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Original Article

Risk Assessment of Chlorination Disinfection Byproducts from Ingestion of Municipal Tap Water Supply in Khon Kaen, Thailand

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Abstract

Introduction This study aimed at assessing for human health risk of disinfection by-products (DBPs) from chlorination of public tap water supply since DBPs have been reported of harms to human health. Methods Water samples were collected from 5 collection points along the municipal tap water supply route during rainy (September-October 2014) and after-rainy periods (November-December 2014). Analysis for THMs (Trihalomethanes) was by Purge and Trap and GC-ECD, for HAAs (Haloacetic acids) by LCMSMS.

Results Our study found THMs occurrence in water from the chlorination process and the concentrations were highest at the last collection point of water supply route. After-rainy periods water had significantly higher THMs than in rainy periods. Comparison of THMs levels from the best case scenario (finished water at the treatment plant) to US.EPA guideline values found the safety factors <1, i.e., for chloroform=0.95, for total THMs=0.72. The risk assessment found the threshold toxicity of THMs in water was within acceptable range, but the lifetime excess cancer risk (non-threshold toxicity) from ingestion exceeded 243 fold the acceptable rate in the best case calculation and 363 fold in the worst case. However, the risks of HAAs in water were all in acceptable range.

Conclusion the cancer risk from THMs was of great concern for consumers of Khon Kaen municipal tap water and people living at the last collection point of the water supply route were at greater risk compared to people living near the water treatment plant, particularly in the dry season.

Keywords: *Trihalomethanes (THMs), Haloacetic Acids (HAAs), Dissolved Organic Carbon (DOC), Free Chlorine, Rainy Season*

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นิพนธ์ต้นฉบับ

การประเมินความเสี่ยงทางการกินสารที่เกิดจากการฆ่าเชื้อโรคน้ำประปาด้วยคลอรีน จ.ขอนแก่น

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บทคัดย่อ

บทนำ งานวิจัยนี้มีวัตถุประสงค์เพื่อประเมินความเสี่ยงต่อสุขภาพจากสารที่เกิดจากการฆ่าเชื้อโรคในน้ำประปา (Disinfection by-products, DBPs) ด้วยคลอรีนเนื่องจากมีรายงานถึงอันตรายต่อสุขภาพมาอย่างต่อเนื่อง วิธีวิจัย ทำโดยการเก็บน้ำตัวอย่าง 5 จุด ตามระยะทางส่งน้ำในช่วงฤดูฝน(กลางกันยายน-ตุลาคม 2557) และหลังฤดูฝน (พฤศจิกายน-ธันวาคม 2557) วิเคราะห์ THMs (Trihalomethanes) โดยใช้วิธี Purge and Trap และ GC-ECD วิเคราะห์ HAAs (Haloacetic acids) โดยใช้ LCMSMS ผลการวิจัย พบว่ามี THMs เกิดขึ้นจากการฆ่าเชื้อโรคด้วยคลอรีนโดยมีความเข้มข้นสูงที่สุดในจุดเก็บตัวอย่างจุดสุดท้าย ช่วงหลังฤดูฝนพบ THMs สูงกว่าช่วงฤดูฝน เมื่อเปรียบเทียบระดับ THMs จากการคำนวณ best case scenario (น้ำที่เพิ่งผ่านกระบวนการผลิต) กับค่ากำหนดใน US.EPA พบว่าได้ค่าความปลอดภัย (safety factors) <1 คือ chloroform=0.95, total THMs=0.72 การประเมินความเสี่ยงพบว่าความเป็นพิษแบบมีระดับกั้น (threshold toxicity) ของ THMs ในน้ำยังอยู่ในช่วงที่ยอมรับได้ แต่ความเสี่ยงต่อการเกิดมะเร็งตลอดช่วงชีวิต (lifetime excess cancer risk) หรือ ความเป็นพิษแบบไม่มีระดับกั้น (non-threshold toxicity) จากการกินสูงเกินกว่า 243 เท่าของค่าที่ยอมรับได้ในกรณี best case และสูงกว่า 363 เท่าของค่าที่ยอมรับได้ในกรณี worst case แต่กรณีความเสี่ยงจาก HAAs ในน้ำยังอยู่ในช่วงที่ยอมรับได้ สรุป ความเสี่ยงต่อการเกิดมะเร็งจากสารประกอบ THMs เป็นเรื่องน่ากังวลสำหรับผู้บริโภคน้ำประปาในเขตเทศบาลเมือง จ.ขอนแก่น และประชากรที่อยู่อาศัยในจุดสุดท้ายที่เก็บตัวอย่างน้ำจะมีความเสี่ยงสูงขึ้นเมื่อเปรียบเทียบกับผู้ที่อยู่อาศัยใกล้สถานีผลิตน้ำประปาโดยเฉพาะอย่างยิ่งในฤดูแล้ง

คำสำคัญ: *Trihalomethanes (THMs), Haloacetic Acids (HAAs), Dissolved Organic Carbon (DOC), Free Chlorine, Rainy Season*

