

Analysis of Volatile Disinfection By-Products in Metro Manila Drinking Water

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A method for microextraction and GC-ECD analysis specific for volatile disinfection by-products (DBPs) in drinking water was optimized based on US EPA Standard Method 551. The method was validated in terms of linearity, recovery, and detection limit and was found to be linear over a wide concentration range (5.00 - 250 µg/L) with acceptable recoveries (70 - 110 % at the 150.0 µg/L level in water). The optimized method was used to determine the levels of volatile DBPs in water samples from various sources in Metro Manila. The DBPs found in the water samples were chloroform (18 - 379 µg/L), bromodichloromethane (2.6 - 9.5 µg/L), dichloroacetonitrile (5.6 - 157 µg/L), dichloroacetone (0.86-1.7 µg/L), trichloroacetone (1.6 - 7.3 µg/L), and bromochloroacetonitrile (1.7 - 1.9 µg/L). The level of chloroform in the samples exceeded guideline values for total trihalomethanes as set in most countries. The levels of the brominated DBPs were also very low compared to those of the chlorinated analogs.

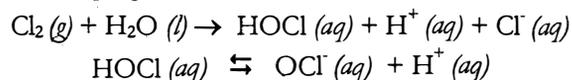
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INTRODUCTION

Chlorination is a widely used method for drinking water disinfection. For many years, it has been proven to be an effective way for reducing infection, and even death, worldwide. Moreover, it is the least expensive water disinfection method available and is effective in preventing microbial regrowth. However, in 1974, it was found that aside from acting on microorganisms in water, chlorine also reacts with natural organic matter (NOM) in water to produce disinfection by-products (DBPs). In bromine-containing water, the presence of

brominated DBP analogs has also been reported [1,2].

Chlorination is carried out by either using chlorine gas or adding hypochlorite ion from HOCl or NaOCl [1,3]. The reactions are as follows:



The hypochlorite ion, OCl⁻, is able to disrupt cell walls and diffuse into a cell leading to the elimination of pathogenic bacteria, slime molds, algae, and fungi [4].

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There are several classes of DBPs. The first class to be identified consists of trihalomethanes (THMs). Studies on THMs gave rise to the discovery of haloacetic acids (HAAs) and haloacetonitriles (HANs). THMs and HANs are volatile compounds while HAAs are not. Recently, more DBPs such as 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone or MX and iodinated THMs and acids were discovered. Contaminants in drinking water produced from anthropogenic activities, such as methyl-tert-butyl ether (MTBE), perchlorate, and organotins, have also been identified [5]. These DBPs and contaminants raise health concerns because of their reported toxicity.

THMs are usually analyzed using classical liquid-liquid extraction with gas chromatography-electron capture detection (LLE-GC-ECD), liquid-liquid extraction with gas chromatography-mass spectrometry (LLE-GC-MS), headspace gas chromatography-mass spectrometry (headspace GC-MS), and purge-and-trap with gas chromatography-mass spectrometry (purge-and-trap GC-MS). LLE-GC-ECD is found to be the most sensitive among the above methods while purge-and-trap GC-MS is found to have high detection limits compared to the other methods [6].

THMs are extracted from the sample matrix using methyl-tert-butyl ether (MTBE) according to Method 551 of the US Environmental Protection Agency (US EPA) [7]. Subsequent identification of analytes is carried out by GC-ECD. GC-ECD has been used for THM determination in chlorinated seawater samples in three French coastal power stations; the THMs were separated from the sample matrix using a purge-and-trap system directly coupled to a gas chromatograph [8].

HANs comprise the second largest group of volatile DBPs after the THMs. These are formed during the chlorination process, if ammonia is present in raw water. HANs are drawing the attention of scientists because of their potential adverse health effects on human beings.⁹ The most common HANs are trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN). Among the HANs, DCAN has exhibited mutagenic properties while DBAN and BCAN were reported to be carcinogenic in mice [9]. As with THM formation, the formation of HANs in water is also

dependent on factors such as chlorine dose, contact time, pH, and temperature. However, longer contact time leads to the decay of the HANs formed. As with THM, HANs are also analyzed using methods such as LLE-GC-ECD, LLE-GC-MS, purge-and-trap GC-MS and headspace GC-MS.

In other countries, the concentrations of the above-mentioned compounds in drinking water are closely monitored, and maximum allowable values for these compounds have been proposed. For example, the maximum allowable value suggested by the US EPA for total THMs is 80 µg/L. Japan, China, and Taiwan are reportedly moving towards implementing regulations and standards for drinking water treatment [10]. In the Philippines, however, no guidelines exist for the regulation of DBPs. Prior to this study, no information on the presence or level of DBPs in local drinking water supplies was available. Thus, this study aims to assess the performance of a modified US EPA procedure for water analysis and apply it to determine the levels of volatile DBPs in various drinking water samples collected in Metro Manila.

