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Occurrence of trihalomethane in relation to treatment technologies and water quality under tropical conditions

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Abstract

Distribution of most prevalent disinfection by-products, trihalomethanes (THMs) in relation to treatment technology and common water quality parameters (turbidity, conductivity, color, pH, and residual chlorine) was examined for two water supply schemes (WSS) in Sri Lanka (locations: Greater Kandy-WSS (GKWSS) (80.56– 80.66 °E, 7.28–7.38 °N) and Kandy South-WSS (KSWSS) (80.49–80.63 °E, 7.21–7.30 °N). In both treatment plants, only CHCl₃ and CHCl₂Br were detected in appreciable concentrations and total THMs (TTHMs) values were well below the WHO limits ($80 \mu g/L$). TTHMs variations ranged from 0 to $16 \mu g/L$ and 0 to $54 \mu g/L$ in GKWSS and KSWSS, respectively. Highest TTHM value ($54 \mu g/L$) was found in KSWSS which employs pulsation treatment technology. Correlations between CHCl₃ and CHCl₂Br in both water schemes are noteworthy, but THM levels relate to most of the water quality parameters ambiguously. However, a distinct relationship is observed between THM levels and degree of chlorination, resident time, pipeline corrosion, and temperature. THM formation increased towards the boundaries of most of the sub-water supply schemes (SWSS).

Key words: disinfection by-products, Sri Lanka, THM, TTHM, water quality

INTRODUCTION

Chlorination is the most common disinfection method used to destroy pathogenic microorganisms in potable water (Morris & Levin 1995). Although the exact chemical structures of natural organic matter (NOM) are unresolved to date, they are ubiquitous in natural waters. It is well known that upon chlorination, the NOM often acts as a precursor in the formation of disinfection by-products (DBPs) (Rook 1974; Li & Mitch 2018). The most prevalent DBP classes are CHCl₃, CHCl₂Br, CHClBr₂, and CHBr₃; the sum of them are designated as total trihalomethanes (hereafter TTHMs) (Rook 1974; Krasner *et al.* 2006).

During the past four decades, many researchers have examined DBP levels in water (Hu *et al.* 2010), their formation pathways (Wang *et al.* 2017), biotoxicity, and mitigation methods (Ashbolt 2004). Epidemiologic studies have shown a relationship between long-term exposure to DBPs and increased cancer risks and adverse reproductive effects (IARC 1991; Singer 1999; Gordon *et al.*

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2008). Thus, the US Environmental Protection Agency (EPA) has promulgated the maximum contaminant level of THMs as $80 \,\mu\text{g/L}$ (Fooladvand *et al.* 2011).

Operational procedures typically implemented in water treatment plants (WTP) such as chlorine dosage, resident time, pH, total organic carbon content, etc., have a marked impact on THM formation (Sadiq & Rodriguez 2004; Navalon et al. 2008). THM formation is also varied with seasonal fluctuations and geography of the water resources (Williams et al. 1997). In different geographical locations, such as Spain, China, South Korea, Greece, the US, and Iran, the average THMs in WTP vary widely, namely, 9-177 mg/L and sometimes exceeding regulatory limits (Krasner & Wright 2005; Platikanov et al. 2012; Hladik et al. 2014; Ramavandi et al. 2015). Particularly in tropical regions, research focus to examine the effects of waterworks' management practices on THM formation are limited (Abdullah et al. 2003; Panyapinyopol et al. 2005; Baytak et al. 2008; Hasan et al. 2010; Amjad et al. 2013). None of these studies specifically assessed the effects of different treatment technologies on THM formation. To address this issue, for the first time in Sri Lanka, we carried out research to compare THM levels in water that resulted from different treatment methods upon chlorination. Two major WTP were selected to monitor THM levels and their impact on treatment technology. The selection of treatment plants was made due to the following reasons. Greater Kandy treatment plant (80.6203 °E, 7.3166 °N) (hereafter GKWTP) follows conventional technology whereas Kandy South treatment plant (80.5943 °E, 7.2487 °N) (hereafter KSWTP) operates under pulsation technology. Both plants receive water from the same surface water source (intake locations; GKWTP 80.6220 °E, 7.3064 °N and KSWTP 80.5946 °E, 7.2487 °N). Both plants received ISO: 9001 accreditation under a common source to tap water quality. THM monitoring and speciation was carried out using ECD-GC coupled with automated headspace analyzer systems.

