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Evaluation of Trihalomethanes in Drinking Water of Mosul, Iraq

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Abstract. This study investigates the occurrence and associated health risks of trihalomethanes (THMs)—specifically bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (BF)—in the domestic water supply of Mosul, Iraq. Water samples were collected from ten locations across the city between 2019 and 2020, including Al-Zuhoor, Al-Muthanna, Al-Sukar, Al-Mansour, Al-Majmoua Al-Thaqafiya, Al-Wahda, Al-Maliya, Al-Hadbaa, Al-Arabi, and Al-Tamim neighborhoods. Analysis was performed using gas chromatography with electron capture detection (GC-ECD) following USEPA Method 551.1. THM concentrations ranged from non-detectable to 69.4 µg/L, remaining below the WHO guideline of 100 µg/L. Health risk assessments were conducted using both WHO and USEPA models. Non-carcinogenic risks via ingestion pathways were found to be within acceptable limits (hazard quotient < 1), while the estimated total lifetime cancer risk from combined exposure (1.03×10^{-6}) slightly exceeded the USEPA benchmark of 1.0×10^{-6}, a threshold typically used for carcinogenic risk, indicating a marginal yet notable concern. The assessment primarily focused on oral ingestion, and further investigation into inhalation and dermal pathways, as well as impacts on sensitive subpopulations (e.g., children, elderly), is recommended. To mitigate potential health risks, improvements in water treatment—such as the implementation of advanced technologies like activated carbon filtration and better optimization of chlorination practices—are advised. The findings contribute valuable insights into water quality management and chemical exposure in urban environments of developing regions.

1. Introduction

Water disinfection using chlorine as a disinfectant is an economic and effective in water treatment for disinfection strategy and inactivation of microorganisms (Chowdhury and Champagne, 2013). Nonetheless, the hazardous organic compounds that produces as a disinfection by-product (DBP) that causes a cancer risks, as well as other acute and chronic hazards on human health.

Disinfection by chlorination, is that the medical care methodology accustomed make clean of potable, and has cause a significant decrease in mortality and morbidity from most varied diseases far-famed to be waterborne [1]. However, the potable that contain a chlorinated medical care by-products (DBP) is of concern from a public health side as a result of they will be malignant neoplastic disease [2-4]. The medical care by-product compounds that fashioned throughout medical care method is that the CHCl3, $CHBrCl_2$, $CHBr_2$, and $ClCHBr_3$, the $CHCl_3$ is assessed in cluster 2B as a probably malignant neoplastic disease to humans, supported comfortable proof of carcinogenicity in experimental animals [6-7]. CHBrCl2 may be an agent and classified as in all probability

malignant neoplastic disease to humans, with comfortable proof in animals. CHBrCl2 is to be the foremost potent eutherian mammal matter. CHBr2Cl and CHBr3 area unit classified in cluster three thanks to the inconclusive genotoxicity [6-8]. The THMs risks area unit cancer and adverse copy issues like abortion, miscarriage, and feebleminded foetal development [1-3].

Chlorine chemically is a very reactive compound and also known as a strong oxidizing agent. In the 1970s, some studies cited that the chlorinated drinking water may be produces a **halogenated disinfection by-product (DBPs)**, the formation of DBPs are correlated with the concentrations of natural organic carbon (TOC) and retention time, water pH, and water temperature, so the mono-chloramine uses are increased as a secondary disinfectant in order to control the formation of DBPs in drinking water [1-2].

Trihalomethanes (THMs) compounds that formed in chlorinated water are trichloromethane (TCM, chloroform), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM, bromoform). Brominated DBPs are formed by the competing chlorine agent during oxidation of bromide to HOBr/OBr− a brominating agent.

Halo organic compounds (THMs and HAAs) are represents the bigger mass portion of the halo-organo compounds, these organo compounds have been regulated in all states of the world. The THMs were regulated in the USA by the USEPA. The maximum permissible limit level (MPL) of 100 μg/L for total trihalomethanes (TTHM), which is the sum of the four trihalomethanes compounds. The TTHM maximum permissible limit was calculated based on water treatment and chlorination disinfection, controlling waterborne of microbial risks. The TTHMs were used as indicators to determine the treatment type and for reduce the other DBPs, and and controlling the coliforms and Escherichia coli bacterial indicators of pathogenic microorganisms [1-2, 8-10].

