The effect of boiling water on disinfection by-product exposure

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Abstract

Chloraminated and chlorinated waters containing bromide were used to determine the impact of boiling on disinfection by-product (DBP) concentrations. No significant changes were detected in the concentrations of the dihalogenated haloacetic acids (DXAAs) (i.e., dichloro-, bromochloro-, dibromoacetic acid) upon boiling of chloraminated water, whereas the levels of the trihalogenated haloacetic acids (TXAAs) (i.e., trichloro- (TCAA), bromodichloro- (BDCAA), dibromochloroacetic acid (DBCAA)) decreased over time (e.g., 9–37% for TCAA). Increased DXAA concentrations (58–68%) were detected in the boiled chlorinated sample, which likely resulted from residual chlorine reacting with DXAA precursors. TCAA concentration was unchanged after boiling chlorinated water for 1 min, but a 30% reduction was observed after 5 min of boiling. BDCAA concentrations decreased 57% upon boiling for 1 min and were completely removed after 2 min of boiling, whereas DBCAA was removed after boiling chlorinated water for 1 min. Trihalomethane concentrations were reduced in both chloraminated (74–98%) and chlorinated (64–98%) water upon boiling. Boiling chloraminated water for 1 min reduced chloroform concentration by 75%. Chloroform was reduced by only 34% in chlorinated water after a 1 min boil, which indicates that simultaneous formation and volatilization of chloroform was occurring. Most of the remaining DBPs (e.g. haloketones, chloral hydrate, haloacetonitriles) were removed by at least 90% after 1 min of boiling in both samples. These data suggest that other mechanisms (e.g., hydrolysis) may have been responsible for removal of the non-volatile DBPs and further highlight the importance of examining individual species when estimating thermal effects on DBP concentrations.
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1. Introduction

Disinfection by-products (DBPs) are ubiquitous in chemically disinfected water containing natural organic matter and/or bromide. Carcinogenic and reproductive effects of DBPs have been reported in toxicological and epidemiological studies (Nieuwenhuijsen et al., 2000;

Villanueva et al., 2003). Epidemiologic studies of DBPs have often relied on ecologic measures, including type of treatment, type of source water, and trihalomethane (THM) compliance monitoring data (e.g., utility average concentrations) to estimate individual-level exposures. These indirect measures of exposure lead to measurement error, which can result in bias and reduced statistical power to detect associations. Key DBP research needs have been identified to address these exposure assessment limitations, including collection of detailed individual water use data, examination of

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non-volatile DBPs, use of sensitivity and uncertainty analysis, and development of exposure prediction models (Arbuckle et al., 2002; Nieuwenhuijsen et al., 2000). Recent DBP research has begun to address some of these DBP exposure assessment issues (Whitaker et al., 2003; Waller et al., 2001; Wright and Bateson, 2004; Wright et al., 2004; Dodds et al., 2004; Fenster et al., 2003; Windham et al., 2003), but it remains unclear which of these needs are most critical.

Information on exposure modifying factors, such as point-of-use filtration and boiling water prior to consumption (e.g., hot water-based beverages) needs to be considered in epidemiologic studies, because these activities can influence estimates of DBP ingestion exposure (Egorov et al., 2003; Eslinger and Weinberg, 2003). Experimental data have shown that boiling water prior to consumption can greatly impact DBP concentrations (Table 1). Batterman and colleagues (2000) examined thermal effects on THM concentrations by heating chlorine-free distilled water in an electric kettle. Average volatilization rates of 81% for chloroform (trichloromethane (TCM)) and 73% for bromodichloromethane (BDCM) were reported at 100 °C, with a 69% reduction in the four regulated THMs (THM4). Wu and colleagues (2001) conducted boiling experiments of Seattle tap water typically containing 0.9 mg/L chlorine residual and 0.9–1.5 mg/L of dissolved organic carbon (DOC). As boil time increased from 1 to 5 min, reductions of 68% and 83% for chloroform and 75% and 94% for BDCM were observed. Lahl and colleagues (1982) reported THM4 volitalization losses of 73% for a 1-min boil and 88% following a 5-min boil. Chloroform had the highest loss, and the amount removed during boiling decreased with increasing bromine substitution. Kuo and colleagues (1997) found similar removals of chloroform and BCDM upon boiling chlorinated water from Taiwan.

