

# Factors Affecting on Formation of DBPs in Greater Cairo Drinking Water

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## Abstract

The formation of disinfection by-products (DBPs) from chlorination of treated drinking waters was determined. Formation potential tests were carried out to determine the THMs, DCAA and TCAA formed by chlorination. All waters had the potential to form significant levels of all the HAAs measured. This study aims to determine the factors affecting on the formation of THMs and HAAs in Greater Cairo drinking water. The formation of these by-products is controlled mainly by operating factors ( $\text{Cl}_2$  dosage, total organic carbon (TOC), pH, temperature of the raw water, bromide ion and the contact time with  $\text{Cl}_2$ ). So, the effect of all of these parameters was investigated in this study in addition to THMs formation potential and HAAs formation potential. The batch experiments showed that increasing  $\text{Cl}_2$  dosage leading to increasing in the formation of THMs and HAAs. In the same trend was observed for the contact time and initial TOC concentration. pH 7.5 was recognized as the optimum value for formation of THMs and HAAs.

**Keywords:** Drinking water; THMs; HAA; Water quality

## Introduction

Chlorination is a good servant but a bad master in the sense that it is very economical and effective but if not controlled properly, it forms disinfection by-products (DBPs), some of which are regulated due to their carcinogenic effects. Chlorination is an age old, cheap, efficient and effective biocide process for disinfection of drinking water. The added chlorine can react either directly or after water hydrolysis to hypochlorous acid with naturally occurring organic matter such as humic substances to form halogenated organic compounds. These compounds include trihalomethanes (THMs), haloacetonitriles (HANs), halo ketones (HKs), chloropicrin (CP) and haloacetic acids [1-3]. According to the World Health Organization (WHO), more than a billion people in the world have no access to potable water and more than three billion have a lack of adequate hygiene [1], therefore a very careful management of the drinking water is needed. In this respect, the monitoring of chemical parameters in the determination of organic compounds in the drinking water is very important, since these compounds are harmful to human health [2-4]. Of these, highly dangerous are the disinfection byproducts (DBPs) whose main subgroup are trihalomethanes (THMs) which have proved to be cancerous to people. Having this in consideration, the level of awareness of the public opinion in relation to the quality of the drinking water, especially to the THMs has increased lately [5]. The reaction between chlorine and organic compounds present in the drinking water always produces THMs, when the former is used as disinfectant in advance. To have a better understanding of HAAs, THMs and semi-volatile DBPs in treated waters, their formation was evaluated under controlled conditions. Here 11 water treatment works selected from across England and Wales have been surveyed to allow us to determine the potential for formation, relative distribution and speciation of DBPs as well as identify any relationships between water sources. The DBPs selected include THM4 (trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM)), HAA9 (MCAA, MBAA, DCAA, TCAA, bromochloroacetic acid (BCAA), DBAA, bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), and tribromomethane (TBAA)) plus four HANs (DCAN, trichloroacetonitrile (TCAN), bromochloroacetonitrile (BCAN) and DBAN), two HKs (1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP)), two HAs (dichloroacetaldehyde (DCA) and TCA), two

HNMs (trichloronitromethane (TCNM) and dibromonitromethane (DBNM)) and two THMs (dichloroiodomethane (DCIM) and bromochloroiodomethane (BCIM)) [4,5]. This is the first study that has reported the potential for formation of HAAs, THMs and a range of semi-volatile DBPs in drinking water in England and Wales. It is also the first European study to directly assess what impact the switch from chlorine to monochloramine would have on the concentrations of the DBPs found [1,6]. The aim of the paper is to determine the variation of the HAAs concentration and physical-chemical parameters in the drinking water in the Greater Cairo during 2014, in order to conclude the quality of the drinking water and its impact on the health of the population living in this region and investigate the water quality effect on the DBPs formation potential.