The chlorination of water is that the main step in treatment method for the standard of water however may well be causes a formation of undesirable organic compounds thanks to the production of DBPs throughout chlor-amination, chlorination, and ozonation method that react with a natural organic matter. The previous studies have rumored that the water chlorination could also be fashioned a probably dangerous DBPs with quite 600 DBPs detected and determined in drinking waters [9-10]. DBPs compounds square measure includes the THMs, HAAs, HALs, HKs, and element DBPs like HANs, HNMs, and HAcAms [11-15]. However, with the ne techniques in analytical procedures, rising DBPs like halobenzoquinones and iodotrihalomethanes are known [16-18].

Natural organic matter (Humic and fulvic poly organic compounds) that represent the TOC, and act as the organo precursors for the formation of hazardous organo compounds when exist with the chlorine in water treatment process, while bromide ion act as an inorganic precursor for brominated organo compounds [19-21].

Alternative disinfectants use in water treatment is also turn out unregulated DBPs that probably have a health hazard in beverage. several medicine studies have cited that health risks, related to liver, system, kidney, and central systema nervosum, magnified risk of cancer attributable to a consumption of beverage that have a DBPs and exceeds than the utmost stuff level (MCL) [5, 11–16].

Many studies have been identifying and describe the THMs formation potential and related health hazardous effects (5), where the maximum contaminant levels (MCLs) of THM was 0.080 mg/l according to USEPA (2018).

2. Methodology

2.1 Sampling

Water samples were collected from ten selected sites across the drinking water distribution network of Mosul City, covering residential and municipal zones. Sampling was conducted at different intervals over the 2019–2020 period to account for seasonal variations. Each sample was collected in 100 mL amber glass bottles containing 0.3 g of sodium thiosulfate to neutralize residual chlorine. Samples were stored at 4°C and analyzed within 24 hours to maintain integrity.

2.2 Material

All material, reagents and standards used in the present study are high quality and American Chemical Society (ACS) vendors which used in analytical laboratories.

2.3 Analytical Methods

Water samples were taken from the selected ten sites, in different periods during 2019/2020, were subjected to analysis of the trihalomethanes. Samples were collected in hundred mille Amper glass after adding 0.3 g sodium thiosulfate. The collected water samples were refrigerated at 4oC for subsequence laboratory tests.

Trihalomethanes (THMs) were extracted employing a liquid-liquid extraction with HPLC grade n-hexane, and

analyses were administrated employing a gas chromatograph (GC) (7890A, Agilent, USA) with auto-sampler (7683B, Agilent, USA) equipped with Associate in Nursing lepton capture detector (ECD) supported USEPA technique 551.1 [25].

Triplicate analyses were performed among twenty-four hours once extraction for all the water samples. The calculated limit of detection (LOD) for dichlorobromomethane, dibromochloromethane, bromoform, and chloroform was ≥ zero.1 µg/L. The accuracy of the GC-ECD technique for the trihalomethanes were ninety-nine.1, 98.9, 99.3, and 99.2% for chloroform, dichlorobromomethane, dibromochloromethane, and haloform, severally.

In this study, 2 approved risk assessment models were approved by the globe Health Organization (WHO) index for additive toxicity, and also the USEPA-Approved risk assistant model. The WHO index for additive toxicity, WHO, for THMs is Associate in Nursing overall guideline price to estimate the poisonous (developmental and non-carcinogenic) risk related to chlorinated drink. The IWHO price ought to be ≤ one for compliance with WHO tips and was calculated as follows:

Where C is that the concentration of every master's degree during this study, and GV is that the WHO guideline values are established. The GV for CF is three hundred, BDCM 60, DBCM one hundred and BF one hundred, bushed µg/l [22].

The USEPA approved Risk model that interested in several researchers [5-9]. The USEPA Risk assessment model is ready to estimating the toxicologic risks (toxic and non-carcinogenic risks) and malignant neoplastic disease risks.

Toxicologic risks, expressed because the hazard quotient (HQ), were calculated supported the comparison of actual exposure to the reference dose (RfD) as follows**:**

HQ = (Total amount ingested / body weight × exposure time × RfD)

The reference doses were cypher from toxicologic studies of exposure that demonstrate a essential result. they're expressed in units of mg/kg/day, and square measure obtainable within the Integrated Risk data system info [22] info maintained by the USEPA [25].

