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Experimental Investigation into the Occurrence and Effects of Individual Parameters on THM Formation

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ABSTRACT

Disinfection of drinking water for removal of water borne microorganisms has been in use for past many years. Common disinfectant used is Chlorine. Reaction between chlorine and naturally occurring organic matter (NOM) results in formation of trihalomethanes (THMs) which are possible carcinogen to humans. This study presents the results of an experimental investigation on different parameters from two water supply systems in twin cities Islamabad and Rawalpindi, Pakistan. Research was carried out in two phases. In first phase factors affecting the formation behaviour of THMs were studies and in the second phase drinking water samples of the twin cities were investigated for likely occurrence of THMs. To identify factors that influence the THM formation, the chlorine decay and THM formation kinetics were carried out in laboratory experiments. Water quality characteristics that influence the formation of DBPs e.g. type and concentration of organic precursors, pH, temperature, and disinfectant were monitored. Gas chromatographic method was established to analyse the samples on GC apparatus. The present study also assessed that main factors influencing THM formation in the main water distribution system were the chlorine dose and presence of the naturally occurring organic matter (NOM) in water. The results of the study indicated that temperature and chlorine dosage tends to effect formation of trihalomethanes more as compare to pH. In the second phase of experimentation samples were collected from 20 different sampling sites of the twin cities including water filtration plants, underground water storage areas and consumer taps. The results showed occurrence of THMs in 90% of chlorine treated drinking water samples. Results from the investigation indicated the occurrence of Trihalomethanes in the water sample collected from 16 stations. Few sites met the standard value of 80 µg/L..

INTRODUCTION

Clean and safe drinking water is most important to support life. Consumption of poor quality drinking water containing high level of organic pollutants may cause damage to liver and kidney, immune system, reproductive system disorders and different types of cancers [1,2]. Therefore, making to necessary to treat drinking water prior to human use. Chlorine is one of the most important and widely used water disinfectants due to its low cost and effectiveness [3-5]. Besides many advantages of using chlorine as disinfectant in drinking water treatment plants, it may result in formation of disinfection byproducts (DBPs) such as trihalomethanes (THMs) due to presence of natural organic matter (NOM).

Trihalomethanes have reported to be potential carcinogens in several studies [5,6]. Various factors such as pH, contact time, residual chlorine and temperature of water affects formation of THMs. Chemical composition of organic matter is also an important factor according to many studies [7,8]. As reported in various studies THMs consist of a group of four compounds including chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform [9,10].

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Since identification of THMs in drinking water, substantial research have been focused toward the formation kinetics of DBP, its occurrence, and health effects. The Maximum Contaminant Level (MCL) currently regulated by the US-EPA for total THM are 80 µg/l [11,12]. To safeguard public health continuous monitoring and regulation of THMs formation is required and to ensure that it comply with the standards set by health organizations. The current study was carried out in two major cities of Pakistan with a population of more than 2.1 million [13].

This study is aimed to investigate the formation behaviour of CDBPs, namely THMs in main water supply of the twin cities i.e. Islamabad and Rawalpindi. Experimental procedure was designed to address the objectives mentioned below.

- To identify factors that influence the THM formation such as pH, temperature, chlorine dosage, reaction time and analysis of total organic carbon content (TOC).
- Detection of THMs in spiked water and isolation of these compounds from water through micro-extraction in immersion mode on optical fibres coated with polydimethylsiloxane (PDMS) phase.
- Calculate amount of THMs in twin cities i.e. Rawalpindi and Islamabad drinking water by gas chromatography.

MATERIALS AND METHODS

Sample Collection

Water samples were collected from two main water reservoirs supplying water to Islamabad and Rawalpindi. Sampling was carried out in consultation with Water and Sanitation authority (WASA) and Capital Development Authority (CDA) staff. Surface water of two different water supply systems i.e. Simly Dam and Rawal Dam was collected throughout October 2011 to March 2012. Water from Rawal Lake is supplied to Rawalpindi area, which is monitored by WASA with respect to water quality. Islamabad is receiving water from Simly Dam as well as from Khanpur Dam. Raw water samples as well as treated samples were collected for THM analysis. The pre-treated water samples were collected in 2-litres glass bottles and refrigerated at 4 ± 1°C. Whereas drinking water from 20 different locations across twin cities were also analyzed to define typical concentration of target DBPs.