## Materials and Methods

The city of Cairo is capital of Egypt and has about 15000000 inhabitants. Even though it has sufficient water resources and permanent water flows (River Nile). The statistics show that the average amount of water per inhabitant is about 200-250 liters per day. The drinking water in Cairo is disinfected with gaseous chlorine without any kind of special treatment. The experimental part of the research was done in the laboratories of the Holding Company for Water and Wastewater. The water quality (TOC,  $\text{Cl}_2$ , Br, pH, etc.) were determined according reference methods mentioned in the standard methods for water and waste water ed 22 (2012) [7]. The determined parameters were as follows: Trihalomethanes THMs, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA). Various different chemicals with pro-analysis, superpure and HPLC grade were used. Before sampling, a solution of sodium thiosulfate was added to the

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amber bottles to eliminate any remaining residual chlorine and to stop further THM formation. Each glassware used was previously washed with phosphate-free detergent, rinsed with ultrapure water (Milli-Q) and acetone (HPLC grade). Then, it was placed in an oven at 150°C for 2 h and cooled at room temperature. THMs were extracted and determined according to EPA Method 551. DCAA and TCAA were extracted with a modified version of the US EPA Method 552.2. The HAAs were converted to their methyl esters and quantified using gas chromatography coupled with an electron capture detector (GC/ECD). THM measurements were made using a gas chromatograph equipped with electron capture detector (GC-ECD, Varian, Model CP-3800). Chromatographic separation was accomplished with a capillary column DB-5 (J&W Scientific Inc/Agilent Technologies, 30 m × 0.25 mm × 0.25 μm). The GC oven temperature program was as follows: initial temperature in 60°C for 2 min and then ramped 10°C per min until 220°C. Carrier gas (N<sub>2</sub>) at a flow rate of 0.8 ml min<sup>-1</sup> and split ratio of 1:15 was used in each experiment. It was injected 3 μl of each sample in the capillary column. For the calibration curve, standard solutions of DCAA (Supelco Inc., 99.2%), TCAA (Supelco Inc., 99.4%), in concentrations ranging from 5 to 80 μg/L in ultrapure water [8,9].

## Results and Discussion

### Effect of water TOC on the formation of DBPs

In the laboratory scale, some trials carried out to investigate the

water quality parameters that control the DBPs formation potential. The data represented in Figures 1 and 2, showed that as TOC concentration increased in water, THMs and HAAs concentrations increased.

Singer et al. conducted a study on eight North Carolina water supply systems these results showed that as TOC concentrations increased so did THMs and HAAs levels. Lu et al. showed that when TOC concentration increases THMs and HAAs concentration increases. Kim showed that when TOC concentration increases THMs and HAAs concentration increases. Uyak et al. indicated a higher level of available TOC will provide more THMs. Scheili et al. demonstrated rate of THMs and HAAs formation increase as TOC increases [10-14].

### Effect of chlorine dose and residual chlorine on the formation of DBPs

The present study showed that as chlorine doses increased THMs and HAAs levels increased as indicated in Figures 3 and 4. Scientists have been studying how the disinfectant concentration affects DBPs formation. The studies have shown that as the disinfectant concentration increases, DBP formation also increases. For example, Singer et al. conducted a study in North Carolina on eight conventional water treatment plants that practiced chlorine disinfection. The treatment plant that used the largest chlorine dose had average THMs and HAAs levels of 52 μg/l and 80 μg/l, respectively [10].

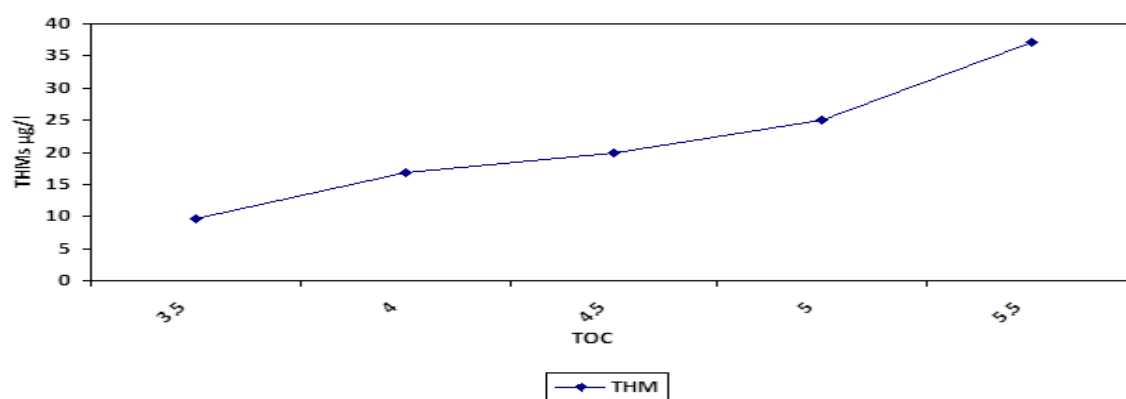


Figure 1: Effect of water TOC on the formation of THMs.