Carcinogenic risks of exposure to THMs concentrations were calculable by victimization the USEPA technique. malignant neoplastic disease material varied from cyanogenetic compounds in this there's no lower limit for the presence of risk. So, substance risk assessment models square measure supported the premise that risk is proportional to total life dose, and therefore the exposure metric used for malignant neoplastic disease risk assessment is that the life Average Daily Dose (LADD). The LADD is often utilized in conjunction with the Cancer Slope issue (CSF) to calculate individual excess cancer risk. it's AN estimate of the daily intake of a malignant neoplastic disease agent throughout the whole lifetime of a personal. The CSF is that the gradient of the road of the dose response curve derived from laboratory toxicologic studies, and levels of every compound square measure obtainable within the USEPA IRIS databases [25]. For master's degree species, the USEPA vary of concern is for AN augmented malignant neoplastic disease risk of 1026 i.e.1:1,000,000 [25].

3. Results & Discussion:

In the present study, the disinfectant water with chlorine was collected from Mousl city districts and analysis in order to estimate the trihalomethanes risk assessment.

The purpose of the risks assessment to ensures that the domestic water supplied for consumers are safe and comply with the local standards and regulations. The probabilistic Model achieve a lot of a total characterization of data, determine the intervals and then the chance of exposure for teams of people, together with proof, which needs additional study. It includes the employment of math empirical formula for the physic-chemical processes that give a spread of values and therefore the chance distribution for the exposure.

3.1 Chloroform (CF)

The observations of CF in El Mousl ranged from 18.3 to 46.4 µg/l with average value 29.65 µg/l, as shown in Table (1) and Figure (1).

Chloroform, is that the most typical THMs compounds, the CF found in high levels in chlorinated-water, as a result of higher OM [4-5]. The levels of chloroform different with totally types of water treatment plant (WTP). Levels of chloroform in chlorinated water in WTP and distribution systems square measure more or less doubly as high throughout hot months as throughout colder months. this can be a result of the excess levels of OMs and particularly of the upper rates of formation of medical care by-products within the raw water throughout the new amount [4-5].

The chlorination of water is one of the treatment steps in order to raising the water quality and to be safe for human uses but could be form an undesirable chemical hazard material because the formation of disinfection by-products

during chloramination, chlorination, and ozonation with natural organic matter.

Since in seventies, studies have concluded that using chlorine as a disinfectant causes a a human risk of DBPs [18-20].

Two classes of DBPs that regulated by US Environmental Protection Agency with maximum permissible level (MPL) of 60 and 80 μg/L for HAAs and THMs compounds, respectively. The THMs are found in treated water through the reactions of applied chlorine and chloramine with fulvic and humic matter that found naturally in water.

Many researchers conducted their work in the monitoring of chloroform and the assessment of their carcinogenic and non-carcinogenic risks connected with public water supplies [2-3].

Table 1. Chloroform in DS of Mosul City
Parameters

samples	Unit	Range	Mean	SD	Notes
1	µg/l	19.2- 44.8		29.2	96.2
2	µg/l	18.3- 43.6		28.4	88.4
3	µg/l	19.6- 45.6		31.1	97.8
4	µg/l	21.2-46.4		32.2	101.2
5	µg/l	18.4-43.1		28.6	94.1
6	µg/l	18.6-43.8		29.6	91.4
7	µg/l	18.8-44.1		29.4	92.5
8	µg/l	18.4-42.9		29.1	94.1
9	µg/l	18.6-43.1		29.5	95.4
10	µg/l	18.7-44.6		29.4	94.6
Average		-	29.65	-	

SD: standard deviation; CF: chloroform

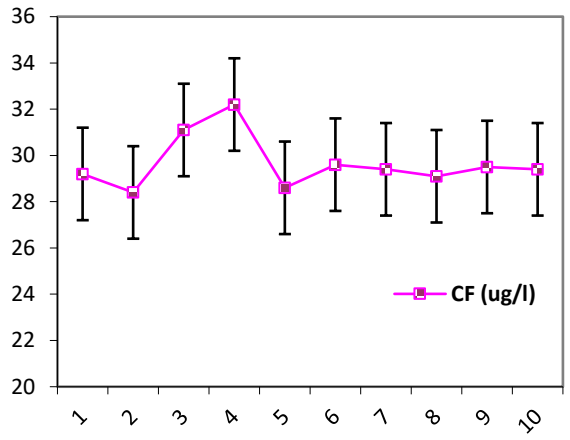

Figure 1. Average values of CF in Mosul City

3.2 Bromodichloromethane (BDCM):

The observations of BDCM in Mousl ranged from 11.3 to 28.2 µg/l with average value 17.17 µg/l, as shown in Table (2) and Figure (2).