METHODOLOGY

Sample Collection and Preservation. The drinking water samples were collected in 1-L bottles that were cleaned with detergent and water and then rinsed with distilled and deionized water. The bottles were oven-dried between 100°C and 110°C. NH₄Cl (1.5 g) was added to the water to bind the free chlorine in the sample and hinder further formation of DBPs (US EPA Methods 551 and 552.2). Drinking water samples were collected by allowing the faucet to flow gently for one minute before filling the bottles to the brim to ensure there was no headspace. The samples were collected from establishments or households supplied by major water concessionaires in Metro Manila. Figure 1 shows a diagram of the sampling sites showing the various sources of drinking water used in this study.

Analysis of DBPs in water. US EPA Standard Method 551 was adapted and modified for the analysis of volatile compounds in water. The volatile components were extracted in 40-mL Teflon-faced vials (Daigger, IL, USA) using diethyl

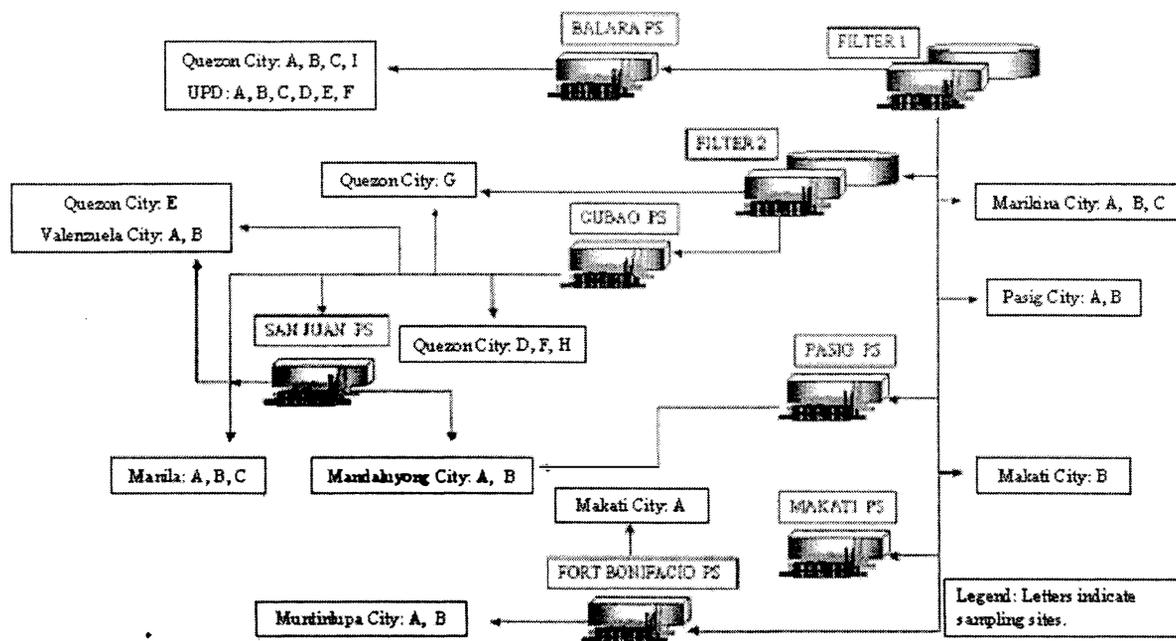


Fig. 1. Diagram of the sampling sites indicating the water pumping stations

ether as solvent. Copper sulfate (3 g) and acidified sodium sulfate (5 g) were placed in a vial prior to addition of a 30-mL sample. Acidified sodium sulfate was prepared by adding 100 μL of concentrated sulfuric acid per 100 g of AR grade Na_2SO_4 . Diethyl ether (3 mL per 30 mL H_2O) was added and extraction was carried out by shaking the vials in a mechanical shaker for ten minutes. After shaking, 1 mL of the diethyl ether layer was transferred to a 2 mL vial and an aliquot of the internal standard mix composed of fluorobenzene and 3-bromo-1-chloropropane prepared in acetone (600 $\mu\text{g}/\text{L}$ in the final extract) was added. The extract was analyzed by GC-ECD using a Shimadzu GC8A equipped with a ^{63}Ni for electron capture detection. The column used was ZB 624 (6% cyanopropylphenyl-94% methylpolysiloxane, 30 m x 0.53 mm id x 3.00 μm film thickness) from Phenomenex, Torrance, USA. Nitrogen gas at 5 mL min^{-1} flow rate was used as carrier gas. The analyses were carried out in a split mode with 1:10 ratio.

