Occurrence of trihalomethanes and haloacetonitriles in water distribution networks of Khon Kaen Municipality, Thailand

Thunyalux Ratpukdi, Sudarat Sinorak, Pradabduang Kiattisaksiri, Patiparn Punyapalakul and Sumana Siripattanakul-Ratpukdi

ABSTRACT

The occurrence of trihalomethanes (THMs) and haloacetonitriles (HANs) in three water distribution networks (Thapra, Kota, and Khon Kaen University (KKU)) in Khon Kaen Municipality, Thailand, from November 2015 to December 2016 was investigated. The highest THMs and HANs were 584 μg/L and 30 μg/L, respectively. Chloroform was the dominant species of the THM pool and trichloroacetonitriles were the dominant species for HANs. Water treatment plants using free chlorine (Thapra and Kota) formed more THMs than the plant using ClO_2 (KKU). In the summer season, more brominate THMs were observed. In many locations, total THM concentrations were found to be higher than the drinking water standard of the Provincial Water Authority of Thailand. The concentration of THMs tended to increase with greater distance from the water plants (as water aged), while HAN concentrations decreased with distance, potentially because they were undergoing hydrolysis in the pipeline.

Key words | chlorine, chlorine dioxide, disinfection byproducts, distribution networks, haloacetonitriles, trihalomethanes

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INTRODUCTION

Chlorination is a commonly used practice to disinfect water in water treatment plants and also provides residuals to inactivate pathogens in the distribution system. When chlorine reacts with organic matter in water, disinfection byproducts (DBPs) can be formed. Trihalomethanes (THMs) comprise one of the most well-known and regulated DBPs that cause adverse health effects. Recently, haloacetonitriles (HANs) known as nitrogenous DBPs (N-DBPs) have received significant attention due to increased contamination of HAN precursors in raw water sources and their toxicity being higher than regulated DBPs. It was reported that HANs have a cytotoxicity approximately 200 times higher than that of regulated haloacetic acids (HAAs) (Muellner *et al.* 2007). The concentrations of HANs in tap water are typically 10-fold less than regulated DBPs and vary from a few micrograms per litre to hundreds of micrograms per litre (Baytak *et al.* 2008; Guilherme & Rodriguez 2014). Due to the health effects caused by DBPs, the World Health Organization (WHO) has provided guidelines for allowable THMs and HANs (WHO 2011). In Thailand, water authorities have adopted these guidelines with respect to regulated chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (BF) at 300, 60, 100, and 100 μg/L, respectively. Thus far, no

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regulation of HANs has been applied in any country, and only guideline values of dichloroacetonitrile (DCAN) and dibromoacetonitrile (DBAN) at 20 and 70 μg/L, respectively, have been reported.

To control DBP levels in distribution systems (DS), information regarding DBP concentrations in DS is required. Such DBP concentrations can be significantly affected by disinfectants, as well as spatial and seasonal variations. Therefore, understanding these factors would support interpretation of the DBP data or allow adjusting of the operation at water plants and DS. Although there have been a relatively large number of studies on THMs in distribution networks, very few studies have investigated the concentrations of N-DBPs (Baytak *et al.* 2008; Shanks *et al.* 2013; Guilherme & Rodriguez 2014; Serrano *et al.* 2015). In addition, all of these works were carried out in North America and Europe, where the climate is different from tropical countries, including Thailand. Khon Kaen Municipality is one of the major municipalities in the northeast of Thailand. Currently, three water utilities supply water to the city in separated DS. Two of them use chlorine (Cl_2) while another one employs chlorine dioxide (ClO_2). Thus far, the level of THMs and HANs has not been reported. This research investigates the seasonal and spatial variations in concentrations of THMs and HANs in these three water distribution networks in Khon Kaen Municipality. This study is the first to report on the occurrence of DBPs in Khon Kaen Municipality DS and the relationship of DBPs and distance along the systems. This information provides fundamental data for tropical countries which can be used for further water treatment plant planning and practice.

METHODS

Water treatment plants and distribution networks

Water quality from three water treatment plants and their DS in Khon Kaen, Thailand, were examined. The treatment plants include: (1) Thapra (TP-WTP) (48,000 m^3/d), (2) Kota (KT-WTP) (139,200 m^3/d), and (3) Khon Kaen University (KKU-WTP) (14,000 m^3/d) water treatment plants, all of which are located in Khon Kaen Municipality (Figure 1), but sources of raw water and disinfectants are different. TP-WTP obtains its raw water directly from the Chi River and the chorine (Cl_2) dose used is 2.4 mg/L. KT-WTP and KKU-WTP both use the same water source (the Pong River). KT-WTP applies chorine as a disinfectant (2.4 mg/L as Cl_2), while KKU-WTP uses ClO_2 at a dose of 2.4 mg/L. It is noted that TP-WTP, KT-WTP, and KKU-WTP service populations in different areas of Khon Kaen Municipality and have separate DS, which are TP-DS, KT-DS, and KKU-DS, respectively.