Different effects of boiling on haloacetic acid (HAA) concentrations have been reported in previous experimental studies (Table 1). Trichloroacetic acid (TCAA), a trihalogenated acid (TXAA), has been shown to be more readily removed (30–70%) upon boiling compared to the other subclasses of HAAs (i.e., dihaloacetic acids (DXAAs) and monohaloacetic acids (MXAAs)). Wu and colleagues (2001) reported more than a doubling of dichloroacetic acid (DCAA) levels in chlorinated water upon boiling for 1 or 5 min, whereas Kim (1997) observed no change in DCAA levels in distilled water following a 5-min boil. These results suggest that DCAA originally present was not impacted by boiling and that, in the presence of chlorine, additional DCAA could form during the boiling process. Changes in MXAA concentrations from previous studies varied from –28% to 46%. The MXAAs are typically present (if detected) at concentrations near their minimum reporting levels (MRLs) in most chlorinated waters, which limits the ability to quantify changes upon heating.

Table 1
Previous experimental studies of boiling effects on disinfection by-product concentrations[a]

Study (boiling time)	TCM (%)	BDCM (%)	DBCM (%)	TBM (%)	THM4 (%)	MCAA (%)	MBAA (%)	DCAA (%)	BCAA (%)	DBAA (%)	TCAA (%)
Kim (1997) (5 min)[b]						−6	−28	0			−40
Dojlido et al. (1999) (10 min)[c]						25	40	−18		−11	−70
Wu et al. (2001) (1 min)[d]	−68	−75				32	46	122	−13		−30
Wu et al. (2001) (5 min)[d]	−83	−94						130	−7		−46
Batterman et al. (2000) (12.5 min)[b]	−81	−73			−69						
Kuo et al. (1997)[d,e]	−79	−79	−93								
Lahl et al. (1982) (1 min)[f]	−80	−76	−71	−62	−73						
Lahl et al. (1982) (5 min)[f]	−91	−90	−87	−82	−88						

Abbreviations: TCM = chloroform (trichloromethane), BDCM = bromodichloromethane, DBCM = dibromochloromethane, TBM = bromoform (tribromomethane), THM4 = sum of the four regulated trihalomethanes, MCAA = monochloroacetic acid, MBAA = monobromoacetic acid, DCAA = dichloroacetic acid, BCAA = bromochloroacetic acid, DBAA = dibromoacetic acid, TCAA = trichloroacetic acid.

[a] Negative value corresponds to decrease in concentration of DBP, whereas positive value corresponds to increase in concentration of DBP.
[b] Distilled water with known DBP concentration.
[c] Ozonated and chlorinated water.
[d] Chlorinated water.
[e] Boil time not reported.
[f] Hypochlorite treated water.

Hot and cold water use is an increasingly important consideration for DBP exposure assessment, because hot water-based beverages can contribute substantially to overall water consumption levels (Kaur et al., 2004; Egorov et al., 2003) and may have higher levels of certain DBPs compared to cold water. Balko and colleagues (2001) reported TCAA and DCAA concentrations up to three times as high in tea, coffee, and juice samples compared to chloraminated tap water, suggesting that the residual chlorine reacted with HAA precursors in the beverages. In the present study, boiling experiments were conducted on chloraminated and chlorinated water containing bromide. The effects of boiling on a wide range of regulated and emerging DBPs of health concern (Woo et al., 2002) were examined in relation to degree of DBP volatility and bromine substitution.