Quantitation of DBPs in Water. The concentrations of the volatile DBPs in the water samples were quantified using an external calibration curve prepared by adding aliquots of the DBP standards in diethyl ether. The method detection limits (MDL) for the analytes were also

determined using external calibration. For MDL determination, aliquots of the DBP standards were spiked in ultrapure water and treated as samples (spike level was estimated to have 2.50 $\mu\text{g}/\text{L}$ of each analyte in the final extract). DBP levels that exceeded the corresponding MDL values were recorded.

DISCUSSION OF RESULTS

Method Validation. The THMs studied were chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform while the HANs studied were TCAN, DCAN, BCAN, and DBAN. Other volatile DBPs studied were dichloroacetone, trichloroacetone and chloropicrin. For most compounds, the percent absolute recoveries were between 70 and 110 % at the 150 $\mu\text{g}/\text{L}$ level (shown in Table 1). These results are comparable to the recoveries reported in US EPA Method 551.⁷ In general, DCAN, DBAN, dichloroacetone, and trichloroacetone showed very good recoveries. For TCAN, the highest recovery was 70 %.

The MDL values for each analyte were determined using eight replicates. Table 1 shows that the optimized method is sensitive for all samples

except chloroform as reflected by their low MDL values. The determined MDL values are also within the allowable concentrations for the DBPs. The allowable value for total trihalomethanes (TTHMs) is 80.0 $\mu\text{g/L}$, which is greater than the sum of the MDL values for chloroform, BDCM, DBCM, and chloroform.

Table 1. Method detection limit (MDL) values for THMs, HANs and other volatile DBPs

Volatile DBPs	MDL, $\mu\text{g/L}$ (n=8)	% Recovery at 150 $\mu\text{g/L}$
Chloroform	17	85
TCAN	1.6	72
BDCM	2.4	94
DCAN	0.70	91
Dichloroacetone	0.55	106
Chloropicrin	1.2	88
DBCM	2.1	95
BCAN	0.35	71
Trichloroacetone	0.31	99
Bromoform	1.1	97
DBAN	1.4	113

DBPs in Water Samples. The actual water samples analyzed for their DBP levels were gathered from two clusters. One set was collected from the UP Diliman campus (6 sites) and another set was collected from outside the campus (25 sites). The samples from UP Diliman were collected and analyzed in October 2002 (samples were collected in one day; data are summarized in Table 2) while the samples from outside the campus were collected and analyzed from December 2002 to June 2003 (data are summarized in Table 3).

The concentrations of the volatile DBPs in actual water samples were calculated using an external calibration curve prepared by adding an aliquot of the standard DBPs in diethyl ether. The quantified volatile DBPs from the UP Diliman sampling sites were chloroform, BDCM, DCAN, dichloroacetone, and BCAN. Chloroform, DCAN, and dichloroacetone were detected in all sites. The chloroform levels in the six sites ranged from 17.8 $\mu\text{g/L}$ to 54.9 $\mu\text{g/L}$ and most sites showed concentrations of chloroform equal to 22.0 $\mu\text{g/L}$. BDCM (detected in two sites) and BCAN (detected in three sites) levels in sites where these DBPs were found were also

low. These indicate that bromine is probably not present in high concentrations in the raw source water. Dichloroacetone levels were also low, with the highest concentration being 1.67 $\mu\text{g/L}$. The levels of DCAN, however, ranged from 5.55 $\mu\text{g/L}$ to as high as 122 $\mu\text{g/L}$. This could mean that nitrogen-containing organic matter have reacted with the residual chlorine present in water from the distribution lines.

For the second set of samples, the compounds quantified were chloroform, BDCM, DCAN, and trichloroacetone. Peaks due to other analytes were present in the chromatogram, but their levels were not quantifiable. The level of chloroform in most sites exceeded the maximum values recommended by the US EPA. BDCM was the only brominated DBP quantified. DBCM levels in most sites were low, which indicates that bromine is probably not present in high concentrations in the raw source water. DCAN was the only HAN quantified. The spread in DCAN levels in the samples ranged from as low as 1.6 $\mu\text{g/L}$ to as high as 157 $\mu\text{g/L}$. The site-to-site differences in DCAN concentrations may be due to the differences in the distances between the sampling sites and the treatment plants. The levels of trichloroacetone in the samples, which range from 1.6 $\mu\text{g/L}$ to 7.30 $\mu\text{g/L}$, were also low.