Sampling locations

For each system, five sampling locations were chosen in order to assess water quality along the DS. In water treatment plants, two sampling locations including after filtration (AF) and after chlorination (AC) were selected. The other three sampling locations were spread throughout the entirety of the distribution lines (Table 1). Maps of sampling locations are provided in the Supplementary Material (Figures S1–S3), available with the online version of this paper.

Sampling plan

The sampling period was from November 2015 to December 2016 (13 months). Grab sampling was performed once per month (approximately the middle of each month). For seasonal analysis, there was a division of four timeframes including winter (November to December 2015), summer (February to April 2016), rainy season (May to October 2016), and winter (November to December 2016). Prior to sampling, tap water was run for 5 min. Two litres of water were sampled. The sample was filled in amber plastic bottles without head space and stored in the dark, refrigerated at 4 °C, until analysis.

Analyses

Chlorine residuals, DOC, and DON

Chlorine residuals were measured using the iodometric method (APHA/AWWA/WEF 2005). Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined using an organic carbon analyzer (TOC multi N/C 2100, Analytic Jena, Germany). Inorganic nitrogen species

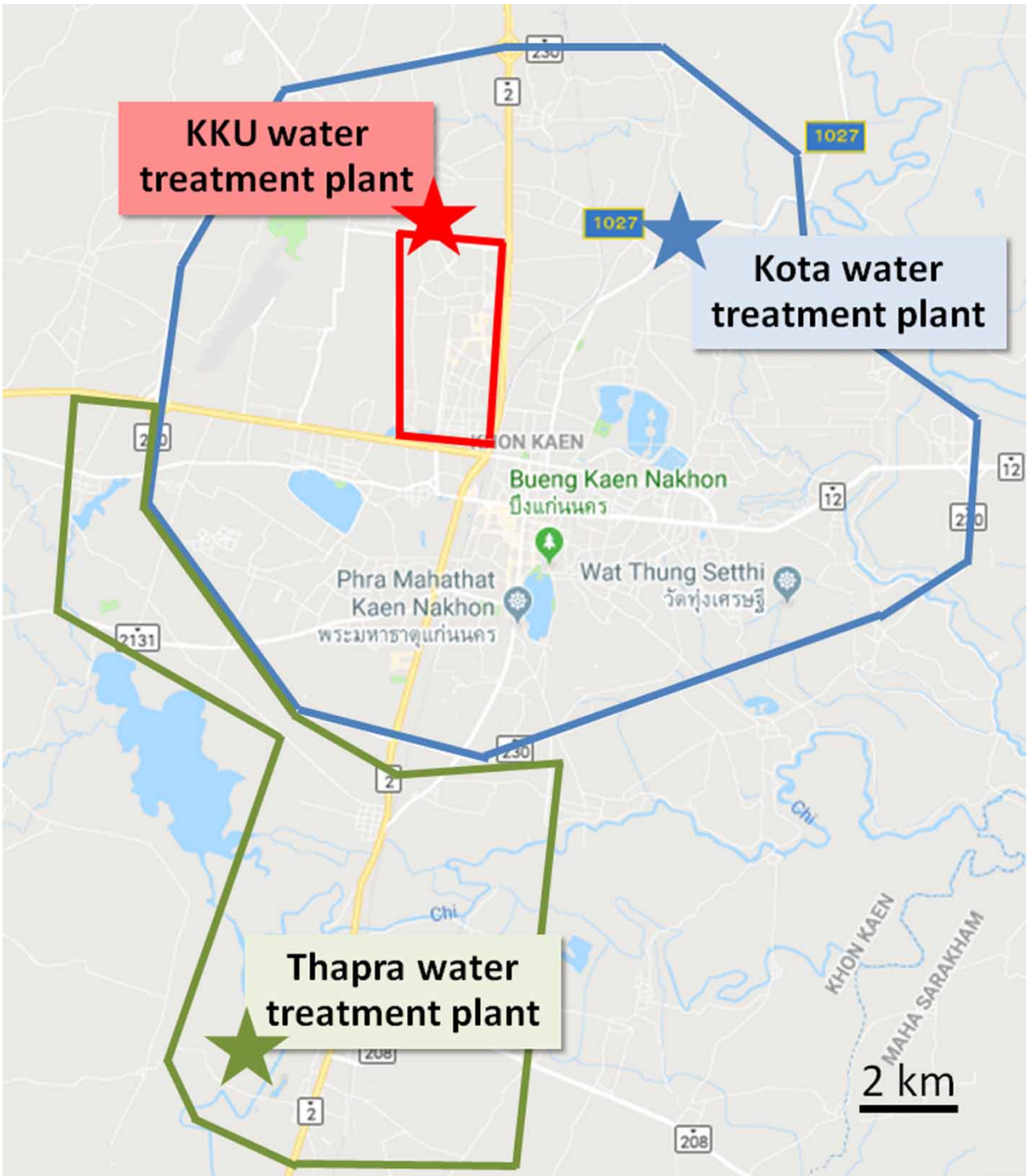

Figure 1 | Water treatment plants in Khon Kaen Municipality and service areas.

including NH_3-N, NO_2-N, and NO_3-N were measured using phenate, colorimetric, and spongy cadmium reduction methods, respectively (Jones 1984; APHA/AWWA/WEF 2005). For dissolved organic nitrogen (DON) determination, TDN was subtracted by inorganic nitrogen species (NH_3-N, NO_2-N, and NO_3-N).

Table 1 | Information on sampling locations

Distribution system and pipe material	Sampling point	Distance from treatment plant (km)	Coordinates	Information on sampling location
Thapra (HDPE pipe)	TP-AF	0	16°19′46.2″N 102°47′05.7″E	Water after filtration and before chlorination
	TP-AC	0	16°19′46.2″N 102°47′05.7″E	Water after chlorination
	TP – 3.2 km	3.2	16°21′06.6″N 102°48′10.2″E	A gas station, Thapra, Khon Kaen