2. Methods

The boiling experiments were conducted on water samples from the Weymouth water treatment plant (La Verne, CA) in winter 2000. Although not measured, the DOC and bromide levels of this water were typically ~3.0 and ~0.1–0.2 mg/L, respectively. Conventional water treatment does not remove bromide, so bromide would have been present in the finished water. The typical pH of this water was ~8.2. Separate aliquots of chlorinated filter effluent and chloraminated plant effluent were collected in 1-L glass bottles. Although not measured, the chlorine and chloramine residuals at these locations were each typically ~2.5 mg/L as Cl_2. Residual chlorine and chloramines were not measured in each sample, but were at comparable levels based on treatment plant specifications. The disinfectant residuals of these samples were not quenched. Shortly after sampling, the water samples were boiled using a 2.5-quart tea kettle on a stovetop in the Metropolitan Water District of Southern California (MWDSC) laboratory kitchen. The experiments consisted of 1-, 2-, and 5-min boil times. The samples were allowed to cool down prior to extraction. Control samples consisted of water that was not boiled (i.e., boil time = 0). Note, the comparisons between the two water treatments are the results from a single set of samples. The samples underwent liquid/liquid extraction (LLE) and were analyzed for DBPs by gas chromatography/electron capture detection (GC/ECD) (Krasner et al., 2001). Additional samples underwent LLE, were derivatized with an acidic methanol solution, and were analyzed by GC/ECD for HAAs (Munch et al., 1995). Sample analysis included standard measures of quality assurance for precision, accuracy, and bias.

Values for Henry's Law constant—a measure of the volatility of a compound—were obtained from the literature or were estimated using a quantitative structure activity relationship model (HENRYWIN version 3.10, part of the Estimation Program Interface for Windows from the US Environmental Protection Agency) (Westerhoff, 2003). HENRYWIN provided experimental values where available and predicted the Henry's Law Constants at 25 °C by the bond contribution method for those DBPs without experimental values. Henry's Law Constants were not determined for boiling water at 100 °C. The Henry's Law Constants served as a tool to ascertain if a DBP was considered volatile (10^{-1}–10^{-3} atm-m^3/mol), moderately volatile (10^{-3}–10^{-5} atm-m^3/mol), slightly volatile (10^{-5}–10^{-7} atm-m^3/mol) or non-volatile ($< 10^{-7}$ atm-m^3/mol). DBPs that are not volatile would still be considered relatively non-volatile in boiling water.

3. Results

3.1. Overview

The HAAs were the most prevalent DBP in the chlorinated and chloraminated samples, followed by the THMs (Tables 2 and 3). Significant amounts of haloaldehydes, haloacetonitriles (HANs), and haloketones (HKs) were also detected. Because of the presence of bromide in the treated source waters, there was a mix of bromine- and chlorine-containing DBP species detected for those DBP classes (i.e., THMs, HANs, haloaldehydes, HAAs) in which brominated species were analyzed. An iodinated THM (dichloroiodomethane) was detected in the chlorinated water, while low levels of chloropicrin (trichloronitromethane (TCNM)) were found in both the chlorinated and chloraminated samples. As shown in Tables 2 and 3, with the exception of the HAAs as a class sum, the sum of the THMs and that of the other DBPs were significantly reduced following a 1-min boil. More modest reductions in these DBP concentrations occurred upon boiling for 2 and 5 min. Within some DBP classes, however, there were significant differences in the impact of boiling on the concentrations of individual DBPs (Fig. 1).

3.2. THMs

Reduction (presumably due to volatilization) in the sum of the THMs (i.e., THM4 and dichloroiodomethane) was (in general) comparable for chlorinated and chloraminated waters, especially after 2 and 5 min of boiling (Tables 2 and 3). THM4 removals ranged from 64% to 98% across the different boiling times.

