plants in Waters Exhibiting High-Precursors Loadings^a

brominated haloacids	
<u>2,2-dibromopropanoic acid</u> <u>dibromochloropropanoic acid</u> <u>3,3-dibromopropanoic acid</u> <u>cis-2,3-dibromopropanoic acid</u> <u>tribromopropanoic acid</u> <u>2-bromobutanoic acid</u> <u>trans-4-bromo-2-butenic acid</u> <u>cis-4-bromo-2-butenic acid</u> <u>trans-2,3-dibromo-2-butenic acid</u> <u>bromodichlorobutenoic acid</u>	<u>3-bromo-3-chloro-4-oxopentanoic acid</u> <u>3,3-dibromo-4-oxopentanoic acid</u> <u>bromoheptanoic acid</u> <u>bromochloroheptanoic acid</u> <u>dibromoheptanoic acid</u> <u>bromochlorononanoic acid</u> <u>cis-2-bromobutenedioic acid</u> <u>trans-2,3-dibromobutenedioic acid</u> <u>cis-2-bromo-3-methylbutenedioic acid</u>
iodinated haloacids	
<u>iodoacetic acid</u> <u>bromiodoacetic acid</u> <u>(E)-3-bromo-3-iodopropenoic acid</u>	<u>(Z)-3-bromo-3-iodopropenoic acid</u> <u>(E)-2-iodo-3-methylbutenedioic acid</u>
brominated halo ketone	
<u>1-bromo-1,3,3-trichloropropanone</u>	
halogenated aldehydes	
iodobutanal dichloropropenal	4-chloro-2-butenal

^a DBPs confirmed with authentic standards are underlined; all other DBP identifications should be considered tentative.

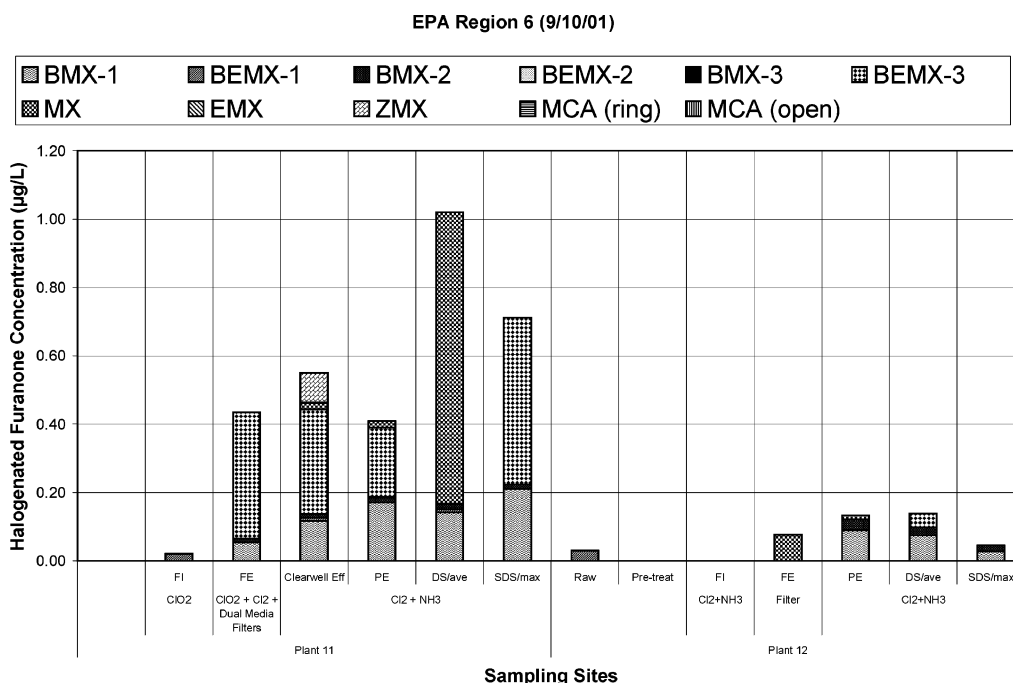


FIGURE 5. Halofuranones (MX and BMX analogues) in drinking water from EPA Region 6. FI = filter influent; FE = filter effluent; PE = plant effluent; DS = distribution system; SDS = simulated distribution system.

acid (Table 5). These iodoacids were found in finished drinking water from plant 12 in November 2001, which used chloramines only and also had relatively high levels of iodine in the overall empirical formulas for these new DBPs. Tentative identifications were confirmed through the analysis of purchased (iodoacetic acid) and synthesized standards (41). Although these iodoacids were not identified prior to the prioritization effort for the selection of high priority DBPs, they are likely to be toxicologically important. Recently conducted mammalian cell cytotoxicity and genotoxicity studies have shown that iodoacetic acid is 2-fold more genotoxic and 3-fold more cytotoxic than bromoacetic acid (which is the most potent genotoxin/cytotoxin of the chloro/

bromo acetic acids) (41). Iodoacetic acid has also been shown to cause developmental effects in mouse embryos (neural tube closures) at low μM levels (42). Recently, it was demonstrated that iodoacetic acid induced its genotoxic damage via an oxidative stress mechanism (43). The other four iodoacids discovered are the subject of current toxicity studies.