	TP – 9.2 km	9.2	16°23′24.7″N 102°48′16.7″E	Khon Kaen Bus Terminal 3, Khon Kaen
	TP – 15.9 km	15.9	16°26′16.1″N 102°45′53.4″E	Banped Municipality Office, Khon Kaen
Kota (stainless steel pipe)	KT-AF	0	16°28′38.1″N 102°51′49.9″E	Water after filtration and before chlorination
	KT-AC	0	16°28′38.1″N 102°51′49.9″E	Water after chlorination
	KT – 4.8 km	8.4	16°26′38.0″N 102°50′26.4″E	Khon Kaen Inland Fisheries Research and Development Center, Khon Kaen
	KT – 8 km	8	16°26′26.5″N 102°49′05.6″E	A gas station, Nai Mueang, Khon Kaen
	KT – 10 km	10	16°26′48.5″N 102°47′08.2″E	Khon Kaen Institute for Skill Development Region 6, Banped, Khon Kaen
KKU (stainless steel pipe)	KKU-AF	0	16°28′46.3″N 102°49′17.3″E	Water after filtration and before ClO_2 disinfection
	KKU-AC	0	16°28′46.3″N 102°49′17.3″E	Water after ClO_2 disinfection
	KKU – 0.3 km	0.3	16°28′41.4″N 102°49′10.8″E	KKU Food and Service 2, Nai Mueang, Khon Kaen
	KKU – 3.1 km	3.1	16°27′55.7″N 102°48′54.4″E	Agricultural farm, KKU, Khon Kaen
	KKU – 5.7 km	5.7	16°26′43.3″N 102°48′52.2″E	KKU Art and Cultural Hall, Khon Kaen

THM and HAN analysis

Water samples were extracted using a liquid/liquid extraction method modified from USEPA method 551.1 (USEPA 1995). The samples were analyzed using a gas chromatograph (GC) equipped with a SPB-608 fused silica capillary column (30 m × 0.53 mm × 0.5 μm) and an electron capture detector (GC-ECD) (4890D, Agilent, USA). Helium as a carrier gas was applied. The extract of 1.0 μL was injected. A temperature gradient program was started at 40 °C for 2.5 min, then ramped to 240 °C at a rate of 40 °C/min, and held at 240 °C for 1 min. The retention times for CF, BDCM, DBCM, and BF were 0.8, 1.5, 3.0, and 4.1 min, respectively, while their method detection limits were 0.05, 0.01, 0.01, and 0.01 μg/L, respectively. The retention times for monochloroacetonitrile (MCAN), DCAN, trichloroacetonitrile (TCAN), and DBAN were 1.7, 1.9, 1.1, and 4.5 min, respectively, whereas their method detection limits were 0.25, 0.10, 0.50, and, 0.10 μg/L, respectively. Note that the concentration of THMs in this study refer to the sum of CF, BDCM, DBCM, and BF while the concentration of HANs refer to the sum of MCAN, DCAN, TCAN, and DBAN hereafter.