Table 2
Cumulative percent change (from time 0) in DBP concentrations (µg/L) from boiled chloraminated water[a]

DBP class	Analyte	Time (min)			
		0	1	2	5
Regulated trihalomethanes (THMs)	Chloroform (trichloromethane) (TCM)	18	4.6 (−75%)	3.0 (−84%)	0.6 (−97%)
	Bromodichloromethane (BDCM)	26	6.3 (−75%)	4.2 (−84%)	0.6 (−98%)
	Dibromochloromethane (DBCM)	13	4.1 (−70%)	2.1 (−84%)	ND (−100%)
	Bromoform (tribromomethane) (TBM)	0.9	0.4 (−60%)	ND (−100%)	ND (−100%)
	Sum of 4 regulated THMs (THM4)	58	15 (−74%)	9.3 (−84%)	1.2 (−98%)
Haloacetonitriles (HANs)	Dichloroacetonitrile (DCAN)	4.3	0.2 (−96%)	0.1 (−98%)	ND (−100%)
	Bromochloracetonitrile (BCAN)	1.1	0.05 (−96%)	0.07 (−94%)	ND (−100%)
Haloaldehydes (HAs)	Dichloroacetaldehyde (DCA)	1.5	0.5 (−70%)	0.4 (−75%)	0.2 (−85%)
	Chloral hydrate (CH) (trichloracetaldehyde)	5.1	0.1 (−98%)	0.1 (−98%)	ND (−100%)
Haloketones (HKs)	1,1-Dichloropropanone (1,1-DCP)	0.5	ND (−100%)	ND (−100%)	ND (−100%)
	1,3-Dichloropropanone (1,3-DCP)	0.1	0.07 (−42%)	ND (−100%)	ND (−100%)
	1,1,1-Trichloropropanone (1,1,1-TCP)	2.2	ND (−100%)	ND (−100%)	ND (−100%)
	1,1,3-Trichloropropanone (1,1,3-TCP)	0.1	ND (−100%)	ND (−100%)	ND (−100%)
Halonitromethane (HNM)	Chloropicrin (trichloronitromethane) (TCNM)	1.4	0.7 (−50%)	0.5 (−67%)	ND (−100%)
Sum of other DBPs (i.e., HANs, HAs, HKs, HNM)		16	1.6 (−90%)	1.1 (−93%)	0.2 (−99%)
Haloacetic acids	Dichloroacetic acid (DCAA)	38	34 (−9%)	37 (−3%)	40 (7%)
	Bromochloroacetic acid (BCAA)	14	14 (4%)	15 (9%)	15 (12%)
	Dibromoacetic acid (DBAA)	4.5	4.2 (−7%)	4.1 (−9%)	4.3 (−4%)
	Sum of dihalogenated HAAs (DXAAs)	56	53 (−6%)	56 (−1%)	60 (7%)
	Trichloroacetic acid (TCAA)	26	23 (−9%)	20 (−21%)	16 (−37%)
	Bromodichloroacetic acid (BDCAA)	15	7.1 (−53%)	3.2 (−79%)	1.1 (−93%)
	Dibromochloroacetic acid (DBCAA)	3.9	ND (−100%)	ND (−100%)	ND (−100%)
	Sum of trihalogenated HAAs (TXAAs)	45	30 (−32%)	23 (−48%)	17 (−61%)
Sum of HAAs		100	83 (−17%)	79 (−22%)	77 (−23%)

Abbreviations: DBP = disinfection by-product, ND = not detected.

[a]Percent changes were calculated from the values of the concentrations before those values were rounded to the number of significant figures given in this table.
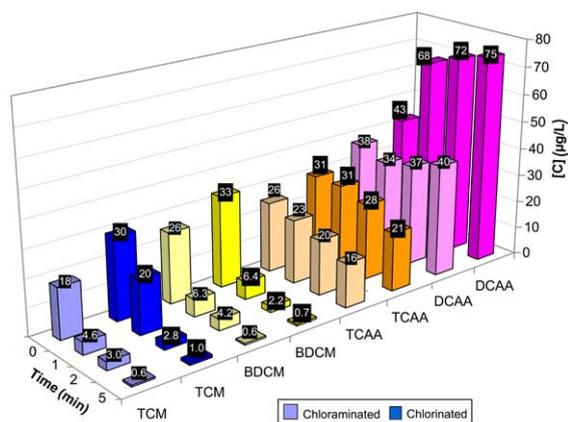
Table 3
Cumulative percent change (from time 0) in DBP concentrations (µg/L) from boiled chlorinated water[a]