Table 2. BDCM in DS of Mousl City

Parameters					
Sample	**Unit**	**Range**	**Mean**	**SD**	**Notes**
1		12.5-28.2	17.4	74.2	
2		11.3-26.5	16.5	71.4	
3		12.4-25.8	17.2	77.4	
4		13.4-27.2	18.2	81.4	
5		14.2-27.8	18.6	82.4	
6	µg/l	13.2-26.4	17.2	81.1	
7		13.6-26.4	17.8	84.1	
8		13.1-26.6	17.7	82.4	
9		14.3-27.5	18.1	83.6	
10		13.6-27.4	18.6	85.4	
Average		-	17.7	-	

•SD: standard deviation; DCBM: dichlorobromomethane

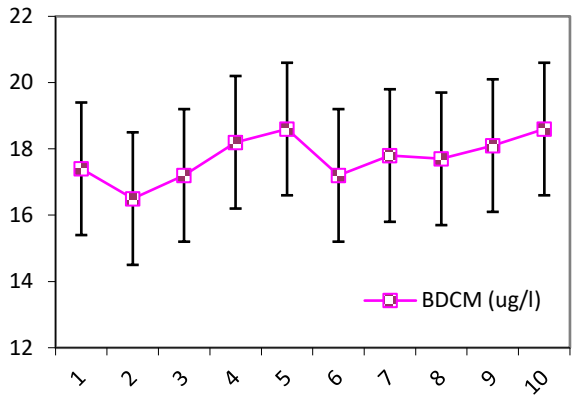

Figure 2. Average values of BDCM in Mosul City

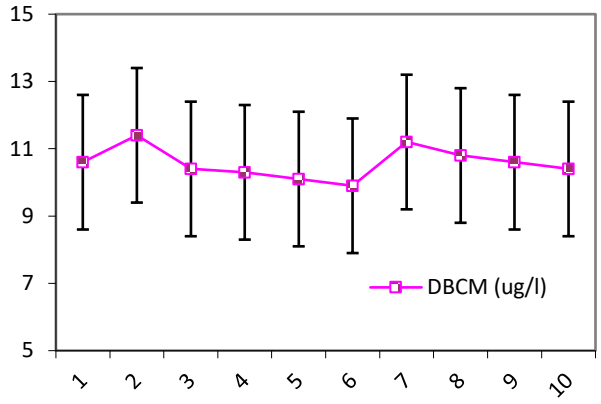

Figure 3. Average values of DBCM in El Mosul City

3.3 Dibromochloromethane (DBCM):

The observations of DBCM in El Mousl ranged from 7.2 to 14.6 µg/l with average value 10.6 µg/l, as shown in Table 3 and Figure 3.

Table 3. DBCM in DS of Mousl City

Parameters

Sample	Unit	Range	Mean	SD
1	µg/l	7.2-12.8	10.6	62.5
2	µg/l	8.2-13.1	11.4	66.2
3	µg/l	7.6-12.4	10.4	61.3
4	µg/l	7.3-12.6	10.3	58.6
5	µg/l	7.6-12.4	10.1	62.1
6	µg/l	7.3-13.8	9.9	76.2
7	µg/l	7.7-14.6	11.2	91.4
8	µg/l	7.4-13.5	10.8	75.1
9	µg/l	7.6-13.1	10.6	68.4
10	µg/l	7.2-12.8	10.4	66.2
Average		-	10.6	-

•SD: standard deviation; DBCM: dibromochloromethane.

3.4 Bromoform (BF)

The observations of BF in El Mousl ranged from ND to 3.7 µg/l with average value 1.7 µ1g/l, as shown in Table 4 and Figure 4.

Table .4. BF in DS of Mousl City

Parameters

sample	Unit	Range	Mean	SD	Notes
1	µg/l	ND-3.6	1.8	31.2	
2	µg/l	ND-4.1	2.1	36.2	
3	µg/l	ND-3.4	1.6	28.6	
4	µg/l	ND-3.4	1.7	29.6	
5	µg/l	ND-3.5	1.8	32.1	
6	µg/l	ND-3.3	1.6	29.5	
7	µg/l	ND-3.2	1.5	29.1	
8	µg/l	ND-3.4	1.7	30.5	
9	µg/l	ND-3.7	1.9	32.1	
10	µg/l	ND-3.3	1.6	29.6	
Average		-	1.7	-	

•SD: standard deviation; BF: bromoform.