Reagents and Standards

Reagents Stock Standard Solutions (SSS)

Bromodichloromethane, dibromochloromethane, chloroform and bromoform (Standard analytes) were purchased from Dr. Ehrenstrofer. Methanol was purchased from Merck. Stock standard solutions were prepared by measuring accurately in 10 mL and 100 ml volumetric flasks with GC grade methanol and stored at 4°C.

Sample Storage

Samples were stored at 4°C until analysis. The sample storage area must be free of organic solvent vapours. All collected samples were tested within 14 days. Treated water samples were tested within 2-4 hours of collection. Whereas pre-treated water samples were collected and stored at 4°C. The chlorine demand for 1, 3, 6, 24 and 48 hours was assessed for each of the source waters.

Setting of formation potential test

Potential tests set formed are given in **Table 1**. One factor was varied at time. Remaining two were remained constant. Four doses of chlorine were used 3.5, 6, 8 and 10 mg/l. Two doses that gave maximum and minimum THMs in the samples were used in remaining study. pH was varied five time. Temperature used in the study was 4, 20 and 30°C

Table 1. Setting of formation potential test.

Test set	Influencing factor	TOC mg/L	Chlorine dose (mg/L)	pH	Temp.(°C)
1	Chlorine dose	5, 9	3.5, 6, 8, 10	8	8.2
2	pH	5, 9	3.5, 10	6.5, 7.0, 7.5, 8.0, 8.5	8
3	Temp	5, 9	3.5, 10	6.5, 8.5	4, 20, 30

RESULTS AND DISCUSSION

Gas Chromatographic Analysis

Water samples were collected from various selected sites of Rawalpindi and Islamabad. A Schimadzu GC (model 2010) equipped with electron-capture detector (ECD) was used to assess and quantify trihalomethanes. Solid phase micro extraction technique (SPME) with a manual solid-phase microextraction fiber assembly (57344-U) fitted with 85 µm carboxen/polydimethylsiloxane (85-CAR/PDMS) fiber was used to analyse samples. Previously optimized extraction time of 15 minutes was used for the current study. The fiber was transferred to the injection port of the gas chromatograph after extraction. 10 min desorption time was optimized and selected at 200°C. Trihalomethanes were analysed according to standard US-EPA methods

551.1 and 552.2, respectively [14,15]. **Figure 1** signify relationship between retention times and peak areas of stock solutions of standard analytes. It is obvious from figure that with increase in retention time peak areas also increases. Chloroform has retention time of 4.17 min with peak area of 3989. Whereas bromoform elutes at 7.02 min which is later than all the analytes. Bromoform has the peak area of 41763.

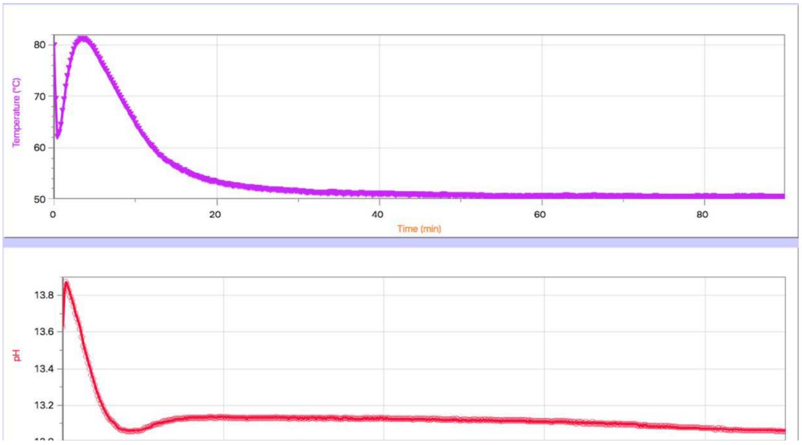

Figure 1. Graph representing correlation between peak area and retention time.

Physiochemical Analysis

Physical and chemical analysis of water samples from both treatment plants along with surface water samples is given in **Table 2**.

Table 2. Physiochemical analysis of surface water samples.

Parameters	Treated water		Surface water samples	
	Rawal Dam	Simly Dam	Rawal Dam	Simly Dam
TOC	4.89 mg/L	2.25 mg/L	9.0 mg/L	5.0 mg/L
pH	8.17	8.0	8.2	8.15
Temperature	8.5°C	8.8°C	14.3°C	15.6°C
TDS	160.4 mg/L	150.8 mg/L	160 mg/L	158.5 mg/L
EC	334 µS/cm	327 µS/cm	329 µS/cm	321 µS/cm
Turbidity	3.41	2.21	8.5	7.8
Free chlorine	0.38 ml	0.35 ml	0.0	0.0
Monochloramines	0.0	0.0	0.0	0.0
Dichloramines	0.0	0.0	0.0	0.0

Parameter Investigation

Although there are many parameters that play role in THMs formation. However, this study focuses on the most frequently used parameters: chlorine dose, TOC, pH, and temperature.