This study demonstrates that in waters high in bromide (and iodide), more brominated and/or iodinated compounds (e.g., THMs, haloacids) can form. The ICR (and some previous research) focused on one- and two-carbon structures. This work demonstrates that analogues of previously identified structures are found for longer carbon chain lengths (even up to nine carbons).

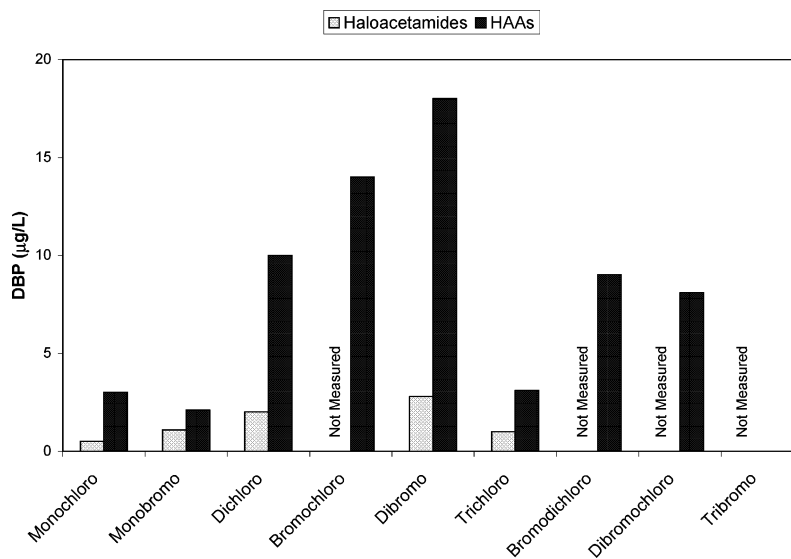


FIGURE 6. Relative formation (and speciation) of haloacetamides and HAAs in plant 12 effluent (2/12/02, bromide = 0.33 mg/L). Haloacetamides not measured in this study included bromochloro, bromodichloro, dibromochloro, and tribromo species.

Haloketones. The priority haloketone 1-bromo-1,1-dichloropropanone reached a maximum of 3 µg/L in a distribution system sample for plant 5 in November 2000 (which used ozone-chlorine disinfection). In addition to the target haloketones, mixed bromochloro analogues were detected in selected samples by the broadscreen GC/MS methods. For example, at plant 7 (where the raw-water bromide was 0.12 mg/L), six tetrahalogenated species were detected after chloramination and ozonation (1,1,3,3-tetrachloro-; 1-bromo-1,3,3-trichloro-; 1,1-dibromo-3,3-dichloro-; 1,3-dibromo-1,3-dichloro-; 1,1,3-tribromo-3-chloro-; and 1,1,3,3-tetrabromopropanone). One of these haloketones, 1-bromo-1,3,3-trichloropropanone, was identified in drinking water for the first time and was found in many of the waters sampled, although the range of concentrations is unknown.

Haloaldehydes. The priority haloaldehyde dichloroacetaldehyde reached a maximum of 16 µg/L in a simulated distribution system sample for plant 7 in December 2000 (which used chloramine-ozone disinfection). Ozonation without biological filtration and chloramination was found to increase the formation of dihaloaldehydes. For example, chlorine-chloramines disinfection at plant 8 (12/11/00) produced 13 µg/L of chloral hydrate and 3 µg/L of dichloroacetaldehyde, whereas ozone and chloramines at plant 7—which treated groundwater from the same aquifer as plant 8—produced 0.3 µg/L of chloral hydrate and 12 µg/L of dichloroacetaldehyde. McKnight and Reckhow found that acetaldehyde (an ozone DBP) can react with chlorine to initially form chloroacetaldehyde, which in the presence of excess free chlorine, can rapidly react to form chloral hydrate (44). At plant 7, it is possible that with only a small free chlorine residual (if any) that the conversion to the trichlorinated species was concentration-limited and the reaction terminated with dichloroacetaldehyde.