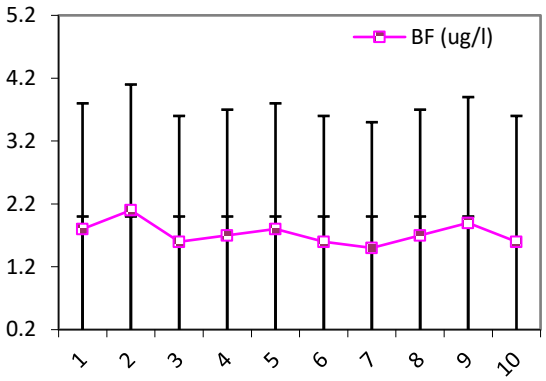

Figure 4. Average values of BF in Mousl City

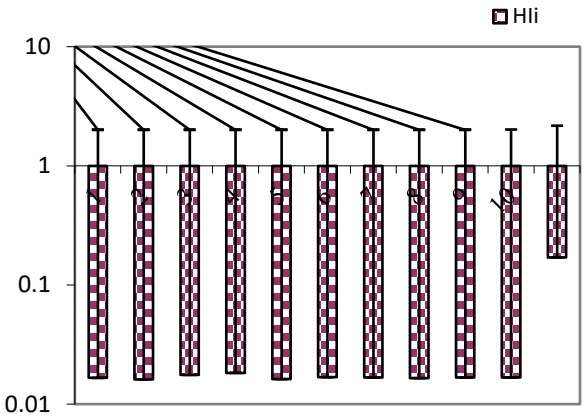

Figure 5. CF risk assessment in Mousl City

Estimation of cancer risk for brominated compounds

3.5 Chloroform

The carcinogenic risk for CF is shown in Fig.5. The mean calculated value of hazard risk for amount trihalomethanes in domestic water samples was acceptable level (0.1702). The risk assessment of chloroform trichloromethane (HIi) ranged from 0.0161 to 0.0183 with average value 0.0168, as shown in Figure 5. THM could be existing in water for human public supply at high levels that may be healthy causing adverse effects for the inhabitants. Consumptions of drinking water that had THMs may be reaching to liver and kidney and causing adverse impacts for both liver and kidney, and also immune, nervous, and reproductive systems disorders [8-12]. Observation data of THMs and estimated jeopardy concluded that a correlation between the cancers of bladder, colon and rectum and these compounds in water uptake. Different countries put regularization Synonyms/Hypernyms (Ordered by Estimated Frequency) of noun value that shouldn't be to exceed those values.

Table 5. CF risk assessment

Site	C_{ai}	EF	ED	BW	AT	IR_a	RfD_i	HI_i
1	0.0292	365	70	75	25550	2	0.047	0.0166
2	0.0284	365	70	75	25550	2	0.047	0.0161
3	0.0311	365	70	75	25550	2	0.047	0.0176
4	0.0322	365	70	75	25550	2	0.047	0.0183
5	0.0286	365	70	75	25550	2	0.047	0.0162
6	0.0296	365	70	75	25550	2	0.047	0.0168
7	0.0294	365	70	75	25550	2	0.047	0.0167
8	0.0291	365	70	75	25550	2	0.047	0.0165
9	0.0295	365	70	75	25550	2	0.047	0.0167
10	0.0294	365	70	75	25550	2	0.047	0.0167
Control	0.3	365	70	75	25550	2	0.047	0.1702

HIi: non-cancer hazard quotient, EF: exposure frequency (d/y); ED: exposure duration (y); BW: body weight (kg); RfDi: reference dose for chloroform (mg/kg^{-d})

3.6 BDCM

The carcinogenic risk for BDCM is shown in Figure 6. The mean calculated value of hazard cancer risk for trihalomethanes due to treated water uptake is in the acceptable low risk (99.2×10^{-6}). The risk assessment of BDCM (HIi) ranged from 27.3×10^{-6} to 30.8×10^{-6} with average value 2.9×10^{-5} as shown in Figure 6.