Introduction

Various disinfection methods for public water supply are available nowadays, but chlorination is the most popularly used method around the world due to the lowest cost and high efficacy. However, several harmful disinfection byproducts (DBPs) are produced such as trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), of which THMs and HAAs are used as indicators for DBPs since these 2 groups compose for about 80% of all DBPs (Health Canada, 2008). Studies showed that THMs (including chloroform or CF, bromodichloromethane or BDCM, chlorodibromomethane or CDBM, and bromoform or BF) could be carcinogens in animals and humans (WHO, 2004). Several analytical epidemiological studies reported that ingestion of chlorinated drinking water was associated with human colorectal cancer and bladder cancer (WHO, 2004). Although it is not possible to attribute the excess cancer rates from DBPs to CF, however, CF has been found the highest concentration in water. According to IARC monographs (IARC, 2016), CF and BDCM are classified in Group 2B (Possible carcinogenic to human), while CDBM and BF are classified in Group 3 (Not classifiable as to its carcinogenicity to humans). In addition to carcinogenicity, some DBPs are also toxic to the reproductive system (Minera and Amy, 1996), cardiovascular system, and may affect internal organs like liver and kidney (Hogan, 1979) and many other health effects (Faust and Aly, 1998). As chlorination is the sole method used for disinfecting public tap water supply in Thailand, this study was aimed to detect the occurrence of THMs and HAAs, the 2 representative groups of DBPs, and calculate the risk on health of consumers.

Methods

1. Water samples

Municipal tap water supply in Khon Kaen Province (Figure 1) was used in this study. Tap water supply from Kotha Water Treatment Plant was followed for the main route of 9 km long supplying around 4,800 consumers of Sila and Baan Samran Districts. The water samples of this main route were collected from 5 collection points, point1 was raw water at Kotha Water Treatment Plant just before entering the treatment process, point2 was finished water at Kotha Water Treatment Plant (at the start point of the municipal water supply route after chlorination disinfection of water), point3 was water at 4.5 km from Kotha Water Treatment Plant, prior to re-chlorination (just before entering Ratanapa water re-chlorination station, where water was chlorinated for the second time), point4 was water after the re-chlorination process (just after Ratanapa water re-chlorination station, 4.6 Km from Kotha Water Treatment plant), point5 was at Baan Samran District (9 km from point4) (Figure 2).

2. Water sample preparation and analysis

Water was collected in rainy period (during September-October 2014, within 7 days after rains) and after-rainy period (November-December 2014, no rains for at least 7 days before collection). This study was first designed to compare between rainy period and dry period. However, in the year 2014 the rainy period extended for longer duration than expected. Since November and December are usually a dry period, but it rained occasionally through the end of the year. Therefore, in this study, there were no sample collections in a real dry period. Only at least 7 days without rain before the collection time was used. Water was collected in a 1 litre-cleansed-sterile storage bottle, to full level (filled up until over flowed), closed with air-tight screwed cap and kept in an iced box until arrival at the laboratory room. Then 4 portions of water samples were prepared and processed as in New Hamshire Sample Collection and Preservation Manual for Drinking Water (N.H. Department of Environmental Services, 2011). Portion1, 100 ml in Erlenmeyer flask was titrated for free chlorine by Argentometric method (Standard method for the examination of water and wastewater (APHA, 2012). Portion2, 40 ml of 0.45 μm filtered water was detected for dissolved organic carbon (DOC) using Analytikjena, multi N/C 2100S. Portion3, 40 ml was detected for THMs using Purge and Trap (P&T) sample concentrator -Tekmar 3100 and GC-ECD -Agilent 4890 D following the modified method from Allonier et al. (2000). Portion4, 1 ml of 0.2 μm-filtered water was detected for HAAs using LC-MS/MS (AB SCIEX® / API 3200 Triple quadrupole) following the modified method from Zaffiro et al. (2009).

3. Chemical analyses conditions

GC-ECD system (Agilent 4890 D, Tekmar 3100: SPB-608 fused silica capillary column -30 m length x 0.53 mm inner diameter x 0.5 μm film thickness, J & W Scientific), injector temperature 150°C, oven temperature 50°C for 15 min, carrier gas 2 ml/min, detector temperature 250°C, total time 15 min. Reference THMs were THMs calibration mix in methanol (Supelco, USA)

Purge & trap (P&T) sample concentrator system: Valve oven temp 150°C, Transfer line temp 150°C, Sample mount Temp 40°C, Purge ready temp 40°C, Purge temp 40°C, Purge ready time 5 min, Desorb preheat temp 225°C, Desorb time 1 min, Desorb temp 225°C, Bake time 5 min, Bake temp 250°C.

LC-MS/MS system: C18 column (Synergi 4u 150 × 4.60 mm 4 micron), mobile phase was by 2 solvents system, solvent A - Ultrapure water 0.1% (V/V) acetic acid (pH3.1), solvent B-Acetonitrile, gradient analysis, flow rate 0.3 ml/min, injection volume 10 **μl**, column temp 40°C, total time 10 min. For MS/MS, negative ion mode was used in Electrospray ionization (ESI) with source/gas temp 400°C, Ion source gas 1 (GSI1) 40, Ion source gas 2 (GSI2) 50, Curtain gas (CUR) 25, IS Voltage (IS) -4500 V. Ions were analyzed by Selective Reaction Monitoring (SRM) mode. Reference HAAs were a Haloacetic acid mix in methyl tert-butyl ether (MTBE) (Supelco, USA).

4. Risk assessment estimation (ATSDR, 2011; US EPA., 2009)

In the calculation for the risks from ingestion of municipal tap water supply, for the worst case scenario: daily ingestion dose was calculated from the highest concentration of DBPs detected in this study. In the best case scenario: daily ingestion dose was calculated from the concentration of DBPs detected in finished water at Kotha Water Treatment Plant (the start point of tap water supply route).

4.1 Comparison of THMs detected to guideline values (GVs)

The highest concentrations of THMs detected (as for the worst case scenario) and the concentrations of THMs at the start point of water supply (finished water at Kotha Water Treatment Plant as for the best case scenario) in the municipal water supply were compared to the guideline values (US.EPA, n.d.) for safety factors.