An iodinated DBP—characterized by high-resolution MS as a product with the empirical formula C_4H_7OI and molecular weight of 198—tentatively identified as iodobutanol, was found in finished waters from two treatment plants (3 and 6). Plants 3 and 6 used chlorine-chloramine and chlorine dioxide-chlorine-chloramine disinfection. This iodoaldehyde was not detected at plant 12, which had relatively high levels of iodo-THMs. This is the first report of an iodoaldehyde as a DBP in drinking water. It is highly likely that the molecule is an iodoaldehyde with four carbons, but its exact structure is not currently known. Broadscreen analyses also revealed the presence of two other haloaldehydes that have not been

previously identified, which were tentatively identified as dichloropropenal and 4-chloro-2-butenal.

Halonitromethanes. The priority halonitromethane bromopicrin reached a maximum of 5 µg/L in the effluent of plant 12 in February 2002 (which used chlorine dioxide-chloramine disinfection). This sample also had the highest halonitromethane sum (10 µg/L). In addition, preozonation was found to increase the levels of selected halonitromethanes at other plants. Figures 6 and 7, Supporting Information, illustrate this for a comparison of the same source water treated (8/13/01) with ozone-chlorine (plant 5) or chlorine dioxide-chlorine-chloramines (plant 6) and another source water treated (July 2001) with ozone-chlorine-chloramines (plant 1) or chlorine-chloramines (plant 2). Other research has shown that preozonation can increase the formation of chloropicrin (45) or other halonitromethanes (15, 16) upon postchlorination.

Preozonation and moving the point of chlorination until after coagulation at plant 1 (chlorine was added to the raw water at plant 2) also caused a shift in speciation to the more brominated forms of the trihalonitromethanes; similar shifts were also observed for the THMs. At plants 1 and 2 (July 2001), the THM bromine incorporation factors (molar sum of bromine incorporated into THMs divided by molar sum of THM4)—where the bromine incorporation factor ranges from 0 (all chloroform) to 3 (all bromoform) (46)—were 1.8 and 1.0, respectively, whereas the bromine incorporation factors for trihalogenated nitromethanes—where the bromine incorporation factor ranges from 0 (all chloropicrin) to 3 (all bromopicrin)—were 2.3 and 1.3, respectively. The bromine incorporation factor for each class of DBP was similar at each plant; in other words, the shift in bromine speciation for each class of DBP was similar at each plant. The difference in speciation between the two plants (i.e., higher bromine incorporation at plant 1) was explained (in part) by the higher bromide-to-TOC ratio at the point of chlorination at plant 1 (36). In addition, the result was also related to differences in chlorine doses. Plant 1 applied a lower chlorine dose (2.2 mg/L) than plant 2 (total chlorine dose = 4.25 mg/L). Therefore, the chlorine/bromide ratio was lower at plant 1, resulting in a higher bromine incorporation (46).

Halogenated Furanones (MX Analogues). The highest levels for halogenated furanone sums occurred at a plant (plant 8) that disinfected a water with 11.3 mg/L of TOC and 0.27 mg/L of bromide with chlorine-chloramines (2380 ng/L

in plant effluent drinking water, Supporting Information) and at a plant (plant 11) that disinfected a water with 3.5 mg/L of TOC and 0.21 mg/L of bromide with chlorine dioxide-chlorine-chloramines (1000 ng/L in the distribution system, Figure 5). Because many of the source waters in this study were relatively high in TOC and/or bromide, high occurrence of some of the halogenated furanones was observed at selected plants (Figure 8, Supporting Information). MX levels >100 ng/L were detected in 7 of 42 filter effluent, plant effluent, and distribution system samples. MX levels reached a high of 850 ng/L in the average detention time distribution system sample from plant 11 on 9/10/01. The median and 75th percentile plant effluent levels of MX were similar to the levels found in other studies (8–10). However, the maximum occurrence was high compared to previous limited surveys (e.g., 80 ng/L in two U.S. studies (8, 9), 260 ng/L in a Californian study (47), 90 ng/L in an Australian study (48), and 586 ng/L in a Russian study (49)).

The results of this survey indicate that BMXs and brominated EMXs (BEMXs) can occur at relatively high concentrations in some high-bromide waters (Table 4). However, the median plant effluent levels of the six BMX and BEMX species was each <20 ng/L. In a study in Japan (12), the maximum occurrence of BMX-1, BMX-2, and BMX-3 was 2, 6, and 11 ng/L, respectively, but the maximum MX formation was also relatively low (6 ng/L) compared to this study or to other surveys (8–10, 47–49).