RESULTS AND DISCUSSION

Occurrence and speciation of trihalomethanes

THMs of TP-DS, KT-DS, and KKU-DS are shown in Figure 2. It was observed that substantial amounts of THMs were formed after Cl_2 disinfection (TP and KT) while less THM was formed for ClO_2 disinfection (KKU). For the TP-DS, four types of THMs were found (Table 2 and Figure S4, Supplementary Material, available with the online version of this paper). THM species and concentrations (μg/L) were as follows: CF (5.37–147), BDCM (0.33–149), DBCM (0.39–64), BF (2.28–20). During summer 2016, the concentration of brominated THMs (BDCM, DBCM, and BF) tended to increase. This result could be due to increasing bromide concentration, which is a precursor of BF (bromide measurement was not available). The low precipitation and reduced surface runoff in summer time caused the ratio of

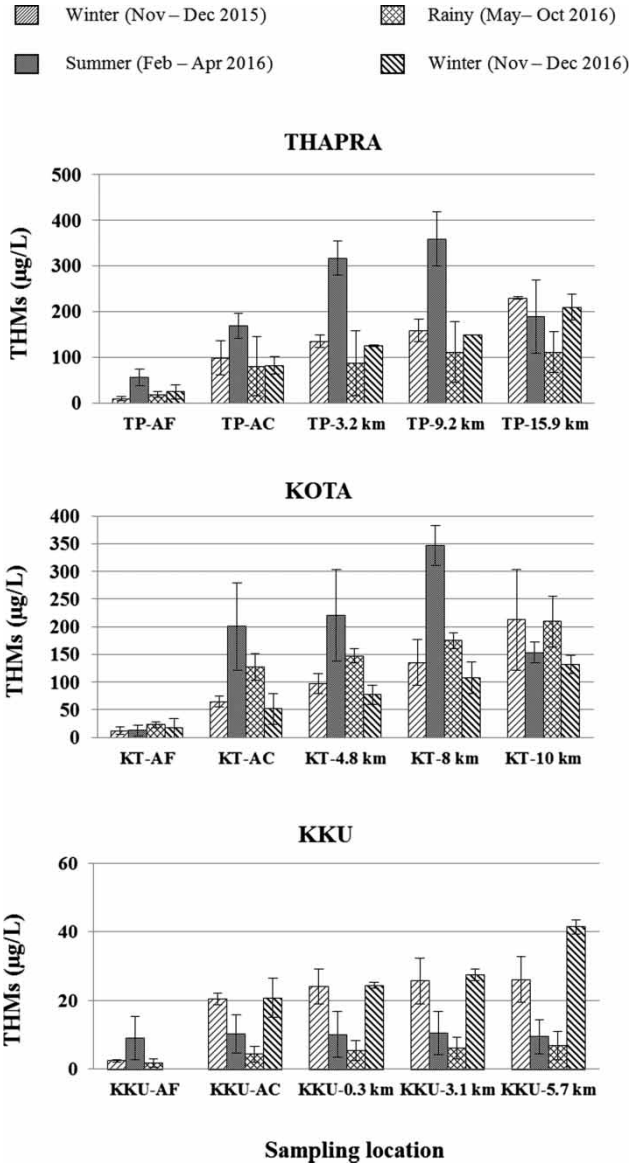

Figure 2 | THM concentrations of TP-DS, KT-DS and KKU-DS.

groundwater inflow to the Chi River to increase. Several areas in the northeast of Thailand are on a rocksalt layer formation (Pholkern *et al.* 2018). Therefore, groundwater is typically saline and can thus contain bromide. The magnitude of THM concentration and speciation in KT-DS and TP-DS was approximately the same (Figures S4 and S5, available online). CF (10–211 µg/L), BDCM (1.77–126 µg/L), and DBCM (2–20 µg/L) were found in all seasons. However, BF (2–4 µg/L) was the lowest among the 4-THM pool and only found in summer 2016 and rainy season 2016 (Table 2 and Figure S5). For the KKU-DS, CF was the most abundant THM species, while BDCM was only detected in summer 2016 and DBCM was found only in rainy season 2016 (Table 2, Figure 2 and Figure S6, available online). Concentrations of BDCM and DBCM were in the range of 0.28–0.64 µg/L and 0.08–0.16 µg/L, respectively. BF was found only in summer and rainy season 2016. It is interesting that concentrations of BF in KT-DS and KKU-DS formed similar patterns. This phenomenon could be explained by KT-WTP and KKU-WTP using the same water source from the Pong River and the type of disinfectants (Cl_2 vs ClO_2) not having a significant effect on BF formation. In the presence of bromide ions in water, BF can be formed because ClO_2 is able to oxidize bromide ions to hypobromous acid, which consequently reacts with natural organic matter (NOM) (Al-Otoum *et al.* 2016).