MATERIALS AND METHODS

Materials

Methanol (HPLC grade), THMs certified standards (reference number: 4S8746), and $Na_2S_2O_3$ (analytical grade) were obtained from Sigma-Aldrich (USA). The chemicals used for free Cl_2 and total Cl_2 measurements were purchased from HACH (USA).

Analytical method

THMs were analyzed by head space method as proposed in Kuivinen & Johnsson (1999). Dedicated head space gas chromatography coupled with an electron capture detector (ECD) and a built-in auto sampler (Thermo trace 1300 GC-ECD and TRIPlus RSH auto sampler) was used for THMs analyses under split/split-less mode (TRACE – TR5). The auto sampler consists of agitation and incubation steps that automatically convert samples into headspace. Data processing was carried out using dedicated quality assured software (Choromelen 7, version 7.2, USA). Free chlorine was measured using DPD standard colorimetric method 4500-Cl F (APHA 2005) with DR 5000 colorimeter (HACH, USA). The pH, EC, and turbidity measurements were determined using a pH meter (Hansen's ION+ pH3, USA), conductivity meter (Model: ELE 470, EU), and a turbidity meter (HACH 2100P, USA), respectively. Sampling sites were located using Gramin global positioning system GPS (Graminetrex, USA).

Quality assurance and quality control

In compliance with QA & QC protocols, quality of the THM analysis was controlled utilizing ten external standards with different THM concentrations; the relative standard error was always less

than 9% with an excellent linearity of calibration ($R^2 > 0.99$). To evaluate possible matrix effects, samples were spiked with 20 µg/L THMs at each 20th point; in all cases, over 95% spike recoveries for all THMs examined were observed. The THMs were analyzed in replicates. Field and laboratory blank analyses were used for background corrections.

Water treatment systems

Process flow charts of GKWTP and KSWTP are shown in Figure 1(a) and 1(b), respectively. Both plants utilize the same surface water from the River Mahaweli (intake locations: GKWTP 80.6220 °E, 7.3064 °N and KSWTP 80.5946 °E, 7.2487 °N). GKWTP is located 10.8 km downstream along the river from KSWTP. In the GKWTP, the raw surface water was pumped directly into the treatment plant. At the chemical mixing point, poly-aluminum chloride (PAC) was added as a coagulant. Chemically mixed water was then transferred to the flocculation basin under gravity. Baffle walls of the basin increase residence time by increasing water flow paths that are essential to enhance coagulation and



(a) Greater Kandy Water Treatment Plant

Figure 1 | Process flow diagram of (a) GKWTP and (b) KSWTP.

flocculation. Most of the settled flocs in the sedimentation basin were regularly removed by scraping and transferred to a lagoon for dehydration. The water with fine unsettled flocs then flowed into sand filters for removal of fine particulates. After sand filtration, to raise water pH, lime was added. The treated water after chlorination was transferred to a clear water tank.

In the KSWTP, before entering into the pulsator-clarifier, water was pumped into a cascade aerator. PAC coagulant was added to the raw water at the inlet point of the cascade aerator. The coagulated water was then transferred to a vacuum chamber located in the pulsator clarifier. By the vacuum pressure created by the vacuum fan, the water level was raised to a pre-determined level. At this point, a vacuum breaker was opened automatically which surged water into bottom perforated distribution pipes. As water was distributed through the stilling plates, gently stirring turbulence created by 'pulses' enhanced coagulation. The flocs accumulated on the plates as a sludge blanket overflowed to sludge concentrators for periodic removal. The treated water was collected from the top part of the clarifier. When the water level was lowest in the vacuum chamber, the automatic vacuum breaker closed, repeating the cycle. The treated water was filtered by rapid sand filters and disinfected, and stored in the clear water tank for distribution.