The halogenated furanones were often stable in the distribution systems and in simulated distribution system tests, most of which were in chloraminated water. Previous controlled laboratory studies had suggested that MX may not be stable in chlorinated distribution systems (8). In two instances, MX levels increased in concentration from the plant effluent to the distribution system point sampled (for plant 6 during one sampling event and for plant 11 during one sampling event). In another instance, MX levels decreased in the distribution system (for plant 3).

Haloamides. Several haloacetamides were quantified for the first time in this study (Figure 1, Supporting Information) and found to be present at levels similar to other commonly measured DBPs (Table 4). The highest level for the haloacetamide sum (14 µg/L) occurred in a simulated distribution system sample for plant 6 that disinfected a water with 9.5 mg/L of TOC and 0.06 mg/L of bromide with chlorine dioxide-chlorine-chloramines. Alkaline hydrolysis of haloacetonitriles can form haloacetamides (and ultimately HAAs) (50). For example, dichloroacetonitrile can hydrolyze to form dichloroacetamide, which can further hydrolyze to form dichloroacetic acid. Therefore, it is possible that some or all of the haloacetamides were formed by the hydrolysis of haloacetonitriles. The occurrence of 2,2-dichloroacetamide was similar to that of dichloroacetonitrile (Table 4). Figure 6 shows the relative formation of haloacetamides and HAAs at plant 12 (2/12/02, bromide = 0.33 mg/L). Although not all of the bromine- and chlorine-containing haloacetamide species were analyzed in this study, it does appear that the relative concentrations of the haloacetamides compared well to the HAAs (i.e., similar degree of halogen incorporation), where the haloacetamides were in a concentration range of ~10 times less than the HAAs. The dichloro species of each DBP class were formed at higher concentrations than the trichloro species, where the presence of an elevated level of bromide resulted in a shift in speciation of the dihalogenated species to the more bromine-substituted compounds. Thus, it is likely that brominated analogues of trichloroacetamide were also formed in this water. Haloamides are a new family of DBPs of health concern (51).

Nonhalogenated Carbonyls. Several nonhalogenated carbonyls were quantified in drinking water for the first time in this study (Figure 1, Supporting Information; Table 4). Of

the nonhalogenated priority carbonyls, dimethylglyoxal was consistently the most prevalent.

Impact on Drinking Water Treatment and Future Health Effects Studies

The quantitative information provided through this study was critical for prioritizing future health effects research. Toxicity studies continue for the newly identified iodoacids, and *in vivo* studies are currently being conducted for some of the bromonitromethanes. New toxicity studies are also underway for haloamides and haloacetonitriles (51) as well as the iodo-THMs. It is likely that other priority DBPs will be studied for potential adverse health effects. Because the magnitude of the risk of a particular chemical includes both its concentration and toxic potency, assuming a health priority for specific DBPs from this study without the health effects data would be premature. For this reason, concentrations shown in this paper should be considered along with health effects data. For example, brominated and iodinated DBPs are much more potent than their chlorine-containing counterparts, which may be because bromine and iodine are better leaving groups than chlorine (22). Thus, DBPs such as the brominated MX analogues, bromonitromethanes or iodo-THMs should not be dismissed because they are present at lower levels than some of the other DBPs, because their potency could be much greater than other DBPs present at higher concentrations. Conversely, DBPs present at higher concentrations should not necessarily be assumed to be the most important until their toxic potencies are known.

This study also has important implications for drinking water treatment. Because the commonly used alternative disinfectants (ozone, chloramines, and chlorine dioxide) produce lower levels of the four regulated THMs and most of the HAAs as well as TOX, many water utilities have switched (or are in the process of switching) from chlorine to these alternative disinfectants to meet the Stage 1 and/or Stage 2 DBP Rules. Although the four regulated THMs and most HAAs are minimized with the use of alternative disinfectants, some of the priority DBPs were higher in concentration with the use of alternative disinfectants. For example, iodo-THM levels were highest in a water disinfected with chloramines only; dichloroacetaldehyde was highest in a water disinfected with chloramines and ozone (with no biological filtration); selected halonitromethanes were formed at higher levels during postdisinfection when preozonation was used; and MX precursors were better controlled at plants using ozone than those using chlorine dioxide. Because disinfection with chloramines only may not always meet virus or *Giardia* inactivation requirements, this disinfection scenario is not used at many plants that treat surface water. When chloramines are used as the secondary disinfectant at a drinking water treatment plant, it should be possible to limit the formation of iodo-DBPs through a sufficient free-chlorine contact time before the addition of ammonia to form chloramines or through the use of preozonation (19, 21). For example, in this study, iodinated THM formation was low at plants using free chlorine or ozone for primary disinfection. In addition, it should be possible to minimize the formation of haloaldehydes at ozone plants through the use of biological filtration. One of these haloaldehydes, dichloroacetaldehyde, is of moderate health concern, because it is a potential cross-linking agent (22).