Natural organic matter (NOM)

The main precursors of THMs are NOM, they do not have direct measurements The NOM can be expressed in terms of TOC, DOC or U_{254} [16]. Trihalomethanes (THMs) will develop as a result of chlorine reaction with organic carbon leading to a serious water quality issue.

Total and Dissolved Organic Carbon

Total organic carbon (TOC) and dissolved organic carbon (DOC) are directly related with THMs formation. An increase in TOC will lead to increase formation of THMs [17]. It has been put forward in various studies that the organic matter could be measured in terms of DOC or UV_{254} [18].

pH

Various researches indicated that pH has direct relation with formation of THMs. A study was conducted to understand relation of various pH values at the Cincinnati treatment plant using Ohio River water [19]. Another lab study showed that as the pH values increased from 7 to 11, THMs formation also escalated 30% to 50%. Source of organic compounds and chlorine dose also played vital role [20]. The effect of pH on THMs formation is presented for Simly dam and Rawal dam water samples in **Figure 2**. Trihalomethanes formation rise considerably with increase in pH, which agrees to result noted in preceding researches [21].

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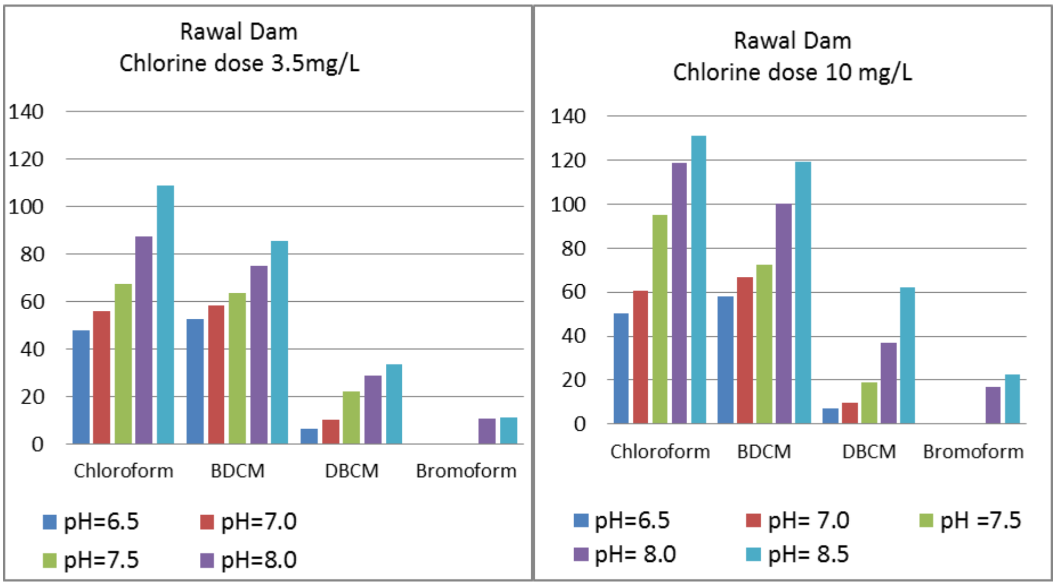

Figure 2. Effect of pH on THMs formation.

In the current study, formation of THMs was found to be approximately 50% higher when pH was changed from 6.5 to 8.5 in Rawal Dam water samples; whereas in Simly Dam water samples there was approximately 25% increase in THMs when pH was changed from 6.5 to 7.5. In Simly Dam water samples although chloroform found to 50% increased when pH was increased from 6.5 to 8.5 but the overall concentration was fairly low due to lower level of TOC in the original water sample.

Reaction time

Though considerable amounts of THMs are produced rapidly after chlorination [22], long reaction time also contribute to higher levels of THMs in drinking water [21]. A research conducted by Chang and his coworkers concluded that maximum THMs occurs within first 8 hours of reaction time [22]. However, no significant increases in THMs formation happens after 48 hours of chlorine treatment [23]. However, the practice of maintaining free chlorine residuals in water distribution systems to keep drinking water safe from microbial contamination may result in further formation of THMs in drinking water [24].