Safety factors of THMs = $(GV_{CF}/C_{CF}) + (GV_{DCBM}/C_{DBCM}) + (GV_{DBCM}/C_{DBCM}) + (GV_{BF}/C_{BF})$

When C = concentration of each THM detected

GV = guideline value of each THM
CF = chloroform,
DCBM = dichlorobromomethane,
DBCM = dibromochloromethane,
BF = bromoform

4.2 Calculation for risk of threshold toxicity (non-carcinogenic effects)

Total hazard index (HI) = HQ_{CF} + HQ_{DCBM} + HQ_{DBCM} + HQ_{BF}

HQ=hazard quotient of each compound from ingestion of water containing THMs= ADD /RfD

Where ADD = average daily ingestion dose of each compound

RfD = reference dose of each THM from ingestion

4.3 Calculation for risk of non-threshold toxicity (carcinogenic effects)

Total cancer risk = Cancer $risk_{CF}$ + Cancer $risk_{DCBM}$ + Cancer $risk_{DBCM}$ + Cancer $risk_{BF}$

Cancer risk of each compound from ingestion of water containing THMs = SF x LADD

Where SF = slope factor (carcinogenic potency factor) of each THM

LADD = lifetime average daily ingestion dose of each compound

4.4 Calculation for daily ingestion dose

In this study, the average daily ingestion dose (ADD) to evaluate for threshold toxicity (non-carcinogenic effects) and lifetime average daily ingestion dose (LADD) to evaluate for non-threshold toxicity (carcinogenic effects) for THMs and HAAs detected from municipal tap water supply were assumed the same for average Thai adult consumers, using ingestion rate of water at 2.5 L/d (DEQ, 2015), average body weight of 63 kg (male and female combined (Size Thailand, 2007-2008; U.N., 2015), and that the averaging time (AT) was equal to a lifetime (LT).

ADD = (C_w x IR) / BW

LADD = (C_w x IR x AT) / (BW x LT)

C_w = THMs or HAAs concentration in water, IR = daily ingestion rate of water 2.5 L/d (DEQ, 2015), BW = average body weight = 63 kg (male and female combined, Size Thailand, 2007-2008; U.N., 2015), AT=averaging time, LT = lifetime = 74 years (male and female combined, SizeThailand, 2007-2008; U.N., 2015).

5. Statistical analysis

Differences between groups were tested by one-way ANOVA, then Tukey HSD for post-hoc multiple comparisons, using statistix10 (Analytical Software, USA).

Results

1. Validation of chemical analysis methods

From GC-ECD, Purge and Trap sample concentrator, the detection found the retention time of Chloroform (CF) =0.9, Bromodichloromethane (BDCM) =1.4, Chlorodibromomethane (CDBM) =2.4, Bromoform (BF)=5.4 (min), respectively. The linearity range of these 4 THMs was 0.02-20.0 μg/L with a correlation coefficient R^2= 0.993, 0.999, 0.998, 0.998, respectively. The limits of detection (LODs) of these 4 THMs=0.28, 0.09, 0.12, 0.17 μg/L and limits of quantitation (LOQs)=0.39, 0.15, 0.22, 0.25 μg/L, respectively. The interday and intraday precisions were acceptable and within 15% relative standard deviations (RSDs).

From LCMSMS, the detection found the selectivity of Monochloroacetic acid (MCAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Monobromoacetic acid (MBAA), Dibromoacetic acid (DBAA), were precursor ion (m/z)/product ion (m/z)=93/34.9, 126.7/83, 160.6/116.6, 136.8/78.9, 216.8/172.7, respectively. The linearity range of these 5 HAAs was 2.0-120.0 μg/L with a correlation coefficient R^2= 0.997, 0.981, 0.996, 0.992, 0.989, respectively. The LODs of these 5 HAAs were 0.0049, 0.0067, 0.03, 0.0023, 0.005 μg/L, the LOQs 0.0078, 0.0088, 0.086, 0.0035, 0.0068, respectively. The interday and intraday precisions were acceptable and within 15% relative standard deviations (RSDs).

2. Characteristics of Khon Kaen municipal tap water

In rainy period, the raw water at point1 contained none of detectable free chlorine. Finished water at the treatment plant (point2) was found 0.18±0.10 mg/l of free chlorine. After point2, significant increase of free chlorine was found at each farther distance (point3 and point4), until point5 where the free chlorine was the same as point4. Dissolved organic carbon (DOC) was found the highest concentration in raw water (point1) at 9.71±0.83 mg/l. At point2, DOC in finished water was reduced significantly from raw water at point1. After that DOC remained similar at point3 and point4 but significantly increased at point5. The pH of water remained similar all through the collection route (Table 2).

After-rainy period, the raw water at point1 was found trace of free chlorine, even before chlorination process (0.06±0.01 mg/l). Finished water at point2 had lower free chlorine than the raw water at point1 and remained the same at point3. However, free chlorine sharply increased at point4 (after re-chlorination) and remained the same at point5. These free chlorine concentrations at point4 and 5 were the same as in rainy period. DOC was found significantly higher in after-rainy period than in rainy period in all sampling points, except for point5 where similar level was found. The pH of water was found similarly in after-rainy period and in rainy period at all sampling points (Table 2, 3).

Overall, water in rainy and after-rainy periods contained the same free chlorine concentrations at the 2 last collection points (points 4-5) but significantly higher free chlorine in rainy period than after-rainy period at the 2 first collection points (points 2-3). Re-chlorination significantly increased free chlorine. DOC concentrations were significantly higher in after-rainy period than in rainy period.