For some waters with high TOC and/or high bromide, relatively high MX and BMX levels were detected in this study. This new occurrence information should be considered with existing health effects information to address the potential risk of these DBPs at those plants. Also, higher-chain haloacids (such as the 3,3-dichloropropenoic acid) should be considered along with the commonly measured HAAs. It is

important to acknowledge that three- and four-carbon haloacids can be formed in drinking water treatment—not only the two-carbon HAAs that are regulated. Finally, the new information on haloacetamide concentrations is important because this is the first quantitative data for this DBP class, and the data demonstrate that their levels can be comparable to other commonly measured DBPs. Health effects information is needed for the haloacetamides as well as other DBPs identified in this survey.

Since this project was completed, many of the priority and newly identified DBPs have been incorporated into new studies. However, these compounds are not the end of the story. Emerging DBPs of health and regulatory concern (e.g., nitrosamines) are being identified in disinfected drinking water. Because all chemical disinfection processes produce DBPs, it is important to include a wide range of potential DBPs in treatment studies to determine how best to minimize the formation of as many DBPs as possible, recognizing that not all will be minimized (and some may be maximized).

Acknowledgments

The U.S. EPA funded and collaborated in the research described here. Acknowledgment is given to other chemists and laboratory technologists who helped develop the analytical methods, synthesized standards, and conducted or supervised the analyses at Metropolitan Water District of Southern California (Alicia Gonzalez, Lely Suhady, Jacob Nikonchuk, Leslie Bender, Tim Albrecht, Vaheh Martyr, Sylvia Barrett, Hsiao-Chiu Wang, Suzanne Teague, Ching Kuo, Robert Alvarez, Jesus Vasquez, Jr., Bart Koch, Eric Crofts, Sikha Kundu, Tiffany Lee, Pat Hacker, and Himansu Mehta), University of North Carolina (UNC) (Ramiah Sangaiah, Karupiah Jayaraj, Christine N. Dalton, Lindsay Dubbs, Gary L. Glish, Katrina Jamison, Vanessa Pereira, Petra Strunk, and Zhengqi Ye) and the U.S. EPA (Terrance L. Floyd and F. Gene Crumley). We express appreciation to Leif Kronberg (Åbo Akademi, Finland) and Angel Messegue (Institute of Chemical and Environmental Research, Barcelona, Spain) for providing samples of furanone standards as well as Bruce McKague (CanSyn Chem Corp., Toronto, Canada), Francesc Ventura (Aigues of Barcelona, Spain), and George Majetich (Majestic Research, Athens, GA) for providing standards used in the quantitative methods and new DBP identification work. The authors acknowledge Philip Singer of UNC for helping to select and solicit the participating utilities for this study as well as for his assistance in developing the sampling plans for many of the plants. We gratefully acknowledge the assistance of the participating utilities that collected the samples, provided operational and water quality data, and ensured a successful survey. We are also grateful to the U.S. EPA Office of Water and Office of Prevention, Pesticides, and Toxic Substances scientists—Yin-tak Woo, Jennifer McLain, Vicki Dellarco, David Lai, and Mary Ko Manibusan—who undertook the initial DBP prioritization effort that provided the focus for this study. We are especially grateful to Vicki Dellarco for her vision in recognizing the importance of such a prioritization effort. This paper has been reviewed in accordance with the U.S. EPA's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

Supporting Information Available

Concentration of nonregulated DBPs in plant effluents; percentage of TOX accounted for in plant effluents in U.S. occurrence study (on a median basis); percentage of TOCl accounted for in plant effluents; formation of HAAs after chlorine dioxide and chlorine disinfection at two plants; EI mass spectrum for DBP identified as 3,3-dibromo-4-oxo-

pentanoic acid methyl ester; effect of preozonation on halonitromethane formation at two plants; concentration of halogenated furanones in plant effluents; DBPs measured and identified in finished water at drinking water treatment plants; list of synthesized standards; selected analytical methods; and discussion of how a new DBP was identified. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review February 15, 2006. Revised manuscript received June 9, 2006. Accepted June 13, 2006.

ES060353J