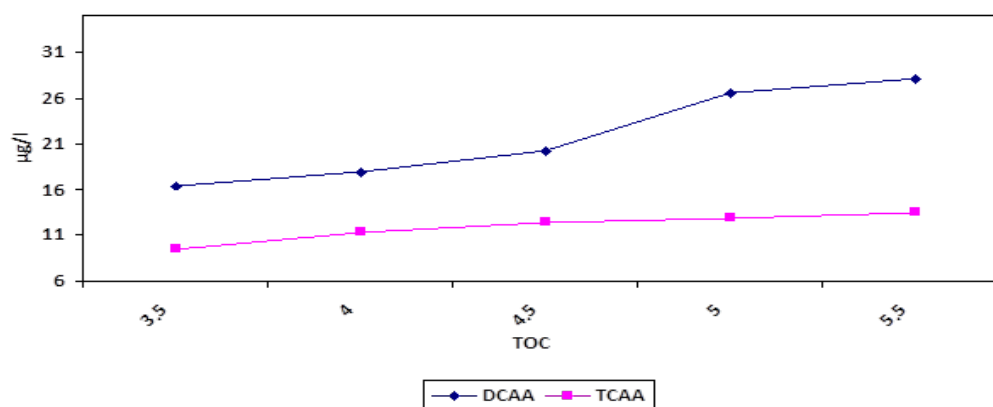


Figure 2: Effect of water TOC on the formation of HAA.

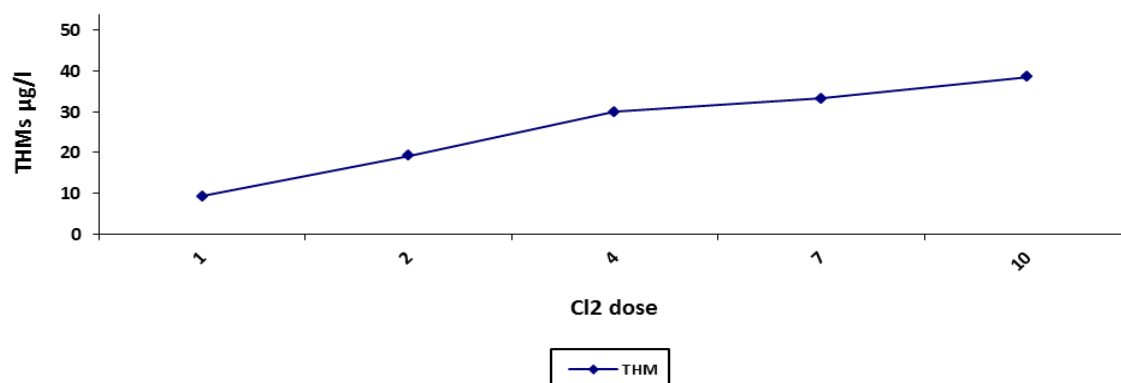


Figure 3: Effect of water Cl<sub>2</sub> dose on the formation of THMs.

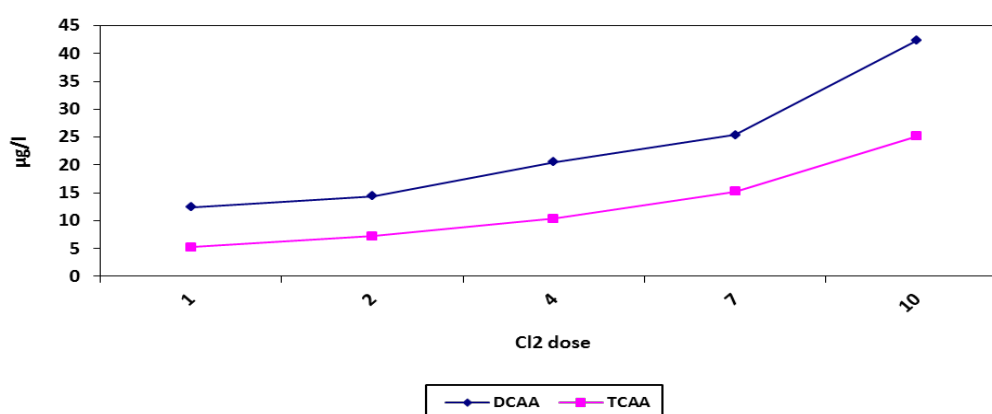


Figure 4: Effect of water Cl<sub>2</sub> dose on the formation of HAA.