For THMs detection (Table 4, 5), even the raw water at point1 was detected a little amount of THMs both in rainy and after-rainy periods. Total THMs (TTHMs) and each compound of THMs was found significantly higher in after-rainy period than in rainy period. Of all THMs at every collection point, CF was found the highest concentration while BF was the lowest concentration with some collection points at non-detectable level. In both rainy and after-rainy periods, water after chlorination (point2) increased its THMs concentrations sharply compared to the raw water, and water at the last collection point (point5) contained the highest TTHMs and CF compared to all collection points. In both collection periods, CF and BDCM at point3 were significantly lower concentrations than that at point2 but CDBM and BF were significantly higher than that at point2. Point4 (water after re-chlorination) was found TTHMs and CF significantly higher than point3. And water at the last collection point (point5) contained the highest concentration of each THMs of all collection points except for BF. The highest TTHMs at point5 was found 122.44±2.61 and 144.27±8.8 μg/l in rainy and after-rainy periods, respectively.

Overall, after chlorination (point2) significant increases of every THM and TTHMs were found, and after re-chlorination (point4) significantly further increases of TTHMs, CF, and BDCM were found, but not CDBM and BF.

For HAAs detection (Table 6, 7), the findings were different from THMs for concentrations of compounds were almost the same at every collection point and in both collection periods, with DCAA was found the highest concentration of all HAAs.

3. Risk assessment estimation

3.1 Comparison of DBPs detected from municipal tap water supply to guideline values (GVs)

When compared to guideline values suggested by US.EPA (n.d.), it was found that even water of the best case scenario (calculation from point2, finished water at the start point of water supply in rainy period), THMs concentration already exceeded GVs, with safety factors <1, i.e., safety factors for CF=0.95, for TTHMs=0.72. The safety factors of THMs for the worst case scenario (from point5, water of after-rainy period) were undoubtedly lower, i.e., for CF=0.76, for TTHMs=0.55. Only CDBM was found with safety factor >1, i.e., safety factors = 8.05 for the best case, and = 3.38 for the worst case (Table 8). Fortunately, even in the worst case of HAAs, safety factors were >1, i.e., for MCAA =29.54 and for THAAs =3.97 (Table 9).

3.2 Risk of threshold and non-threshold toxicity from municipal tap water supply

In calculating for the worst case, the risk of threshold toxicity from municipal tap water supply was found within acceptable range with total HI=0.4696. However, the risk of non-threshold toxicity was found unacceptable with the total lifetime excess cancer rate =3.63×10^{-4}. It was 363 fold of acceptable lifetime excess cancer rate (10^{-6}). For the best case calculation, the risk was a little better with the total HI=0.3303, the total lifetime excess cancer rate =2.43×10^{-4} (Table 10).

Discussion and conclusion

Chlorination disinfection was confirmed in this study to be the source of THMs production since point2 (after chlorination) obviously increased every THM compound from point1, and re-chlorination further increased every THM compound (point4 significantly higher than point3). Point1 (raw water) was also found THMs. This may be due to natural production in the environment although there were only traces. DOC was found higher in after-rainy period than rainy period. This may be due to less dilution from rain in water at after-rainy period. Studies reported that carbon species in rainwater were varied by atmospheric transformation, transport, removal mechanisms of carbonaceous particles, different biogenic/anthropogenic emission and meteorological conditions, thus resulted in spatial and temporal variability of carbon species in rainwater (Siudek, Frankowski, & Siepak, 2015). The loading of organic carbon to water resources varies with climate, vegetation, and the season of year (Thurman, 1985 cited by Kim et al., 2000). Rains at the beginning of seasons are important factor loading organic carbons into water resources (Kim et al., 2000). However, this factor should have little effect in our study since the water samples were collected at mid of the season. Chlorination process could reduce DOC and increase THMs levels since free chlorine from chlorination could react with DOC to produce chlorination byproducts including THMs (Yee et al., 2006; Rodriguez, Serodes, & Levallois, 2004; Pentamwa, et al., 2013; Gough, 2014; Chatsantiprapa et al., in press). In our study point2 (after chlorination) was found significantly lower DOC and higher THMs than point1. This should reflect at least partly the transformation of DOC to THMs. However, re-chlorination did not reduce DOC levels since point4 was not lower than point3, but remained the same. The different factor involving between these 2 chlorination stations was the filtration process in the water treatment methods at point2 not provided at point4. Therefore, the filtration process may have explained the significantly lower DOC at point2 more than the transformation reaction of DOC producing THMs. DOC should have remained insignificantly changed all through the tap water route if there was no more chlorination process. However, in rainy period (Table2), point5 was found a significant increase of DOC from points 2-4. This could be due to inevitable errors in water collection or DOC analysis of this point5 water samples. This error was not found in after-rainy periods.

In this study, distance of the collection points did not affect DOC or free chlorine levels. But chlorination and re-chlorination significantly increased free chlorine. The significantly higher free chlorine in rainy period than after-rainy period at the 2 first collection points (points 2-3) should be due to more chlorine addition during water chlorination to compensate the dilution from rains. In the water treatment process, it was said that the pH of water was monitored before chlorine addition. Thus, pH of water remained indifferent all through the supply route. But free chlorine was highest after re-chlorination and remained unchanged thereafter as detected at the last 2 collection points (points 4-5). For THMs, it could be that the distance of collection points if long enough may have increased every THM compound (except BF) since the levels at point5 were always higher than point4. The distance between point2 and point3 may have been too short to see this effect. Longer distance provided longer reaction time producing more THMs. The warm temperature in Thailand could be another activation factor for the reactions while water was being carried in the supply pipes as the temperature effect was also mentioned (Faust and Aly, 1998). The significantly lower CF and BDCM concentrations at point3 than that at point2 could be due to decomposition or transformation of the chemicals after being carried in the pipe for some time but concentrations increased again at point4 due to re-chlorination. However, the levels of CDBM and BF was not able to explain by the same logic. This could be because the levels of these 2 chemicals were much lower, thus, inevitable errors in detection or other chemical principles might have interfered.