Sample collection and preservation

Figure 2(a) and 2(b) show the coordinates of WTP, service reservoirs, and distribution networks used for sampling. Fixation of residual chlorine was carried out in the field by adding sodium thiosulfates (10 mg per 40-mL sample for up to 5 mg/L chlorine) to empty amber-colored bottles prior to sampling. Water samples of distribution pipe lines were taken from the tap at the nearest possible point to the main pipeline. Before sampling, water was allowed to run for 5 min and then sample bottles were filled with water without leaving a headspace. Sampling details are shown in Table 1. A total of 56 samples were collected from GKWSS and 73 samples from KSWSS in the year 2014.

Data processing

Statistical analysis was carried out using public domain R statistical software (R Foundation for Statistical Computing, version 1.14.4). Spatial variation maps of THM and TTHM concentrations were developed using Surfer surface mapping software (Golden Software Inc., Version 11.0.642).

RESULTS AND DISCUSSION

The variations of THMs, TTHMs, and other water quality parameters, namely, pH turbidity, conductivity, residual chlorine, and color, at different locations of GKSSS and KSWSS are shown in Figures 3 and 4. For both plants, a common water source is used; this ensues similarity in water composition, particularly with respect to major constituents. Therefore, upon chlorination, we expect a similar formation mechanism/s of THMs. Out of the THMs (CHCl₃, CHCl₂Br, CHClBr₂, and CHBr₃) examined, only CHCl₃ and CHCl₂Br were detected in service reservoirs (SR) and sub-water supply schemes (SWSS). In the presence of NOM particularly enriched with phenolic groups, bromide readily converts HOCl \rightarrow HOBr forming CHCl₂Br by bromination of CHCl₃ (Heeb *et al.* 2014; Criquet *et al.* 2015). The provenance of Br⁻ in the receiving water is inconclusive to date; however, natural bromide is often concentrated in top layers of soils (upper 60 cm) that can be leached into surface water upon intense precipitation. Further enhanced soil erosion resulting from farming may also accelerate the migration of Br⁻ into natural waters (Wang *et al.* 2010).





Variation of $CHCl_3$ and $CHCl_2Br$ in GKSS and KSWSS

In the GKWSS, the CHCl₃ concentration range is 13.9–16.2 (GKWTP), 0–19.5 (NG), 0.00–18.3 (KH), 8.79–18.8 (KL), 0.00–18.0 (AS), and 3.76–18.2 (KN) μ g/L and in the KSWSS it is 11.5–13.8 (KSWTP),

Locations and SWSS in GKWSS	Number of samples	Locations and SWSS in KSWSS	Number of samples
Nugawela-SWSS(NG)	6	Maligathanna-SWSS(ML)	31
Kahalla-SWSS(KH)	6	Angunawala-SWSS(AG)	14
Kulugammana-SWSS(KL)	8	Mahakanda-SWSS(MH)	11
Asgiriya-SWSS(AS)	8	Service reservoirs (SR)	12
Kondadeniya-SWSS(KN)	10	KSWTP	5
Service reservoirs (SR)	15		
GKWTP	3		

Table 1 | Number of samples collected from GKWSS and KSWSS



Figure 3 | Variations of THMs, pH, turbidity, conductivity, residual chlorine, and color in GKWSS.



Figure 4 | Variations of THMs, pH, turbidity, conductivity, residual chlorine, and color in KSWSS.

0–42.5 (ML), 8.46–25.7 (AG), and 7.74–32.1(MH) μ g/L. As shown in Figures 3 and 4, the highest concentration of CHCl₃ is detected at NG (19.5 μ g/L; GKSS), ML (42.5 μ g/L; KSWSS), and MH (54.9 μ g/L; KSWSS). Distance between NG/ML or MH and corresponding WTP is higher than

other SWSS; therefore, the water residence time is increased with a concomitant increase of $CHCl_3$ formation. At different localities in the GKWSS, the $CHCl_2Br$ concentration range is 2.43–3.76 (GKWTP), 0.0–5.99 (NG), 0.0–6.16 (KH), 0.0–5.64 (KL), and 0.0–6.17 (KN) µg/L. Similarly in the KSWSS, the $CHCl_2Br$ concentration range is 2.67–3.73 (KSWTP), 0.0–12.3 (ML), 0.0–13 (AG), and 0.0–6.15 (MH) µg/L. The highest concentration of $CHCl_2Br$ is detected at KN (6.17 µg/L; GKWSS) and ML (12.3 µg/L; KSWSS). However, for the KSWTP, KN is not located at the highest distance; due to low water demand of the plant, the water stagnation resulted in high residence time yielding high $CHCl_2Br$ concentration.