### Effect of water contact time on the formation of DBPs

The present study showed that as chlorine contact time increased THMs and HAAs levels increased as indicated in Figures 5 and 6. LeBel et al. who performed an experiment on a conventional water treatment system that used chlorine for its primary and secondary disinfectant. Four sampling points were used at an increasing distance from the treatment plant. The results showed that THMs levels increased [15]. Lu et al. found a similar trend that DBPs THMs and HAAs concentrations increased with increasing reaction time [14].

### Effect of water pH on the formation of DBPs

The present study showed that as water pH increased THMs levels increased as indicated in Figure 7. While in case of HAAs, the effect of pH did not clear as indicated in Figure 8. Diehl et al. conducted a series of experiments to determine the effect of pH on DBP formation in water supplies treated with chloramines. These results lead Diehl et al. to state that as pH increases; THM levels increase [16]. Nieminski et al. evaluated 35 water treatment systems in Utah which used chlorine disinfection. The findings support the conclusion that higher pH conditions cause that higher pH conditions cause HAA concentrations to decrease and THMs concentrations to increase [17]. Lu et al. THMs formation during chlorination in the pH range 6-9. As far as the HAAs formation is concerned, the yield of HAAs increases as pH increases from 6 to 7, but decreases obviously when pH further increases [14]. Hong THMs

formation during chlorination in the pH range 6-8. As far as the HAAs formation is concerned, the yield of HAAs increases as pH increases from 6 to 7, but decreases obviously when pH further increases [18]. The present study showed that as bromide concentrations increased THMs and HAAs levels increased as indicated in Figures 9 and 10. High bromide concentrations in a raw water source and chlorine is added to the water supply, more brominated THMs will be formed because there is more bromide present in the water source for the organics to react with. In typical raw water supplies when chlorine is added, chloroform is the major compound of THMs found in the water supply. Diehl et al. performed experiments on three different water sources and tested the effect of bromide levels on DBP formation [17]. Results showed that as the bromide concentration increased, the THMs concentration also increased. Uyak and Toroz performed experiments and tested the effect of bromide levels on HAAs formation, as the bromide concentration increased the brominated HAAs concentration increase and chlorinated HAAs (DCAA, TCAA) concentration decrease due to enhance formation of brominated HAAs (Table 1) [13].

### Conclusions

This study showed that

- Increasing the chlorine dose, temperature and the contact time enhancing the formation of THMs.

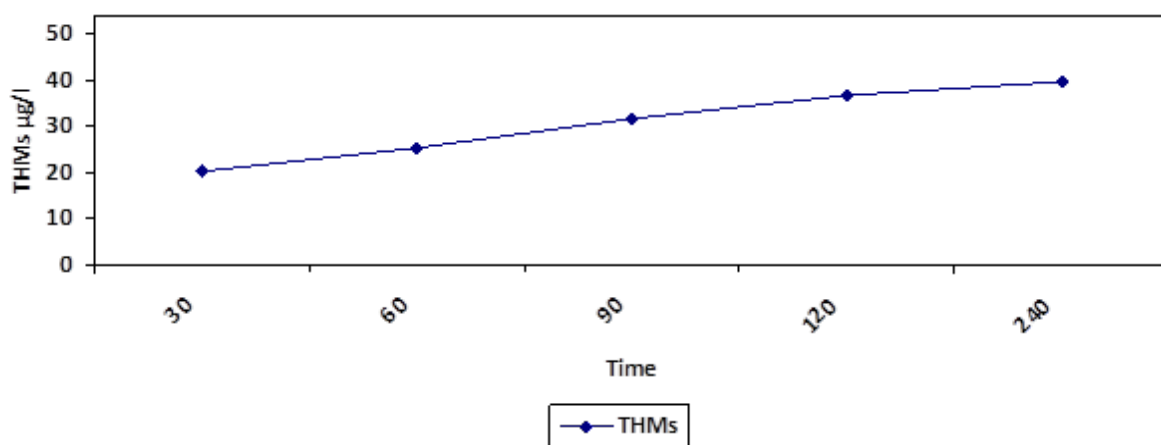


Figure 5: Effect of water Time (T) on the formation of THMs.