Less rain was proved in this study to be a factor increasing every THM compound (except BF) since the THMs levels in after-rainy period were always higher than in rainy period at every collection point. This may be due to lesser water to dilute the chemical concentrations in after-rainy period. In this study, people living at the last collection point were at increased risk of health hazards than people living near the start point of water supply route. Although the risk of threshold toxicity from THMs was within acceptable range, the lifetime excess cancer risk of non-threshold toxicity exceeded far out the acceptable rate even for the best case scenario calculation (from water at the start point of municipal tap water supply in rainy period). In this study CF was always the predominant substance in TTHMs in all situations, i.e., every collection point and every collection period, in the municipal water supply. The predominance of CF has always been reported elsewhere. Therefore, CF distributed the highest excess cancer risk of all THMs in municipal tap water supply. However, CDBM and BDCM in our study also individually gave unacceptable excess cancer risk since each risk was $>10^{-6}$. Nevertheless, HAAs in Khon Kaen municipal tap water were in acceptable range both for threshold and non-threshold toxicity estimations.

In this study, the estimations of risks were based on many assumptions. The physiological parameters (body weight 63 kg, daily water ingestion rate 2.5l/d) were assumed the average values from Thai male and female combined (SizeThailand, 2007-2008; U.N., 2015; DEQ, 2015).

The ADD (average daily intake dose) was assumed equal to LADD (lifetime average daily intake dose) when calculating for ingestion of municipal tap water since people were assumed to consume water regularly at the same rate as daily basis for a lifetime and that the substances levels and all physiologic parameters remained unchanged at any time points all through a lifetime. However, in reality the use of water could vary between individuals, hence the risk of these chemicals in water could vary. For example, some people might filter water or boil water before use. These variations could reduce the ingeston dose of the chemicals since filtration and boiling could reduce the chemicals through filter or evaporation from boiling heat (Chatsantiprapa et al., in press). The different ways of using water could change the chemical levels in the water. Some people might use water from mixed sources, e.g., commercially bottled water. Some people might ingest more or less water than the rate used in this study. Male or female population and different weight of individuals also vary from the average values. These factors could vary the risks from ingestion of this water. Despite the awareness of these uncertainties, our findings still raised high concern since the lifetime excess cancer rates were already too high for a life even without the addition of the risks from other routes of exposure to this water, e.g., inhalation while using as studied by Chatsantiprapa et al. (in press), or the risks from other chemical contaminants encountered in daily life. Our findings supported the too high lifetime excess cancer rates from public water supply reported in some other regions in Northeast of Thailand (e.g., Chongsamoe, Chaiyaphum) by Pentamwa et al. (2013). Their study reported the highest TTHMs detected at 48.46 µg/l giving the excess cancer rate 4.96E-5 for male and 1.04E-4 for female, although our study's findings were higher. Our findings were TTHMs 99.36±1.01 µg/l for the best case and 144.24±8.8 µg/l for the worst case giving the excess cancer rate 2.43E-4 (the best case) and 3.63E-4 (the worst case) which were 2.3-3.6 fold of their female's cancer risk and 4.9-7.3 fold of their male's cancer risk. The studied locations of Pentamwa et al. (2013) were neighbours of Khon Kaen Province - our study location. These findings reflected that public tap water in the northeast region of Thailand should be of concern. In our study, the standard values used in calculation were all commonly used in most published articles (Basu et al., 2011; Pentamwa et al, 2013; Siddigue et al., 2015), e.g., the oral slope factor of chloroform was used at 0.061 $(mg/kg.d)^{-1}$, not 0.031 $(mg/ kg.d)^{-1}$ (RAIS, n.d). The differences in standard values used in calculations would result in different risk values. Still the excess cancer rates were too high. In our study even in after-rainy period, not a real dry period, THMs were found significantly higher than in rainy period and the lifetime excess cancer rate was already 363 fold the acceptable cancer rate at the last collection point (point5, the worst case). It could be predicted that in the real dry period, the situation could be worse.

Nine approaches for removal of THMs and their precursors as suggested by Faust & Aly (1998) were oxidation, adsorption, aeration, clarification, ion exchange, biodegradation, pH adjustment, source control and intense mixing during disinfection. Of these approaches, the effectiveness and estimated costs of 19 techniques for control of THMs were presented. For safety of the Thai consumers in the northeast region, therefore, we recommend urgent measures should be pursued.