The effects of reaction time on THMs formation is showed in **Figure 3** using Simly Dam and Rawal Dam water samples subjected to various temperature and chlorine doses, respectively. It can be observed that the formation of THMs considerably increases at pH 8.5 with temperature 20°C after 24 hours. There is approximately 50% increase in chloroform after the initial reaction phase **Figure 3**. However, it was observed that lower level of TOC resulted in general decreased amount of THMs formation, which is noticeable in **Figure 3**.

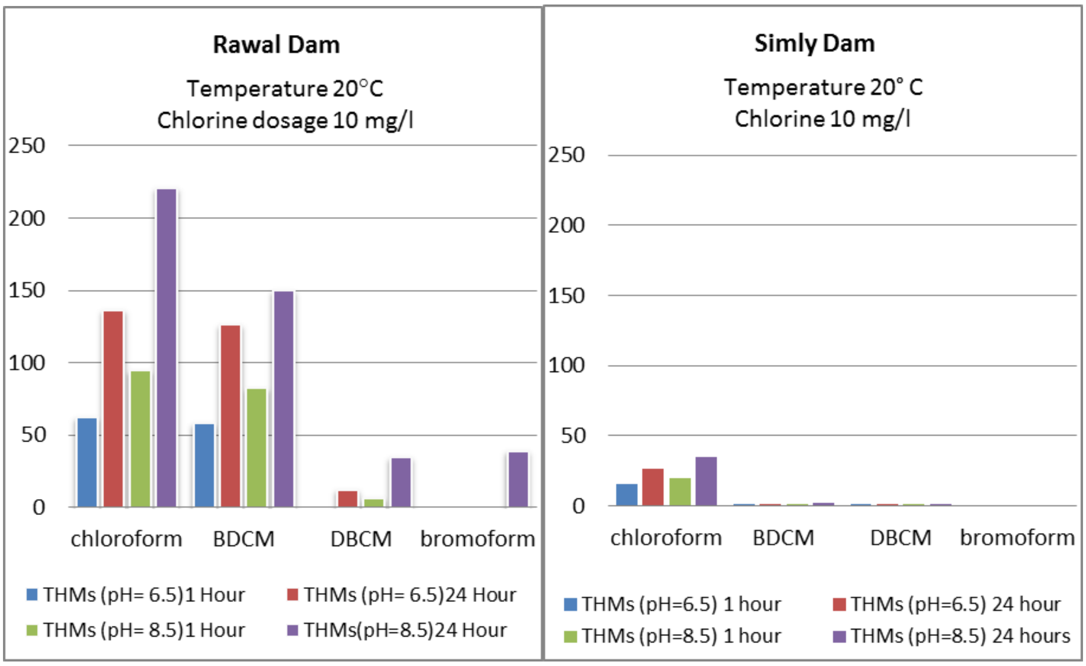

Figure 3. Effect of reaction time on THMs formation.

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Temperature

Temperature also have direct effect on THMs formation in drinking water. Several lab studies were conducted using Ohio River water from Cincinnati water treatment plant. Three different temperatures (3, 25 and 40°C) were used with pH of 7 and chlorine dose 10 mg L^{-1}. The results indicated with each stage in temperature change there is an approximately 2 times higher production of THMs [19]. El-Shahat et al. and Hellur-Grossman et al. also indicated that higher temperature during summer results in higher formation of THMs as compare to lower temperature during the winter months [25,26]. Though, change in occurrence natural organic matter during difference seasons may play important role in elevated levels of THMs.

It is evident from the current study that the temperature also has direct effect on the THMs formation **(Figure 4)**. Experimentation was performed using three different temperatures (4, 20 and 30°C). Constant pH of 6.5 and 8.5 with chlorine dose of 3.5 mg/L and 10 mg/L were used. It was noted that there is 50% increase in THM formation at 8.5 pH with chlorine dose of 10 mg/l which complies with the previous studies mentioned above. Results showed that water samples stored at temperature as low as 4°C resulted in very low production of THMs when tested after 1 hour of reaction time and even after 24 hours, concentration of THMs didn't change much. THMs formed continuously from 1 hour to 24 hours when the temperature was set at 20°C and 30°C.