Among DS, TP-DS and KT-DS had high THM concentrations. Many sampling locations (excluding AF) had average concentrations of THMs > 100 µg/L. At TP-9.2 km and KT-8 km, THM concentrations were more than 350 µg/L in summer 2016 (Figure 2). These relatively high THMs were due to the use of Cl_2 gas as disinfectant. The occurrence of high THMs is also related to DOC, dose of disinfectant, and contact time (Guilherme & Rodriguez 2014; Serrano *et al.* 2015). In this work, it was noticed that water with high DOC (>5 mg/L) tends to have high THMs as it ages in pipelines along DS. Also, high THMs in summer could be from organic precursors that are reactive to chlorine and higher doses of disinfectant (Serrano *et al.* 2015). On the other hand, KKU-DS had THM levels lower than those of TP-DS and KT-DS. The highest THM concentration was 43 µg/L in winter 2016. Relatively low THM concentrations were because ClO_2 was used as a disinfectant. ClO_2 is known to form less THM because it reacts with NOM but does not destroy the C = C bond (Crittenden *et al.* 2012).

Overall, the concentration of THMs in several locations of TP-DS and KT-DS was higher than the drinking water standard (80 µg/L) recommended by the United States Environmental Protection Agency. However, in terms of Provincial Waterworks Authority (PWA) regulations, Thailand, each THM species is regulated and only BDCM concentrations were higher than the drinking water standard (60 µg/L) in summer 2016 for the TP-DS and in summer

Table 2 | Summary of THM and HAN speciation in distribution systems

	Water distribution systems		
Information	**TP-DS**	**KT-DS**	**KKU-DS**
Disinfectant	Cl_2	Cl_2	ClO_2
Raw water source	The Chi River	The Pong River	The Pong River
Maximum THM species and concentration (μg/L)	CF (147)	CF (211)	CF (41)
Minimum THM species concentration (μg/L)	BF (2.28)	BF (2)	DBCM (0.08)
Winter (Nov–Dec 2015)	CF (147) > DBCM (43) > BDCM (28) > BF (12)	CF (178) > DBCM (20) > BDCM (14)	CF (26)
Summer (Feb–Apr 2016)	BDCM (149) > CF (128) > DBCM (64) > BF (20)	CF (211) > BDCM (126) > DBCM (13) > BF (2)	CF (10) > BF (1.48) > BDCM (0.64)
Rainy (May–Oct 2016)	CF (48) > BDCM (44) > DBCM (24) > BF (6)	CF (121) > BDCM (72) > DBCM (13) > BF (4)	CF (4) > BF (3) > DBCM (0.24)
Winter (Nov–Dec 2016)	CF (145) > DBCM (44) > BDCM (18) > BF (3)	CF (119) > DBCM (11) > BDCM (2)	CF (41)
Maximum HAN species and concentration (μg/L)	TCAN (14)	TCAN (12.66)	TCAN (14)
Minimum HAN species and concentration (μg/L)	DBAN (0.45)	DBAN (0.1)	DBAN (0.19)
Winter (Nov–Dec 2015)	TCAN (14) > DCAN (11) > DBAN (1.75)	TCAN (12.66) > DCAN (7) > DBAN (4.5)	TCAN (14) > DCAN (4.3) > DBAN (3.8)
Summer (Feb–Apr 2016)	DCAN (7) > DBAN (6) > TCAN (5)	DCAN (10) > TCAN (7) > DBAN (2.5)	TCAN (6) > DCAN (2) > DBAN (1.6)
Rainy (May–Oct 2016)	DCAN (4.4) > DBAN (2.4) > TCAN (1.3)	DCAN (11) > DBAN (1.2) > TCAN (0.63)	TCAN (1.45) > DCAN (1.23) > DBAN (0.9)
Winter (Nov–Dec 2016)	DCAN (0.39) > TCAN (0.14) > DBAN (2)	DCAN (0.37) > TCAN (0.23) > DBAN (0.16)	DCAN (0.50) > TCAN (0.34)

Note: PWA standard: CF < 300 μg/L, BDCM <60 μg/L, DBCM <100 μg/L, and BF < 100 μg/L. USEPA standard: sum of CF, BDCM, DBCM, and BF < 80 μg/L.