DBP class	Analyte	Time (min)			
		0	1	2	5
Regulated trihalomethanes (THMs)	Chloroform (trichloromethane) (TCM)	30	20 (−34%)	2.8 (−91%)	1.0 (−97%)
	Bromodichloromethane (BDCM)	33	6.4 (−81%)	2.2 (−93%)	0.7 (−98%)
	Dibromochloromethane (DBCM)	16	2.9 (−82%)	0.4 (−97%)	ND (−100%)
	Bromoform (tribromomethane) (TBM)	1.0	0.2 (−76%)	ND (−100%)	ND (−100%)
	Sum of 4 regulated THMs (THM4)	80	29 (−64%)	5.4 (−93%)	1.6 (−98%)
Iodinated THM	Dichloroiodomethane (DCIM)	0.8	ND (−100%)	ND (−100%)	ND (−100%)
Sum of THMs		81	29 (−64%)	5.4 (−93%)	1.6 (−98%)
Haloacetonitriles (HANs)	Dichloroacetonitrile (DCAN)	6.2	0.1 (−98%)	ND (−100%)	ND (−100%)
	Bromochloracetonitrile (BCAN)	1.6	0.1 (−94%)	ND (−100%)	ND (−100%)
Haloaldehydes (HAs)	Dichloroacetaldehyde (DCA)	1.2	0.9 (−27%)	0.2 (−85%)	0.06 (−95%)
	Chloral hydrate (CH) (trichloracetaldehyde)	12	0.4 (−97%)	ND (−100%)	ND (−100%)
	Tribromoacetaldehyde (TBA)	0.4	0.4 (0%)	ND (−100%)	ND (−100%)
Haloketones (HKs)	Chloropropanone (CP)	1.1	0.08 (−93%)	ND (−100%)	ND (−100%)
	1,1-Dichloropropanone (1,1-DCP)	0.3	ND (−100%)	ND (−100%)	ND (−100%)
	1,3-Dichloropropanone (1,3-DCP)	0.2	ND (−100%)	ND (−100%)	ND (−100%)
	1,1,1-Trichloropropanone (1,1,1-TCP)	6.2	ND (−100%)	ND (−100%)	ND (−100%)
Halonitromethane (HNM)	Chloropicrin (trichloronitromethane) (TCNM)	1.5	0.7 (−57%)	ND (−100%)	ND (−100%)
Sum of other DBPs (i.e., HANs, HAs, HKs, HNM)		31	2.6 (−92%)	0.2 (−99%)	0.06 (−100%)
Haloacetic acids (HAAs)	Monochloroacetic acid (MCAA)	3.4	3.9 (15%)	4.2 (24%)	4.6 (35%)
	Dichloroacetic acid (DCAA)	43	68 (59%)	72 (69%)	75 (76%)
	Bromochloroacetic acid (BCAA)	17	26 (51%)	25 (48%)	25 (49%)
	Dibromoacetic acid (DBAA)	4.3	7.4 (72%)	6.9 (60%)	6.8 (58%)
	Sum of dihalogenated HAAs (DXAAs)	64	101 (58%)	104 (63%)	107 (68%)
	Trichloroacetic acid (TCAA)	31	31 (0%)	28 (−10%)	21 (−30%)
	Bromodichloroacetic acid (BDCAA)	17	7.4 (−57%)	3.1 (−82%)	ND (−100%)

Table 3 (*continued*)

DBP class	Analyte	Time (min)			
		0	1	2	5
	Dibromochloroacetic acid (DBCAA)	4.6	ND (−100%)	ND (−100%)	ND (−100%)
	Sum of trihalogenated HAAs (TXAAs)	52	38 (−27%)	31 (−41%)	21 (−60%)
Sum of HAAs		120	142 (19%)	139 (16%)	133 (11%)

Abbreviations: DBP = disinfection by-product, ND = not detected.

[a]Percent changes were calculated from the values of the concentrations before those values were rounded to the number of significant figures given in this table.

Fig. 1. The effects of boiling chlorinated and chloraminated water on the concentrations of the major THM and HAA species.