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Table 1 Standard values of trihalomethanes used in calculation for risk assessment from ingestion

Terms	Meaning	Value	Unit	Reference
SF	Slope factor, ingestion			
	CF (chloroform)	0.061	**$(mg/kg/d)^{-1}$**	RAIS (2009)
	BDCM (bromodichloromethane)	0.062	**$(mg/kg/d)^{-1}$**	IRIS (2009)
	CDBM (chlorodibromomethane)	0.084	**$(mg/kg/d)^{-1}$**	IRIS (2009)
	BF (bromoform)	0.0079	**$(mg/kg/d)^{-1}$**	IRIS (2009)
RfD	Reference dose, ingestion			
	CF (chloroform)	0.01	mg/kg/d	**U.S. EPA (1987)**
	BDCM (bromodichloromethane)	0.02	mg/kg/d	**U.S. EPA (1987)**
	CDBM (chlorodibromomethane)	0.02	mg/kg/d	**U.S. EPA (1987)**
	BF (bromoform)	0.02	mg/kg/d	**U.S. EPA (1987)**

Table 2 Characteristics of Khon Kaen municipal tap water in rainy period (triplicate collections and analyses) (mean ±SD)

Location	pH	Free chlorine(mg/l)	Dissolved organic carbon (mg/l)
Point 1	6.57±0.36	ND	9.71±0.83
Point 2	6.53±0.71	0.18±0.10^{1}	4.30±1.29^{1}
Point 3	6.63±0.72	0.38±0.18^{1,2}	4.46±0.00^{1}
Point 4	6.58±0.64	0.50±0.00^{1,2,3}	4.46±0.45^{1}
Point 5	6.34±0.00	0.50±0.00^{1,2,3}	5.08±0.23*

Point 1 = raw water (just before entering the treatment plant), point 2 = water at the treatment plant (after chlorination), point 3 = water prior to second chlorination (4.6 Km from point2), point 4 = water after second chlorination (4.6 Km from point2), point 5 = water at 9 km from point 4

^{1,2,3} = significantly different at $p<0.05$ when compared that point with point 1, 2, 3, respectively

* = significant different at $p<0.05$ when compared that point with all other 4 points

ND=not detectable

Table 3 Characteristics of Khon Kaen municipal tap water in after-rainy period (triplicate collections and analyses) (mean±SD)

Location	pH	Free chlorine(mg/l)	Dissolved organic carbon (mg/l)
Point 1	6.61±0.08	0.06±0.01$^{\#}$	10.96±0.59$^{\#}$
Point 2	6.74±0.09	0.02±0.01$^{1,\#}$	6.08±1.08$^{1,\#}$
Point 3	6.90±0.07	0.02±0.01$^{\#}$	5.77±0.01$^{1,\#}$
Point 4	6.90±0.07	0.50±0.00^{1,2,3}	5.89±0.12$^{1,\#}$
Point 5	6.87±0.01	0.50±0.00^{1,2,3}	4.95±0.59$^{*,\#}$

Point 1 = raw water (just before entering the treatment plant), point 2 = water at the treatment plant (after chlorination), point 3 = water prior to second chlorination (4.6 Km from point2), point 4 = water after second chlorination (4.6 Km from point2), point 5 = water at 9 km from point 4

^{1,2,3} = significantly different at $p<0.05$ when compared that point with point 1, 2, 3, respectively

* = significant different at $p<0.05$ when compared that point with all other 4 points

$^{\#}$ = significantly different at $p<0.05$ when compared that point between after-rainy period with rainy period

Table 4 Trihalomethanes (THMs) detected in Khon Kaen municipal tap water supply during rainy period (duplicate collections, each collection with triplicate analyses)

Location	THMs μg/l (mean ±SD)				
	CF	BDCM	CDBM	BF	TTHMs
Point 1	0.67 ± 0.03	0.29 ± 0.01	0.33 ± 0.00	ND	1.29± 0.04
Point 2	67.11 ±0.65*	28.43 ± 0.27*	3.82 ± 0.09^{1}	ND	99.36±1.01*
Point 3	65.77 ±0.35*	27.71 ± 0.32*	4.85 ± 0.26^{1,2}	0.22± 0.06	98.55±0.99*
Point 4	77.87 ± 2.11*	30.79 ± 0.63*	5.00 ± 0.36^{1,2}	ND	113.66±3.10*
Point 5	83.53 ± 1.68*	32.72 ± 0.53*	6.19 ± 0.38^{1,3}	0.02 ± 0.02	122.44±2.61*

CF=chloroform, BDCM= bromodichloromethane, CDBM= chlorodibromomethane, BF= bromoform, TTHMs=total THMs, ND = not detectable

Point 1 = raw water (just before entering the treatment plant), point 2 = water at the treatment plant (after chlorination), point 3 = water prior to second chlorination (4.6 Km from point2), point 4 = water after second chlorination (4.6 Km from point2), point 5 = water at 9 km from point 4,

^{1,2,3} = significantly different at $p<0.05$ when compared that point with point 1, 2, 3, respectively

* = significantly different at $p<0.05$ when compared that point with all other 4 points

Table 5 Trihalomethanes (THMs) detected in Khon Kaen municipal tap water supply during after-rainy period.

Location	THMs µg/l (mean ±SD)				
	CF	BDCM	CDBM	BF	TTHMs
Point 1	1.69 ± 0.20	1.52 ± 0.31	0.40 ± 0.04	ND	3.62± 0.55
Point 2	79.62 ±1.45$^{*,\#}$	31.04 ± 0.77$^{*,\#}$	11.07 ± 1.41$^{*,\#}$	0.35± 0.03$^{*,\#}$	122.08±3.66$^{1,\#}$
Point 3	74.56±2.64$^{*,\#}$	30.50 ± 0.71$^{*,\#}$	16.52 ± 0.54$^{*,\#}$	0.63± 0.88$^{*,\#}$	122.24± 4.77$^{1,\#}$
Point 4	87.25±4.75$^{*,\#}$	32.95 ± 1.50$^{*,\#}$	15.29 ±1.20$^{*,\#}$	0.23± 0.23$^{*,\#}$	136.42±7.68$^{*,\#}$
Point 5	92.39±5.9$^{*,\#}$	33.94±1.53$^{*,\#}$	17.77±0.81$^{*,\#}$	0.17±0.50$^{*,\#}$	144.27±8.8$^{*,\#}$