2016 and rainy season 2016 for the KT-DS. To control THM formation and also comply with the regulations, enhanced coagulation could be applied (Crittenden *et al.* 2012). In addition, formation of specific THM species such as BDCM needs to be investigated in depth with respect to NOM characteristics and its reactivity towards the disinfectant.

Occurrence and speciation of haloacetonitriles

A summary of HAN speciation and total HANs in the examined distribution networks is shown in Table 2 and Figure 3, respectively. It should be noted that no MCAN was detected in any sample (Table 2 and Figures S7–S9 in the Supplementary Material, available online). For TP-DS, TCAN was the dominant species, while DBAN comprised the lowest fraction of the HAN pool (Figure S7). The amount of DCAN was found to increase in summer 2016 and decreased in winter 2016. HANs found in this study were higher (maximum concentration of 30 μg/L) than those in Canada (<2 μg/L) (Shanks *et al.* 2013). This result could be due to a high amount of precursors in water sources in Thailand (DOC = 4–6 mg/L and DON = 0.44–0.89 mg/L) compared with 1–2 mg/L of DOC in Canada (Shanks *et al.* 2013). In addition, the type of DOC or DON could affect the formation of HANs. During winter 2015, HAN concentrations were higher than those of winter 2016 in all DS. This result was due to increased precipitation and surface runoff in winter 2016 causing the dilution of the HAN precursor.

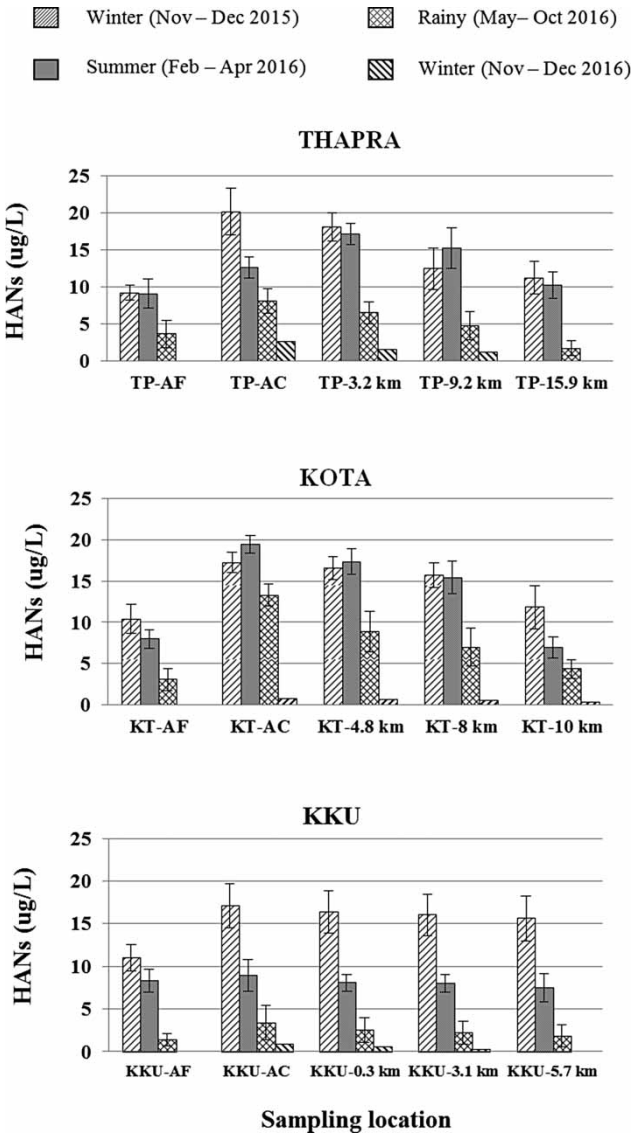

Figure 3 | HAN concentrations of TP-DS, KT-DS, and KKU-DS.

In the case of KT-DS, high HAN concentrations in winter 2015 were observed compared with other seasons (Figure 3). Ranges of DCAN, TCAN, and DBAN concentrations throughout the sampling period were 0.14–10.88, 0.16–12.66, and <0.1–4.47 μg/L, respectively. TCAN and DCAN appear to be the dominant species (Figure S8). Similar to TP-DS, a concentration of HANs in the range of 5–20 μg/L was found in winter 2015, summer 2016, and rainy season 2016. HAN concentration below 2 μg/L was found in winter 2016. The reason for this result was the same as for TP-DS in that high flow in the Pong River occurred during winter 2016.