The levels of volatile DBPs from the two clusters show high concentrations of the analytes. Chloroform levels were higher than the recommended maximum allowable concentration. Dichloroacetone was detected in the UP Diliman sites only while trichloroacetone was detected in the other cluster. Also, chloroform concentrations in the second set of samples were higher than those from the UP Diliman sampling sites. As with the DCAN, the differences in the analyte concentrations and the identities of the quantified DBPs in the two clusters and in-between sites could be due to the differences in the distances between the sampling sites and the water source or to the concentration of the residual chlorine present in the distribution lines. It is also likely that the analyte concentrations were affected by the temperature at which each sample was collected. Further studies should be done to look at variations and trends in DBPs levels along the network of distribution lines of drinking water in Metro Manila.

Table 2. Concentrations of volatile DBPs in water samples collected from the UP Diliman campus in October 2002 (values in parenthesis are standard deviations)

Site	Concentrations of the volatile DBPs in water, $\mu\text{g/L}$ (n = 3)				
	Chloroform	BDCM	DCAN	Dichloroacetone	BCAN
UPD A	22 (1.7)	2.6 (0.47)	76 (12)	0.88 (.015)	1.7 (0.38)
UPD B	55 (2.6)	9.5 (0.50)	5.6 (2.7)	0.89 (0.17)	1.9 (0.23)
UPD C	22 (2.6)	nd	122 (19)	0.86 (0.41)	nd
UPD D	22 (1.7)	nd	77 (7.5)	1.4 (0.12)	nd
UPD E	18 (0.68)	nd	48 (5.1)	1.7 (0.14)	nd
UPD F	20 (1.2)	nd	82 (10)	1.2 (0.12)	1.7 (0.63)

nd = not detected (MDL for BDCM = 2.4 $\mu\text{g/L}$; BCAN = 0.35 $\mu\text{g/L}$)

Table 3. Concentrations of volatile DBPs in water samples collected outside the UP Diliman campus between December 2002 and June 2003 (values in parenthesis are standard deviations)

Site	Concentration of DBPs in actual water sample, $\mu\text{g/L}$ (n = 3)			
	Chloroform	BDCM	DCAN	Trichloroacetone
Marikina City A	nd	nd	22.3 (0.5)	nd
Quezon City A	332 (7.1)	4.8 (0.1)	56.1 (2.6)	3.4 (1.5)
Muntinlupa City A	249 (7.2)	nd	79.3 (3.7)	7.1 (1.7)
Muntinlupa City B	320 (13.0)	7.5 (0.6)	6.7 (0.7)	6.6 (1.6)
Makati City A	312 (9.6)	7.8 (0.1)	nd	6.6 (0.5)
Quezon City B	326 (3.4)	7.5 (0.2)	71.4 (2.1)	3.9 (0.1)
Quezon City C	334 (12.0)	3.4 (0.2)	75.2 (13.1)	4.3 (0.6)
Marikina City B	379 (1.8)	6.2 (0.1)	137 (3.4)	2.9 (0.5)
Valenzuela City A	351 (20.5)	5.6 (0.7)	157 (30.9)	3.8 (0.5)
Mandaluyong City A	352 (20.6)	6.8 (0.4)	70.3 (2.0)	3.1 (0.9)
Manila A	nd	nd	nd	nd
Manila B	nd	nd	18.7	nd
Quezon City D	nd	nd	17.2	nd
Quezon City E	nd	nd	nd	nd
Manila C	nd	nd	nd	nd
Pasig City A	nd	nd	nd	nd
Quezon City F	287 (25.1)	4.3 (0.3)	99.0 (4.6)	6.2 (0.3)
Quezon City G	332 (4.2)	5.6 (0.3)	57.4 (2.9)	4.2 (0.9)
Quezon City H	365 (9.2)	6.4 (0.6)	118 (7.6)	4.1 (0.4)
Quezon City I	291 (12)	3.5 (0.4)	75.2 (3.4)	5.7 (1.2)
Marikina City C	nd	nd	nd	nd
Makati City B	302 (10.2)	7.6 (0.2)	1.6 (0.3)	1.6 (4.0)
Pasig City B	285 (17.8)	2.7 (0.3)	73.0 (2.1)	7.3 (2.4)
Mandaluyong City B	273 (17.3)	3.4 (0.4)	19.3 (0.7)	6.9 (0.9)
Valenzuela City B	315 (16.8)	4.5 (0.5)	nd	4.5 (0.6)

nd = not detected (MDL for Chloroform = 17 $\mu\text{g/L}$; BDCM = 2.4 $\mu\text{g/L}$; DCAN = 0.70 $\mu\text{g/L}$; Trichloroacetone = 0.31 $\mu\text{g/L}$)

CONCLUSIONS

Among the volatile DBPs analyzed, only chloroform, bromodichloromethane, dichloroacetonitrile, dichloroacetone, and trichloroacetone were detected in the drinking water samples that were analyzed. These compounds are potentially carcinogenic and their presence and levels in local water supplies should be studied further.

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