CF-chloroform, BDCM= bromodichloromethane, CDBM= chlorodibromomethane, BF=bromoform, TTHMs=total THMs, ND = not detectable

Point 1 = raw water (just before entering the treatment plant), point 2 = finished water at the treatment plant (after chlorination), point 3 = water prior to second chlorination (4.5 Km from point2), point 4 = water after second chlorination (4.6 Km from point2), point 5 = water at 9 km from point 4,

^{1} = significantly different at $p<0.05$ when compared that point with point 1

* = significantly different at $p<0.05$ when compared that point with all other 4 points

$^{\#}$ = significantly different at $p<0.05$ when compared that point between after-rainy period with rainy period

Table 6 HAAs detected in Khon Kaen municipal tap water supply during rainy period (duplicate collections, each collection with triplicate analyses)

Location	HAAs µg/l (mean±SD)					
	MCAA	DCAA	TCAA	MBAA	DBAA	THAAs
Point 1	2.36 ± 0.04	6.59 ± 0.03	ND	ND	4.46 ± 0.37	13.41±0.44
Point 2	2.39 ±0.00	6.68 ± 0.03	ND	ND	4.47 ± 0.24	13.54± 0.27
Point 3	2.42 ± 0.04	7.00±0.01^{1,2}	ND	ND	4.31 ± 0.73	13.73± 0.00
Point 4	2.42 ± 0.04	7.00 ±0.01^{1,2}	ND	ND	4.31 ± 0.73	13.73± 0.78
Point 5	2.39 ± 0.00	6.27 ± 0.01	ND	ND	4.43 ± 0.20	13.09± 0.21

MCAA=monochloroacetic acid, DCAA=dichloroacetic acid, TCAA=trichloroacetic acid, MBAA=monobromoacetic acid, DBAA=dibromoacetic acid, THAAs= total HAAs, ND = not detectable

Point 1 = raw water (just before entering the treatment plant), point 2 = finished water at the treatment plant (after chlorination), point 3 = water prior to second chlorination (4.5 Km from point2), point 4 = water after second chlorination (4.6 Km from point2), point 5 = water at 9 km from point 4

^{1,2} = significant different at $p<0.05$ when compared that point with point 1 and point 2, respectively

Table 7 Haloacetic acids (HAAs) detected in Khon Kaen municipal water supply during after-rainy period (duplicate collections, each with triplicate analyses)

Location	HAAs µg/l (mean ±SD)					
	MCAA	DCAA	TCAA	MBAA	DBAA	THAAs
Point 1	2.34 ± 0.04	6.24 ± 0.01	ND	ND	4.33 ± 0.74	12.91± 0.79
Point 2	2.36 ±0.02	6.43 ± 0.03	ND	ND	5.2 ± 0.82^{1}	13.99± 0.87
Point 3	2.37 ± 0.02	7.00 ± 0.10^{1}	ND	ND	5.76 ± 0.77^{1}	15.13± 0.89^{1}
Point 4	2.36 ± 0.02	6.39 ± 0.02	ND	ND	5.44 ± 0.62^{1}	14.19± 0.66
Point 5	2.35 ± 0.00	6.55 ± 0.07	ND	ND	5.47 ± 0.52^{1}	14.37± 0.59

MCAA=monochloroacetic acid, DCAA=dichloroacetic acid, TCAA=trichloroacetic acid, MBAA=monobromoacetic acid, DBAA=dibromoacetic acid, THAAs= total HAAs, ND = not detectable

Point1 = raw water (just before entering the treatment plant), point2 = water at the treatment plant (after chlorination), point3 = water prior to second chlorination (4.6 Km from point2), point4 = water after second chlorination (4.6 Km from point2), point 5 = water at 9 km from point4,

^{1} = significantly different at $p<0.05$ when compared that point with point1

Table 8 Safety factors of trihalomethanes (THMs) calculated for individual THMs and total THMs from the worst case calculation (*) and the best case calculation (**) of Khon Kaen municipal tap water supply using the guideline values suggested by US.EPA

THMs	GV (μg/l) (US.EPA, n.d.)	Concentrations detected for the worst case* (μg/l)	Safety factors of the worst case GV/C	Concentrations detected for the best case** (μg/l)	Safety factors of the best case GV/C
CF	70	92.39	0.76	67.11	0.95
BDCM	-	33.94	NA	28.43	NA
CDBM	60	17.77	3.38	3.82	8.05
BF	-	0.17	NA	ND	NA
TTHMs	80	144.27	0.55	99.36	0.72

CF-chloroform, BDCM= bromodichloromethane, CDBM= chlorodibromomethane, BF=bromoform, TTHMs=total THMs, NA=Not applicable, ND= not detectable, GV=guideline value, C=chemical concentration

*the highest THMs concentrations detected at point5 (the last collection point, in after-rainy-period collection period)

**the best THMs concentrations detected at point2 (the start point from the treatment plant, in rainy-period collection period)

Table 9 Safety factors of Haloacetic acids (HAAs) calculated for individual HAAs and total HAAs (THAAs) from the highest concentrations detected (*) of Khon Kaen municipal tap water supply using the guideline values suggested by US.EPA

Chemicals	GV (μg/l) (US.EPA, n.d.)	Concentrations detected for the worst case* (μg/l)	Safety factors of the worst case GV/C
MCAA	70	2.37	29.54
MBAA	NAD	-	-
DCAA	0	7.00	-
TCAA	20	-	-
DBAA	NAD	5.76	-
THAAs	60	15.13	3.97

MCAA=monochloroacetic acid, DCAA=dichloroacetic acid, TCAA=trichloroacetic acid, MBAA=monobromoacetic acid, DBAA=dibromoacetic acid, THAAs= total HAAs

NAD = No adequate data to recommend guidelines values

*the highest HAAs concentrations detected at point3, at after-rainy-period collection period.