For KKU-DS, DCAN, TCAN, and DBAN concentrations were in the range of 0.06–5, 0.14–14, and 0.47–4 μg/L, respectively (Figure S9). At KKU-5.7 km, TCAN was the dominant species in winter 2015. It is notable that the magnitude of HANs in KKU-DS in winter was less than KT-DS, which used the same raw water source. This result could be attributed to the type of disinfectants (ClO_2 for KKU-WTP and Cl_2 for KT-WTP) being used.

From previous works, seasonal variation showed that the concentrations of HANs and other DBPs in summer were higher than in winter (Shanks *et al.* 2013; Serrano *et al.* 2015) due to two main factors – higher DOC in summer and more disinfectant demand. This phenomenon occurred in North America and Europe where there is a significant change of temperature between seasons. For tropical countries, however, the change of season has very little effect on temperature or vegetation. Rather, changes in the amount of rainfall impact DBP precursors as well as DBP formation. Previous research has reported the elevated THM, HAA, and *N*-nitrosodimethylamine formation potential after extreme flooding events (Ruecker *et al.* 2017).

Relationship of DBP concentrations with distance from WTPs and kinetic model

From Figure 2, THMs increased along the distance of the distribution line. This result was not surprising because water aged along the pipeline and the longer contact time between chlorine residuals and NOM in the distribution system resulted in more formation of THMs (Rodriguez *et al.* 2004; Di Cristo *et al.* 2013, 2014). However, in summer 2016, the concentration of THMs in TP-DS and KT-DS decreased at the farthest sampling locations (TP-15 km and KT-10 km). Because the sampling location was far from the treatment and no intermittent chlorine dosing was used inbetween, no chlorine residuals were left in the water to react with NOM. Further, THMs can be degraded by biofilms (Chien *et al.* 2009).

To predict the areas of high THM levels, the relationship between concentrations of THMs and distance away from water treatment plants was developed; a linear relationship was observed (Table 3). Strong correlation was found for KT-DS and KKU-DS with an R^2 of 0.8507 and 0.9266,

Table 3 | Linear equations of DBPs with distance and first-order kinetic model parameters

	TP-DS	KT-DS	KKU-DS
Linear equation fitted with measured DBP data			
THMs	$C = 3.3241X + 127.15$ ($R^2 = 0.4958$)	$C = 7.3468X + 120.95$ ($R^2 = 0.8507$)	$C = 0.7641X + 11.287$ ($R^2 = 0.9266$)
HANs	$C = -3{,}555.0X + 11.015$ ($R^2 = 0.9859$)	$C = -0.7213X + 13.843$ ($R^2 = 0.9031$)	$C = -0.1899X + 6.0268$ ($R^2 = 0.7651$)
First-order kinetic model parameters			
Calibrated K_1 (1/h)	0.24	0.27	0.49[a]
Calibrated D (μg/mg)	148.68	97.76	6.29
f	0.039889	0.053309	0.049108
f_c	0.001546	0.038773	0.038695
f_T	0.038343	0.014537	0.010413
σ_c^2	0.001546	0.038773	0.019347
σ_T^2	0.019171	0.007268	0.005206
Var(P_c)	0.075815	0.067372	0.067826
Var(D)	0.042590	0.005803	0.004126

C, concentration of THMs or HANs (μg/L); X, distance from water treatment plants (km).
[a]ClO_2 decay rate.

respectively. It was observed that different distributions have varying slopes. Higher slopes were from the TP-WTP and KT-WTP that use Cl_2 as a disinfectant.

For all DS, HAN concentrations were found to decrease with distance away from the water treatment plants (Figure 3), a result which was due to the hydrolysis reaction of HANs (Shanks *et al.* 2013). Strong correlations were observed with an R^2 of 0.9859, 0.9031, and 0.7651 for TP-DS, KT-DS, and KKU-DS, respectively. Higher slopes indicate an increased HAN hydrolysis rate, which was found for TP-DS and KT-DS. Differences in reduction rates of HANs indicated that not only is hydrolysis responsible for decreasing HANs, but that biodegradation may cause HAN reduction in DS. However, there is no research evidence to support this proposal.

A first-order kinetic model was used to estimate THM concentration based on chlorine decay (K_1) and THM productivity (D) (Di Cristo *et al.* 2014, 2015). Table 3 shows the values of the first-order kinetic parameters (further detail is provided in the online Supplementary Material). It was found that the first-order kinetic model provided reasonable results for THM and disinfectant concentrations compared with the measurement data (Table S2, available online). The K_1 values of TP-DS and KT-DS were relatively close (0.24 1/h vs 0.27 1/h) due to the fact that the same type of disinfectant (Cl_2) was used. Note that the K_1 and D values obtained from this study were significantly higher than those of previous work by Di Cristo *et al.* (2014), who reported K_1 and D of 3 μg/L, 0.014 (1/h) and 35 (μg/mg), respectively. This discrepancy was due to the difference of water quality and environmental conditions. For uncertainty analyses, the variances of Cl_2 (σ_c^2) and THM measurement (σ_T^2) were relatively low compared with the measured values. In addition, the variances of chlorine decay (Var(P_c)) and THM productivity (Var(D)) with respect to the error of chlorine measurement (σ_c^2) and THM measurement (σ_T^2) were also small. This result indicates that the first-order kinetic model was reliable for fitting field measurement data.