Variations of TTHM and THM in water supply schemes

Similar assessments are performed for TTHMs in the KSWSS and GKWSS. In the GKWSS, the concentration of TTHMs range is 16.7–20.0 (GKWTP), 0.0–25.5 (NG), 0.0–24.5 (KH), 8.89–25.0 (KL), and 0.0–23.6 (KN) μ g/L and in the KSWSS it is 14.1–17.5 (KSWTP), 0.0–54.9 (ML), 8.46–38.7 (AG), and 7.74–38.3 (MH) μ g/L. As expected, the highest TTHMs concentration is found in KH (25.5 μ g/L; GKSS) and in MH (54.9 μ g/L; KSWSS). However, KH (GKWSS) is not located at the highest distance from the plant. As argued earlier, the high TTHM concentration is accounted for by the enhanced residence time of water due to stagnation.

Variations of TTHM and THM in water supply plants

Average concentrations of THMs in the GKWTP (CHCl₃ 14.5 μ g/L, CHCl₂Br 3.27 μ g/L, TTHMs 18.1 μ g/L) are higher than KSWTP (CHCl₃ 6.31 μ g/L, CHCl₂Br 1.48 μ g/L, TTHMs 7.79 μ g/L). In both plants (GKWTP and KSWTP), booster chlorination points are absent. Therefore, the minimum residual chlorine concentration of 0.2 mg/L at the consumers' end point is maintained introducing high chlorine doses. When compared to KSWSS, GKWSS has a lengthy distribution system (Figure 2(a) and 2(b)). Therefore, the formation of THMs is more favored in the GKWSS than in the KSWSS. Additionally, the technologies adapted to the treatment plants differ, which can also be considered as a contributing factor for THM formation.

Variation of THM/TTHM and water distribution

Temperature also exerts an important role on THM retention in the water phase. Even ambient conditions, namely, 25 °C, the loss of THMs and chlorine gas from aqueous phase is marked (Kuivinen & Johnsson 1999; Gordon *et al.* 2005; Danileviciute *et al.* 2012). THM levels increase with the temperature and chlorine residuals (Nikolaou *et al.* 1999). The annual temperature of the locations of treatment plants ranges from 30 to 23 °C with an average of 24.5 °C. The annual fluctuation of temperature is around 2 °C (Climate-Kandy 2017). Therefore, essentially, constant outflux of THMs from treatment plants into the gaseous phase is envisaged. Further, none of the treatment plants is operated continuously; hence, the creation of gaseous headspace in pipe networks also favors TTHM and chlorine residual evaporation.

Variation of TTHM/THM and water quality

Variation of pH, turbidity, conductivity, residual chlorine, and color in the GKWSS and KSWSS is shown by Figures 3(d)-3(h) and 4(d)-4(h), respectively. In the GKWSS, pH and turbidity values ranged from 6.64 to 7.50 and 0.08 to 0.84 NTU, respectively. In the KSWSS, pH and turbidity values ranged from 5.90 to 7.50 and 0.00 to 1.70 NTU, respectively. In some SWSS localities, turbidity, conductivity, and color levels are high both in the GKWSS and KSWSS. This is due to the