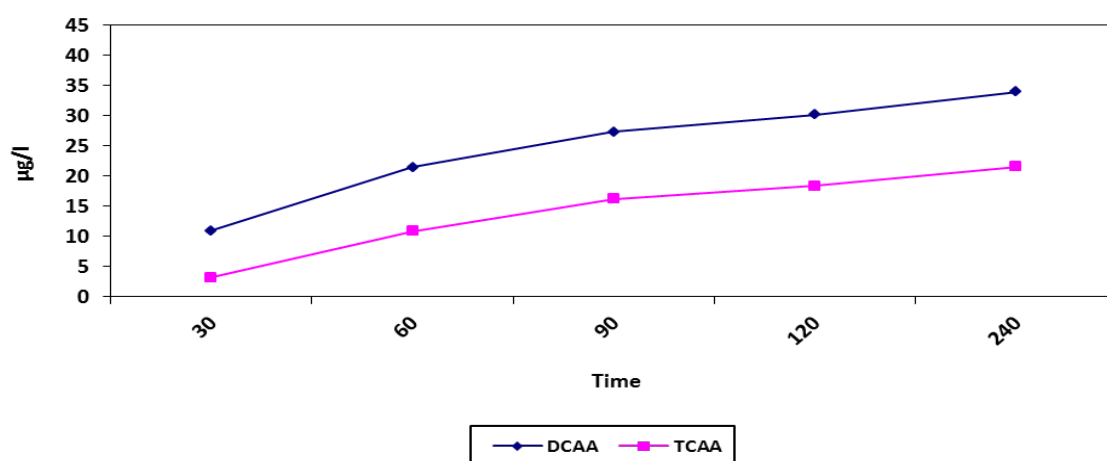


Figure 6: Effect of water Time (T) on the formation of HAA.

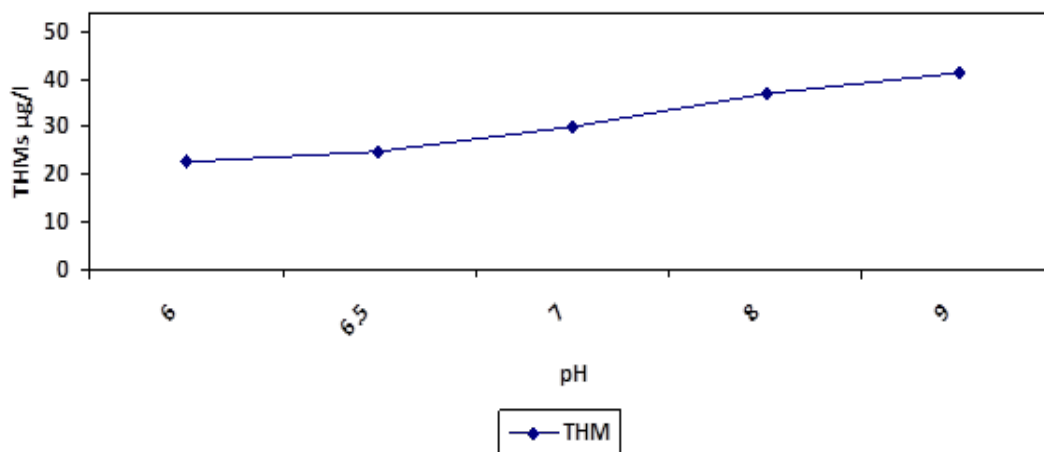


Figure 7: Effect of water pH on the formation of THM.

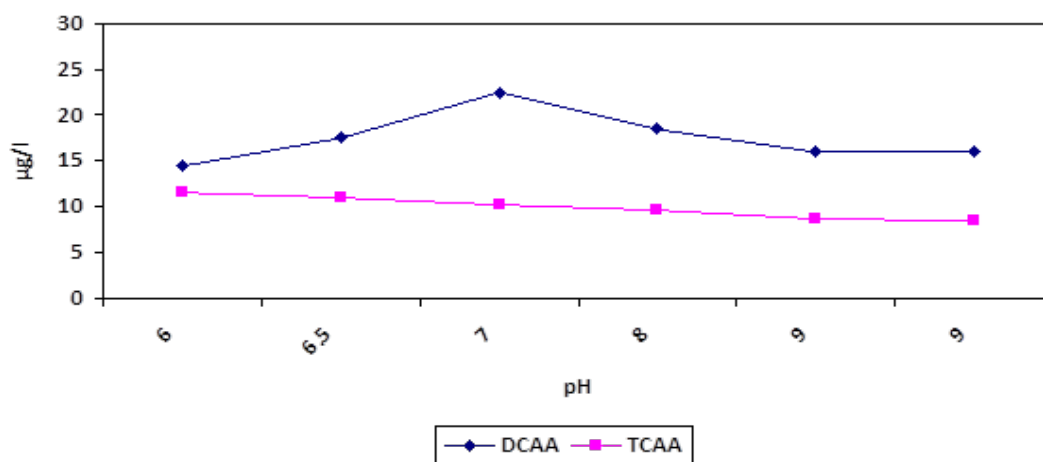


Figure 8: Effect of water pH on the formation of HAA.