DBP exposure

Vulnerability analyses were performed to identify the locations in the DS where populations were at high risk of DBP exposure. In this work, the exposure of populations to THMs and HANs was estimated based on two vulnerability indexes (Quintiliani *et al.* 2018): maximum THM ($THMs^{max}$) (Equation (1)) and HAN concentrations ($HANs^{max}$) and dimensionless exposure time (T_i^E) (Equation (2)) at each sampling point during the entire sampling period (November 2015–December 2016):

$$[THMs^{max}] = \max\{[THMs]_{i,t}\} \text{ or } [HANs^{max}] = \max\{[HANs]_{i,t}\} \quad (1)$$

where $[THMs]_{i,t}$ is the actual THM concentration at time t at the sampling point i and $[HANs]_{i,t}$ is the actual HAN concentration at time t at the sampling point i;

$$T_i^E = \frac{\int_0^{TOT} I(t) \cdot dt}{TOT} \quad (2)$$

where TOT is total observation time and factor $I(t)$ is defined as:

$$I(t) = \begin{cases} 1 \text{ if } [THMs]_{i,t} > [THMs]_{\text{lim}}, \text{ or } [HANs]_{i,t} > [HANs]_{\text{lim}} \\ 0 \text{ if } [THMs]_{i,t} > [THMs]_{\text{lim}}, \text{ or } [HANs]_{i,t} > [HANs]_{\text{lim}} \end{cases} \quad (3)$$

where $[THMs]_{\text{lim}}$ and $[HANs]_{\text{lim}}$ are fixed attention thresholds for THMs and HANs, respectively. In this work, the value of 80 μg/L THMs standard of the USEPA (the sum of CF, BDCM, DBCM, and BF) was used. Note that the USEPA standard was chosen because its concentration was much lower than the PWA standard, Thailand (Table 2). $THMs^{\max}$ of TP-DS and KT-DS were significantly higher than the USEPA standard and T_i^{E} values were close or equal to 1 for TP-DS at 15.9 km and for KT-DS at 4.8, 8, and 10 km (Table S3, available online). These T_i^{E} values indicated that populations at the locations mentioned above were at high risk of chronic THM exposure at all times during the sampling period. On the other hand, $THMs^{\max}$ of KKU-DS at all sampling points was well below the USEPA standard (80 μg/L) and T_i^{E} values were zero. Therefore, there was no vulnerable exposure of customers at KKU-DS to THMs. The fixed threshold for HANs is 90 μg/L, based on the sum of the WHO's guideline concentrations for DCAN and DBAN at 20 and 70 μg/L, respectively. $HANs^{\max}$ for locations in all three DS were found between 20–30 μg/L and T_i^{E} values were zero (Table S3). As a result, there was no vulnerable exposure of customers at TP-DS, KT-DS, and KKU-DS to HANs.

CONCLUSION

This work is the first report on the occurrence of DBPs in Khon Kaen Municipality DS. The results demonstrated that occurrence and speciation of THMs and HANs relied on two main factors – type of disinfectants and characteristics of water. Chlorine could generate 2–10-fold and 1.5–4-fold more THMs and HANs, respectively, compared with ClO_2 for the same water source. With the same disinfectant (Cl_2), two sources of water provided similar trends of THM and HAN formation. From season variations, rainfall was found to be an important factor affecting the characteristics of source waters as well as DBP formation in tropical regions. Spatial variation was observed for both THMs and HANs. The longer the distance away from the water plants, the more THMs were formed, while HANs steadily decreased. A strong linear correlation of THMs and HANs with distance from the water treatment plants was found. This simple model (concentration and distance) can be used to estimate the concentration of THMs and HANs. The first-order kinetic model also provided a reasonable estimation of THMs. Longer sampling periods should be used and several parameters (such as bromide concentration) should be included into the model to more accurately predict DBP concentrations. KKU-DS was found to be non-vulnerable for THMs due to ClO_2 being used as a disinfectant. Although ClO_2 produced less THMs, it could generate other DBPs such as chlorite and chlorate. Formation of these compounds should be further investigated when using ClO_2 as a disinfectant.

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