Table 10 Risk assessment of THMs from Khon Kaen municipal tap water supply as for threshold toxicity (by Hazard Quotients or HQ) and for non-threshold toxicity (by lifetime additional cancer risk) from the daily intake dose (DD) from ingestion.

THMs	Conc (μg/l)	[1]DD (μg/kg.d)	HQ	[2]Cancer risk
The worst case calculation[3]				
CF	92.39	3.5869	0.3587	2.2E-4
BDCM	33.94	1.3468	0.0673	8.4E-5
CDBM	17.77	0.7052	0.0353	5.9E-5
BF	0.17	0.0067	0.0003	5.3E-8
Total			**0.4616**	**3.63E-4**
The best case calculation[4]				
CF	67.11	2.6631	0.2663	1.6E-4
BDCM	28.43	1.1282	0.0564	7.0E-5
CDBM	3.82	0.1516	0.0076	1.3E-5
BF	ND	-	-	-
Total			**0.3303**	**2.43E-4**

[1] DD (Daily intake dose) = average daily intake dose (ADD) and lifetime average daily intake dose (LADD) were assumed equally (explained in text)

[2] Cancer risk = a lifetime additional cancer risk or a lifetime excess cancer rate from ingestion

[3] Calculation for the worst case (THMs concentrations detected at point5, at after-rainy-period collection period)

[4] Calculation for the best case (THMs concentrations detected at point2, at rainy-period collection period)

Figure 1 Map of Khon Kaen province, the central city of the northeast region of Thailand.

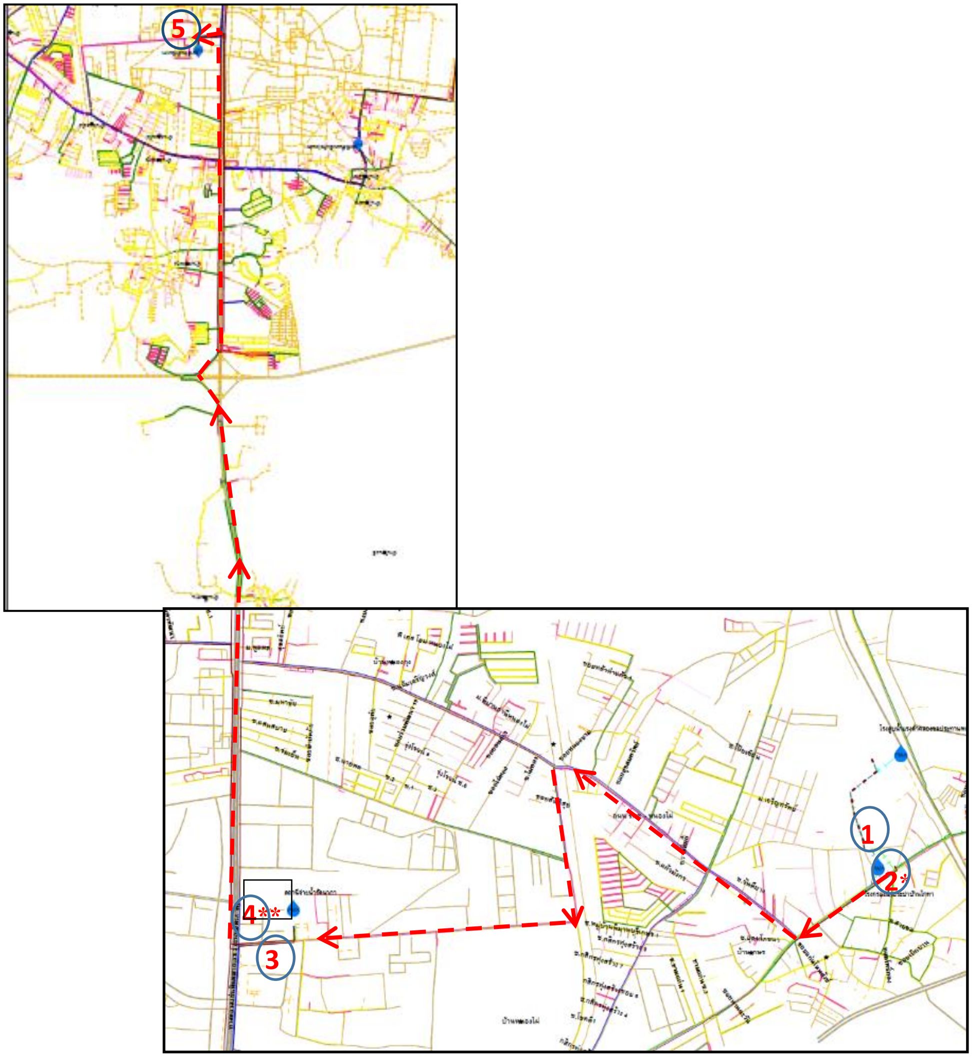

Figure 2 Route of Khon Kaen municipal tap water supply collection points. Point1 was raw water, point2 was finished water at the treatment plant, point3 was water prior to re-chlorination (4.5 Km from point2), point4 was water after re-chlorination (4.6 Km from point2), point5 was water at Baan Samran District (9 km from point4). *Kotha Water Treatment Plant (main and first chlorination station), **Ratanapa water re-chlorination station. Arrows show direction of water sample collection route. Scale in picture may not represent real distance.