Individual THM removals in the chloraminated water ranged from 60% to 75% in chloraminated water boiled for 1 min (Table 4). The THMs are the most volatile group of the DBPs studied, based on their values of Henry's Law constant (the higher the value, the more volatile the compound). Eighty-four percent or more of each species was removed following a 2-min boil, whereas 97% or more of each THM was removed upon boiling for 5 min (Table 2). In the chlorinated water, slightly higher removal of the bromine-containing THMs was detected following a 1-min boil (76–82%), whereas there was limited removal (34%) of chloroform (Table 3). There was little difference between THM removal in chlorinated versus chloraminated water upon further boiling, with both samples having removals of 97% or greater for each THM detected after 5 min of boiling. The only iodinated THM that was detected, dichloroiodomethane, was completely eliminated after boiling chlorinated water for 1 min.

Table 4
Relationship of volatility of DBPs to percent change from time 0 after 1 min of boiling in chloraminated water

DBP	Henry's Law Constant (atm−m^3/mol)	% Change from time 0 at 1 min in chloraminated water[a]
TCM	3.67E−03[b]	−75
BDCM	2.12E−03[b]	−75
TCNM	2.05E−03[b]	−50
DBCM	7.83E−04[b]	−70
TBM	5.35E−04[b]	−60
DCA[c]	8.42E−06	−70
DCAN	3.79E−06	−96
DCAA	3.52E−07[b]	−9
TBA	1.04E−07	N/A
BCAA	2.22E−08	4
TCAA	1.35E−08[b]	−9
BDCAA	7.83E−09	−53
MCAA	9.42E−09[b]	N/A
DBAA	7.27E−09	−7
CH	5.71E−09	−98

Abbreviations: DBPs = disinfection by-products, N/A = not applicable (not detected in chloraminated water at time 0).

[a]Volatility comparisons were made with the test in chloraminated water, to eliminate the confounding phenomena of simultaneous formation of some DBPs in the presence of chlorine.

[b]From literature values provided in HENRYWIN. Other Henry's Law Constants in this table were estimated by HENRYWIN.

[c]Henry's Law Constant was estimated for dichloroacetaldehyde and not for its hydrate.

3.3. HAAs

The overall impact of boiling on HAAs gave different results in the two water samples that were

analyzed. Increased HAA formation occurred in the chlorinated water after 1 min of boiling, and the concentration was still relatively high after 5 min of boiling (Table 3). A reduction in overall HAA concentration was observed in chloraminated water after 1 min of boiling, and the levels changed very little upon further boiling.

Boiling of the chloraminated sample produced no significant changes (−9% to 7%) in DCAA concentrations (Fig. 1), where the coefficient of variation of DCAA and other DBP samples is typically on the order of approximately ±20% (Fair et al., 2002). Similar results were observed in the chloraminated sample for the other DXAAs, with no significant change in bromochloroacetic acid (BCAA) and dibromoacetic acid (DBAA) concentrations (Table 2). DCAA concentrations in chlorinated water increased from 59 to 76% as boiling time increased from 1 to 5 min (Table 3). BCAA and DBAA concentrations increased by at least 50% in chlorinated water for a 1-min boil but remained relatively constant upon further boiling. No change in TCAA concentration was observed for a 1-min boil of chlorinated water, but 10% and 30% reductions were noted in water boiled for 2 and 5 min, respectively (Fig. 1). Among the chloraminated samples, somewhat larger reductions (9–37%) in TCAA concentrations were found as boil time increased. Similar reductions were observed over time for bromodichloroacetic acid in both the chlorinated (57–100%) and chloraminated samples (53–93%). Although found in smaller concentrations compared to the other TXAAs, dibromochloroacetic acid was not detected upon boiling for 1 min. Small increases in the monochloroacetic acid (MCAA) concentration were noted for the chlorinated sample upon boiling.