suspension of the deposited mud on pipelines by turbulence flow, leakages, cross-connection, and pipe material corrosions. Residual chlorine values ranged from 0.4 to 1.2 mg/L and 0.0 to 0.8 mg/L in the GKWSS and KSWSS, respectively. Usually, high water demand reduces water retention time by minimizing water stagnation which reduces chlorine decay. Natural decays of chlorine in the distribution networks have been described extensively (Clark 1998; Ozdemir & Ger 1998; Powell et al. 2000). When compared to the KSWSS, in the GKWSS the variations of pH as a function of sampling locations are marked. However, along the same water flow lines, in the GKWSS the residual chlorine concentration shows a minimal variation, but in the KSWSS it shows rapid fluctuations. However, in both plants, the variation of water color follows opposite trends. Both turbidity and conductivity show intermediate variations with sampling localities. Strikingly, along with the same water flow paths, in the GKWSS the variation of CHCl₃, CHCl₂Br, and TTHM are minimal whereas in the KSWSS some fluctuations occur with respect to CHCl₃ and TTHMs concentrations, in particular. It is important to note that in both cases the composition of inlet water is essentially the same; therefore, the observed variations in water quality parameters and occurrence of TTHMs can largely be ascribed to the different treatment technologies adopted. The results so far presented indicate a complex behavior of THM and TTHM formation even in the inlet water from a common source. The situation is further complicated when different treatment technologies are introduced. Therefore, particular attention is given below to analyze the effects of the aforementioned parameters on THM/TTHM formation.

Correlation of water quality parameters and THM/TTHM

Average concentrations of CHCl₃ and CHCl₂Br in water strongly correlate in most of the sampling localities (locations: KH, NG, AS, KL; GKWTP) and (locations: ML, AG, MH; KSWTP) (Figures 5 and 6). In the presence of precursory NOM, it appears that CHCl₃ is formed first, which shows subsequent conversion into CHCl₂Br via bromine addition (Kumar & Margerum 1987; Krasner 1999; Hua *et al.* 2006). Correlations with turbidity depend on the particular species of TTHM. The formation of THM and CHCl₃ seems to reduce with the increase of turbidity (location GKWSS; NG, KL, KH) whereas in some locations (e.g., GKWTP; KSWSS, KSWTP) an opposite trend is observed. This implies an intimate association between NOM and turbidity. Turbidity measurement peak response is between 400 and 600 nm (APHA 2005). Therefore, the turbidity spectral peak overlaps with humic acids (Hua *et al.* 2014). However, when pipes are ruptured or cracked, the release rates of residual chlorine offset TTHM formation which results in a negative relationship with the turbidity.



Figure 5 | Graphical illustration of correlation matrix for GKWSS. TTHMs: total trihalomethane, RCI: residual chlorine, WTP: water treatment plant, SR: service reservoir, Avg.: averaged.



Figure 6 | Graphical illustration of correlation matrix for KSWSS. TTHMs: total trihalomethane, RCI: residual chlorine, WTP: water treatment plant, SR: service reservoir, Avg.: averaged.

As shown in Figures 3(d) and 4(d), the variations of pH in water throughout sampling sites of GKWSS and GKWTP show minimal fluctuations. The increase of pH is favorable for enhanced THM formation (Rook 1976; El-Dib & Ali 1995). However, our correlation data suggest that even a small change of pH exerts a marked effect on THM formation. Therefore, even minute pH fluctuations may result in wide variations of THMs, CHCl₃, and CHCl₂Br levels rendering data instability in correlation calculations. The same arguments can be made to explain the apparent variability of TTHM formation with the residual chlorine. In the GKWSS, the variations of residual chlorine levels at different localities are essentially constant (Figures 3(g) and 5). As expected, the levels of CHCl₃, CHCl₂Br, and TTHM also show indifferent variations. In the KSWSS, the variations of the concentrations of residual chlorine shown are high; this corresponds to fluctuations of CHCl₃, CHCl₃, CHCl₂, Br, and TTHM concentrations throughout sampling locations (Figures 4(g) and 6).

In both plants, the conductivity exhibits strong negative correlations with THM concentration. Although the exact explanation for this observation is not possible to date, it seems that conductivity plays an indirect role in THM formation. One of the favorable precursors for THMs is hydrophobic NOM (Guanghui & David 2007; Jagatheesan *et al.* 2008). When the conductivity of the aqueous phase is increased (by increasing conductivity), the NOM seems to be aggregated into large moieties due to its water repellency. However, in low conductivity water, this effect seems to be minimized, thus dispersing small grained NOM moieties in the aqueous phase. The surface reactivity of small NOM moieties are expected to be higher than large ones due to its enhanced reactivity sites (Gang *et al.* 2003). Therefore, THM formation is expected to be high in low conductivity water.