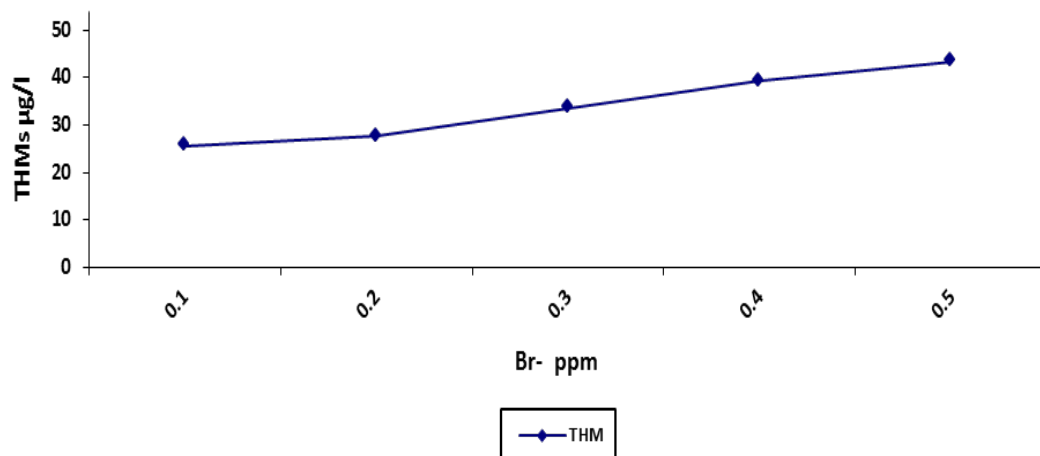


Figure 9: Effect of water Br- on the formation of THMs.

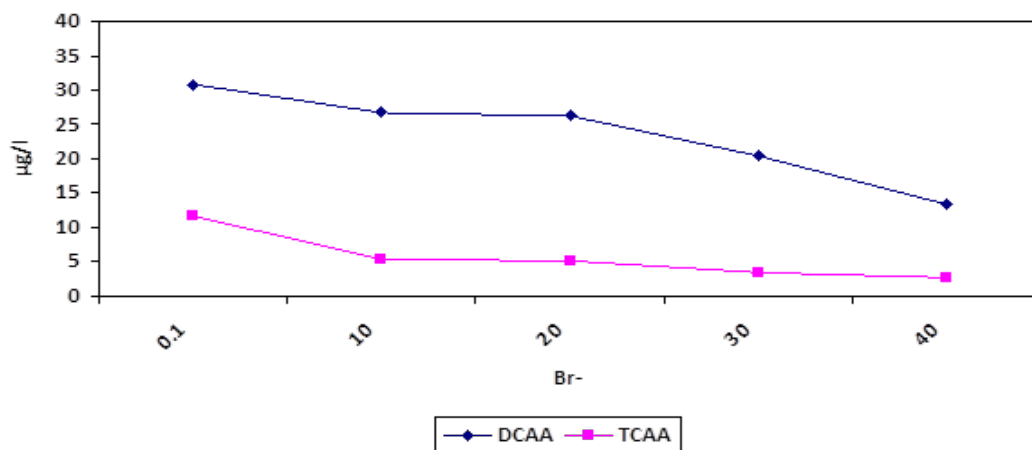


Figure 10: Effect of water bromide on the formation of HAA.

Compound	WHO (2011)	Egypt (2007)
DCAA	0.05	0.06
TCAA	0.20	0.10

**Table 1:** Standards/recommending guidelines for HAAs (mg/L) in the world jurisdictions.

- Increasing the chlorine dose, temperature and the contact time enhancing the formation of THMs and HAAs.
- Increasing the water pH, enhancing the formation of THMs.
- Increasing the bromide concentration, enhancing the formation of THMs.
- Effect of water pH variation has slightly impact on HAAs formation.

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