3.4. HKs

For the chloraminated water sample, substantial reductions in concentrations were noted for most of the other DBPs upon boiling (Table 2). The following HKs were not detected after 1 min: 1, 1-dichloropropanone (1,1-DCP), 1, 1, 1-trichloropropanone (1,1,1-TCP), and 1, 1, 3-trichloropropanone (1,1,3-TCP). The level of 1, 3-dichloropropanone (1,3-DCP) decreased 42% upon boiling for 1 min and was completely removed after 2 min of boiling. Similar reductions were observed in the chlorinated water with complete removal of 1,1-DCP, 1,1,1-TCP and 1,3-DCP upon boiling for 1 min (Table 3). In addition, the concentration of chloropropanone (CP) was reduced by 93% following a 1-min boil and was not detected after 2 min. CP was not detected in the chloraminated water sample, and 1,1,3-TCP was not found in the chlorinated water sample.

3.5. HANs

HAN concentrations in chloraminated water were reduced by 94–98% following a 1- and 2-min boil, and were not detected upon 5 min of boiling (Table 2). Similar removal of the HANs (94–98%) occurred upon boiling the chlorinated sample for 1 min, and no HANs were detected in the chlorinated water after 2 min (Table 3).

3.6. Haloaldehydes

The concentration of dichloroacetaldehyde (DCA) in chloraminated water was reduced from 70% to 85% for 1- to 5-min boil times (Table 2). Boiling chlorinated water for 1 min had a minimal effect on the level of DCA (−27%), but reductions from 85% to 95% were observed upon further boiling (Table 3). Chloral hydrate (CH) (i.e., trichloroacetaldehyde) concentration was reduced by at least 97% following a 1-min boil of both chlorinated and chloraminated water and was not detected after 2 min. Tribromoacetaldehyde (TBA) was not detected in the chloraminated water and a minimal amount was found in chlorinated water (0.37 μg/L). TBA was unchanged upon boiling for 1 min and was not detected after 2 min of boiling.

3.7. Halonitromethane

TCNM concentration was 50–67% lower in the chloraminated water boiled for 1–2 min and was not detected at 5 min (Table 2). A reduction similar in magnitude (57%) was observed for chlorinated water boiled for 1 min, and TCNM was not detected after 2 min of boiling (Table 3).

4. Discussion

Overall, large reductions in most DBP concentrations were observed in boiling experiments of chloraminated and chlorinated finished water samples. Removal rates among the THMs were similar to those noted in previous studies (Lahl et al., 1982; Kuo et al., 1997; Batterman et al., 2000; Wu et al., 2001), although a smaller net removal of chloroform was detected in the chlorinated water (34%) compared to the chloraminated water (75%) for 1 min of boiling (Fig. 1). Because there was a free chlorine residual in the chlorinated water at the time of boiling, it is likely that chloroform was being formed from the reaction of the chlorine with DBP precursors in the water at the same time that chloroform was being volatilized. Although the residuals were not measured after boiling in these tests, preliminary experiments at MWDSC have shown

that the chlorine residual was removed during the first minute of boiling. Thus, the critical issue is that there can be simultaneous formation and volatilization during the first minute, whereas in subsequent minutes of boiling only volatilization can occur. In the chloraminated water, volatilization appeared to be the most important phenomenon, even during the first minute of boiling. In that sample, the two more brominated THMs were removed to a lesser extent (60–70%) than the two more chlorinated THMs (75%). This is similar to the finding of Lahl and colleagues (1982) for a 1-min boil.

Different effects were observed in haloaldehyde concentrations upon boiling. The semi-volatile haloaldehydes, DCA and TBA (Table 4), were not significantly impacted by boiling chlorinated water for 1 min, suggesting that there was simultaneous formation and removal of these haloaldehydes while a free chlorine residual was present. Note, because conventional water treatment does not remove bromide, there can still be bromide in the finished water available to react with free chlorine to form TBA. Their removal at longer boiling times in the chlorinated water and the removal of DCA in the chloraminated water may be due to a combination of volatilization and degradation. Alternatively, the removal of the non-volatile CH (Table 4) was probably due to base-catalyzed hydrolysis. Although hydrolysis is more significant at pH 9 than at pH 7 for CH (Stevens et al., 1989), the combination of elevated temperature and alkaline pH may have resulted in the degradation of this DBP.