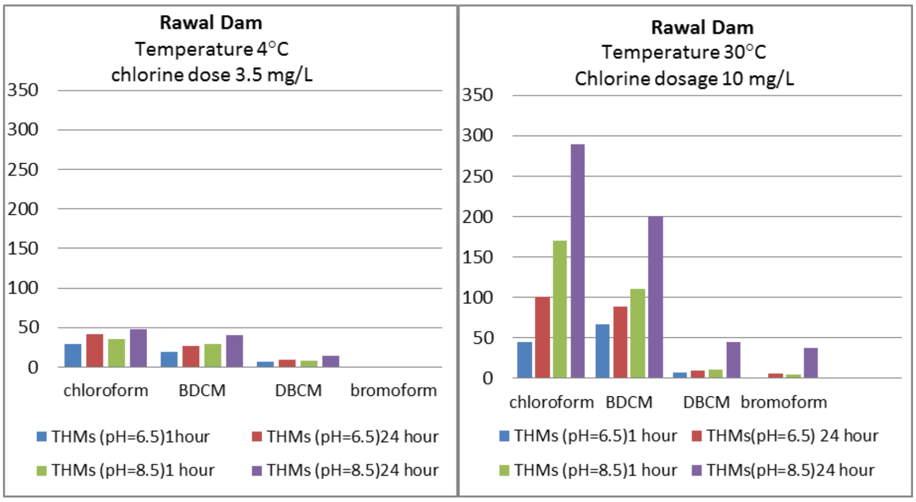

Figure 4. Effect of Temperature on THMs formation.

Chlorine dose

During the THM analyses and laboratory kinetic experimentations it was detected that the main parameter that effects the THM formation was the chlorine dose. Also, in the laboratory kinetic experiments, an increase in $CHCl_3$ concentration was found with increasing chlorine doses. **Figure 5** illustrates the effect of different chlorine dosage on formation of THMs for the Simly Dam and Rawal Dam water samples. Four chlorine dosage were used for water samples from both Dams. From **Figures 5**, it is evident that THMs production was minimum at lowest chlorine dose as compare to intermediate chlorine dose. It was observed that as the dose was increased from 8.5 mg/L to 10 mg/L there wasn't much change in level of THMs. This can be attributed to the fact that the chlorines beyond breakpoints had less organics to react with. Supporting the fact that any chlorine beyond breakpoint does not contribute in higher level of THMs Yet, continuous reactions in water distribution systems between natural organic matter and may affect partial chlorine demand.

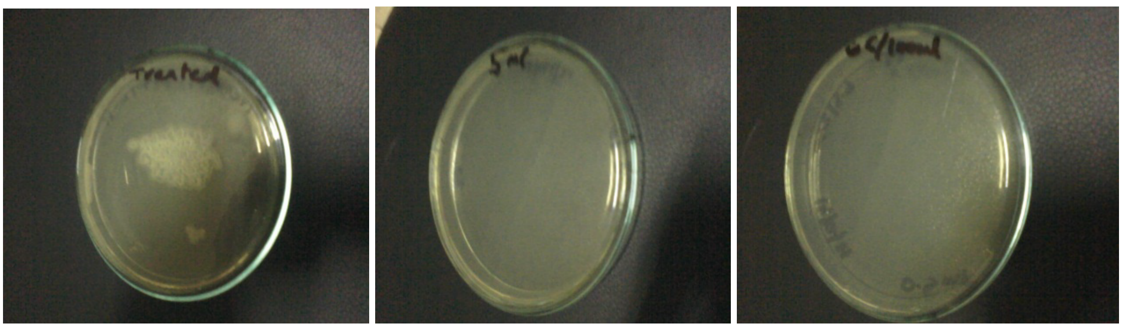

Figure 5. Effect of chlorine dose on microbial contamination.

Increase in chlorine dose lead to increase in reaction extent, therefore causing increase in THMs as well as HAAs [27]. readily oxidisable elements such as Fe^{2+}, Mn^{2+} and S^{2-} in water can also affect the chlorine demand [6,13,21,23,26,28,29], which may not be related with formation of THMs. The chlorine doses used in this study ranged from 3.5 to 10 mg/L for both water samples. Use of higher chlorine dosage in disinfecting drinking water is not an uncommon practice [29].

Microbiological analysis

Microbial analysis of the samples indicated that chlorine dose (3.5 mg/L) used in treated water samples from both treatment plants i.e. Simly dam and Rawal Dam treatment plant was unable to remove microbes from the sample. Although this dose produced least amount of THMs. Whereas maximum THMs with no microbial contamination in samples were produced when chlorine dose was increased upto 10 mg/L. Dose optimized during laboratory kinetic experiments is 5 mg/L. This dose not only resulted in minimum level of THMs but there was also no contamination as shown in **Figure 5**.