In most locations of GKWSS and KSWSS, negative correlations between color and THM levels are observed. Light absorption by dissolved organic carbon has a strong influence on the penetration of ultraviolet and photo-chemically active radiation (Morris *et al.* 1995). High molecular weight fractions of NOM, commonly known as humic acids, contribute to the intense coloration of water. Although water coloration is low, the low molecular NOM fraction favors enhanced THM formation (Xu *et al.* 2015). Therefore THM formation is expected to be inhibited in colored water.

Both in GKWSS and KSWSS, inverse relationships are shown between TTHM concentrations and the distance between the service reservoirs and treatment plants. Residual chlorine concentration is reduced with the distance which retards THM formation. Possibly the increased residence time seems

to implicate THM formation patterns which result in a weak direct relationship. To understand the trends of THM variations, spatial maps are developed for both WSS (Figures 7–10).

Spatial variation of THMs in GKWSS

Spatial distribution of CHCl₂Br, CHCl₃, and TTHMs in the GKWSS based on service reservoirs' THMs are shown in Figure 7. According to these figures, service reservoirs' CHCl₃ and TTHMs levels were higher in the north than the south. A possible reason could be the high retention time. Variation of CHCl₃ was similar to TTHMs, but CHCl₂Br did not show a similar trend since CHCl₂Br concentrations were changed slightly.

Figure 8 shows THM variation in individual SWSS. According to these figures, the trend of variation of major components CHCl₃ and CHCl₂Br were similar to TTHMs. Towards the AS and KN boundary, CHCl₃, CHCl₂Br, and TTHM values were decreased slightly. In NG, THMs were decreased towards the south-west boundary and increased toward the north-east boundary. In KL,



Figure 7 | CHCl₂Br, CHCl₃, and TTHM variation in GKWSS based on THM levels in service reservoirs.



Figure 8 | CHCl₂Br, CHCl₃, and TTHMs variation in SWSS in GKWSS.



Figure 9 | CHCl₂Br, CHCl₃, and TTHM variation in KSWSS based on THM levels in service reservoirs.



Figure 10 | $CHCl_2Br$, $CHCl_3$, and TTHM variation in SWSS in KSWSS.

THM values increased towards its boundary. Therefore, each SWSS has its own tendency of variation of THMs. The possible reasons could be the water stagnation and water demand. However, a slight decrease of THMs was observed in the samples which were away from the service reservoirs.

Spatial variation of THMs in KSWSS

As shown in Figure 9, the spatial patterns of the THMs, TTHMs, CHCl₂Br, and CHCl₃ variations in KSWSS service reservoirs are somewhat similar. They clearly indicate a relation with the retention time on CHCl₂Br, CHCl₃, and TTHMs formation. However, the spatial variations of CHCl₂Br, CHCl₃, and TTHM SWSS are not distinct as in KSWSS (Figure 10). Each SWSS displays its own pattern. In order to understand the THMs variation in SWSS, variation maps for each subscheme were developed. According to the figure, no clear trend of variation of THMs is observed. In ML, THM levels are decreased toward the north boundary. However, in AG, THM concentrations are increased with the distance from the service reservoir. The ML scheme showed a slight decrease of THMs with the increasing distance from its service reservoir. However, each scheme displays its own pattern of spatial distribution of THMs. This could be due to multifactorial reasons such as water demand, TOC level, temperature, as well as residual chlorine concentrations on THM formation.

CONCLUSIONS

For the first time in Sri Lanka, variations of THM and TTHM formation as a function of treatment technology, residence time, pH, residual chlorine, conductivity, turbidity, and color were conducted. In both water schemes, only CHCl₂Br and CHCl₃ were detected which were below WHO and USEPA guidelines. When compared to conventional treatment, the water treated by pulsation technology produced lower THMs. The directional increase of THMs in SWSS is due to increased residence time of residual chlorine. The occurrence of THMs/TTHMs is dependent on temperature, water quality, water demand, and water distribution mechanics.

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