HAN concentrations were dramatically reduced upon boiling of chloraminated and chlorinated water. Dichloroacetonitrile (DCAN) is a semi-volatile DBP (Table 4), which can also undergo base-catalyzed hydrolysis (Croué and Reckhow, 1989). DCAN's degradation product is dichloroacetamide, which can be further hydrolyzed to DCAA (Reckhow et al., 2001). Therefore, it is possible that some of the HANs degraded (e.g., due to hydrolysis), in addition to volatilizing, during the boiling process. TCNM does not undergo base-catalyzed hydrolysis (Croué and Reckhow, 1989) and has a Henry's Law Constant similar to that of the THMs (Table 4), so reductions in TCNM concentrations were likely due to volatilization.

Henry's Law constant values were not obtained for the HKs. Some HKs (e.g., 1,1,1-TCP) are known to undergo base-catalyzed hydrolysis (Croué and Reckhow, 1989). The pH of the samples in the present study was ~8.2; therefore, it is possible that some of the HKs degraded (e.g., due to hydrolysis) during the boiling process. Chloroform is the degradation product of 1,1,1-TCP and CH hydrolysis; therefore, these degradation processes may have contributed to the limited removal of chloroform that was observed during the initial boil of chlorinated water.

In general, the DXAAs were not significantly impacted by boiling in the chloraminated water (Table 2), whereas their concentrations increased significantly in the chlorinated water (Table 3). Most of the increased formation occurred during the first minute of boiling as shown for DCAA (Fig. 1). These data suggest that free chlorine reacted with DBP precursors to form additional DXAAs (and perhaps MCAA), which were not volatilized or degraded by the boiling process. The DXAAs and other HAAs are not volatile (Table 4). A reduction in TXAA concentrations during the boiling process was observed, with the rate of loss higher with increased bromine substitution. Bromine-containing TXAAs have been shown to be less stable with increasing bromine substitution and are subject to thermal- and photo-degradation (Pourmoghaddas and Dressman, 1993). Thus, the loss of the brominated TXAAs in the present study was most likely due to the relative instability of these DBPs. The net impact on the sum of the HAAs (increased concentrations of 11–19% for chlorinated water and decreased concentrations of 17–23% in the chloraminated samples) reflect the very different impact of boiling on the two subclasses of HAAs, DXAAs and TXAAs. These findings highlight the importance of considering the varied formation and degradation processes of individual HAAs when estimating the impact of heating and boiling on exposures.

5. Conclusion

The different effects of boiling within DBP classes in chlorinated versus chloraminated water have important implications for DBP exposure assessment efforts in epidemiologic studies. Previous DBP research has rarely included individual-level water use information, and only two epidemiological studies have examined individual data on hot and cold beverage consumption. Compared to THM water concentrations alone, Klotz and Pyrch (1999) and Waller and colleagues (1998) reported smaller relative risks for reproductive outcomes with THM exposures that considered hot and cold water consumption. Neither study attempted to adjust estimates of individual exposure to account for volatilization or other exposure modifying effects. These studies were also limited in their ability to adequately consider the impact of dermal and inhalation exposures, which may be more important than ingestion for volatile DBPs (Gordon et al., 1998; Keating et al., 1997). THM concentrations can increase upon heating water at lower temperatures than boiling (Weisel and Chen, 1994; Batterman et al., 2000), so future studies should also consider potential exposure modifying activities (e.g., water temperatures during showering or in swimming pools) that may impact overall DBP exposure.

Based on the results of this study and the previous research cited, the effects of heating and boiling on DBPs are dependent on the degree of DBP volatility and compound stability, water temperature, type of residual disinfectant present, as well as the amount of DBP precursors and chlorine residual present in the water. Because chlorine residual can vary considerably within a distribution system, boiling and heating effects may differ between individuals using the same water supply. Failure to directly measure residential DBP concentrations or adequately capture spatial variability in residual chlorine and DBP formation/degradation when estimating individual level exposures can lead to measurement error in epidemiologic studies.

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