THMs monitoring and quantification

Samples were studied using optimized SPME and GC conditions. Level of THMs in drinking water samples is given in **Table 3**. Results showed that THM concentrations vary significantly between treated waters as they leave the treatment plant and in the water distribution network. The concentration increase considerably when the water temperature goes above 15 degrees approximately 2 to 4 times higher. High concentration of TTHMs can be observed at sampling station 15. Probable reason is the distance of this station from the treatment plant and presence of high organic content in the main water reservoirs that is again treated at the main filtration plant supplying water to that area. Practice of booster chlorination is very common during Monsoon season between June till August due higher level of water borne infection in underdeveloped areas. Almost 90% samples were showed higher level of THMs beyond the permissible limit Concentration of Chloroform was maximum in all samples collected from underground tank, overhead reservoir, and various filtration plants. Chloroform was comparatively lower in concentration in underground tank and sampling station 11. Concentration of TTHMs ranged from 36.31 to 577.39 at different sampling station.

Table 3. TTHMs concentration at different sampling station.

Sr. No	Concentrations of THMs (µg/ml)				
	Chloroform	BDCM	DBCM	Bromoform	TTHM
Station 1	109	8.8	6.79	BDL	124.6
Station 2	416.85	26.88	9.6	8.66	461.14
Station 3	249.03	21.6	16.4	BDL	287.03
Station 4	220.45	32.55	23.81	2.21	279.02
Station 5	151.7	18.23	6.73	BDL	176.66
Station 6	409.77	51.1	2.02	BDL	462.89
Station 7	362.9	9.5	3.22	BDL	375.62
Station 8	298.75	10.15	1	BDL	309.87
Station 9	152.6	6.73	2.55	BDL	161.88
Station 10	290	6	1.36	BDL	297.36
Station 11	30.85	5.35	BDL	BDL	36.3
Station 12	212.74	30.28	2.04	BDL	490.12
Station 13	255	8.99	5.69	BDL	363.68
Station 14	114.9	8.66	2.84	BDL	126.4
Station 15	553	16.12	8.27	BDL	577.39
Station 16	298.17	7.65	BDL	BDL	305.89
Station 17	189.62	2.8	BDL	BDL	192.42
Station 18	54.66	8.65	5.24	BDL	68.55
Station 19	272.09	8.85	6.7	BDL	287.45

CONCLUSION

Several factors affecting the formation of THMs were identified: The most important factors were the chlorine dose, the presence of the natural organic matter (NOM) in water, reaction time, temperature/ seasons and pH. Samples were investigated using optimized SPME and GC conditions. The proficiency of this extraction and concentration technique is affected by numerous features, including flow rate and the type of sorbent. Almost 90% samples were contaminated with THMs. Chloroform was found to be highest in all drinking water samples including underground tank, overhead reservoir and filtration plants. Chloroform was relatively lower in concentration in underground tank. Concentration of TTHMs ranged from 33.51 to 576.86 at different sampling station. THMs formation can vary on the nature of the source water. The results presented in the study show strong connections between the selected water quality parameters Natural variability and environmental settings at the particular location of the water sources may affect the correlations among various parameters. The general behaviours of the associated parameters can be generalized as follows:

- The chlorine demand considerably increases with higher NOM content
- THMs formation was approximately 2-4 times higher when pH was increased from 6.5 to 8.5
- The rates of THMs formation significantly rises at pH 8.5 with temperature 20°C after 24 hours

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- The temperature set at 20°C and 30°C. THMs were produced constantly from 1 hour to 24 hours of reaction time.
- The chlorine doses used in this controlled study were in ranges of 3.5-10 mg/L for both water samples.

The research presented herein was conducted to monitor the effects of Reaction time, temperature and pH on formation of THMs using water samples from Simly Dam and Rawal Dam (Pakistan). NOM is considered to be a vital precursor of THMs production. Though, it is difficult to assess actual chlorine demand by the natural organic matter due to its inconsistency in the water distribution system as well as residence time Results indicates that Reaction time, temperature and pH considerably affects the production of THMs. Henceforth, further research is needed to be carried out to characterize and correlate these water quality parameters to have a better understanding of THMs formation kinetics and their potential threats to human health Comprehensive monitoring is required to ensure that reaction time, pH and temperature are not either directly or indirectly overlooked during water disinfection practices.

Further investigation is suggested to better understand the formation of DBPs as the levels found were significant. SPME technique was successfully applied to determine the trihalomethanes in drinking water. As the DBPs issue gains importance in Pakistan, more focus is required to minimize DBP formation while ensuring a microbiologically safe product for human use. Certainly, this poses an operational challenge for concerned authorities.

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