Table 6. BDCM risk assessment

Site	C_{ai}	EF	ED	BW	AT	IR_a	RfD_i	HI_i
1	0.0174	365	70	75	25550	2	0.062	28.8E-6
2	0.0165	365	70	75	25550	2	0.062	27.3E-6
3	0.0172	365	70	75	25550	2	0.062	28.4E-6
4	0.0182	365	70	75	25550	2	0.062	30.1E-6
5	0.0186	365	70	75	25550	2	0.062	30.8E-6
6	0.0172	365	70	75	25550	2	0.062	28.4E-6
7	0.0178	365	70	75	25550	2	0.062	29.4E-6
8	0.0177	365	70	75	25550	2	0.062	29.3E-6
9	0.0181	365	70	75	25550	2	0.062	29.9E-6
10	0.0186	365	70	75	25550	2	0.062	30.8E-6
Control	0.06	365	70	75	25550	2	0.062	99.2E-6

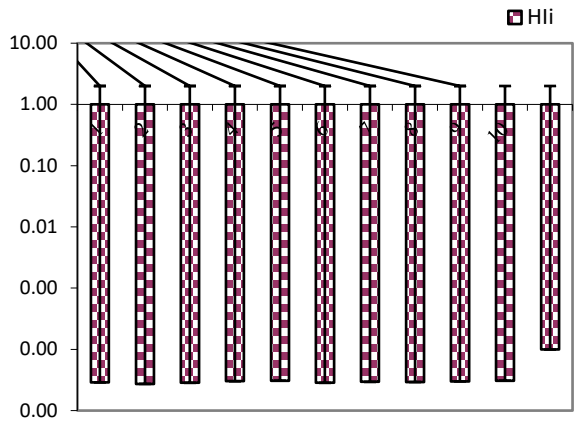

Figure 6. DCBM risk assessment in Mosul City

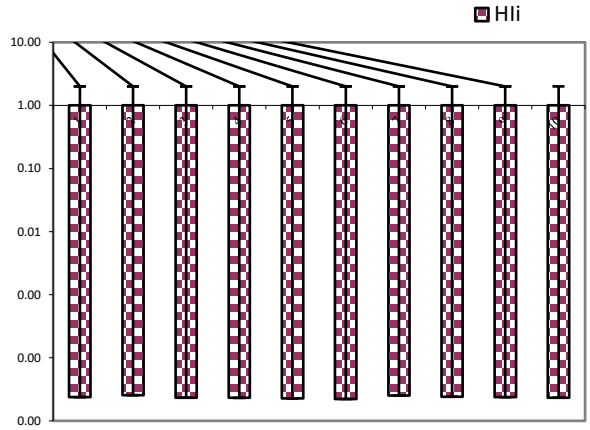

Figure 7. DBCM risk assessment in Mousl City

3.7 DBCM

The carcinogenic risk for DBCM is shown in Figure 7. The mean calculated value of hazard cancer risk for trihalomethanes due to treated water uptake is in the acceptable low risk (134.4 x 10^{-6}). The risk assessment of DBCM (HIi) ranged from 22.2 x 10^{-6} to 25.5 x 10^{-6} with average value 2.37 x 10^{-6}, as shown in Figure 7.

Table 7. DBCM risk assessment

Site	C_{ai}	EF	ED	BW	AT	IR_a	RfD_i	HI_i
1	0.0106	365	70	75	25550	2	0.084	23.7E-6
2	0.0114	365	70	75	25550	2	0.084	25.5E-6
3	0.0104	365	70	75	25550	2	0.084	23.3E-6
4	0.0103	365	70	75	25550	2	0.084	23.1E-6
5	0.0101	365	70	75	25550	2	0.084	22.6E-6
6	0.0099	365	70	75	25550	2	0.084	22.2E-6
7	0.0112	365	70	75	25550	2	0.084	25.1E-6
8	0.0108	365	70	75	25550	2	0.084	24.2E-6
9	0.0106	365	70	75	25550	2	0.084	23.7E-6
10	0.0104	365	70	75	25550	2	0.084	23.3E-6
Control	0.06	365	70	75	25550	2	0.084	134.4E-6

3.8 BF

The carcinogenic risk for BF is shown in Fig.8, the mean calculated value of hazard cancer risk for trihalomethanes due to treated water uptake is in the acceptable low risk (134.4 x $10^{\wedge-6}$). The risk assessment of BF (HIi) ranged from 3.4 x $10^{\wedge-6}$ to 4.0 x $10^{\wedge-6}$ with average value 3.66 x $10^{\wedge-6}$, as shown in Figure (8).

Table 8. BF risk assessment

Site	C_{ai}	EF	ED	BW	AT	IR_a	RfD_i	HI_i
1	0.0018	365	70	75	25550	2	0.079	3.8E-6
2	0.0021	365	70	75	25550	2	0.079	4.4E-6
3	0.0016	365	70	75	25550	2	0.079	3.4E-6
4	0.0017	365	70	75	25550	2	0.079	3.6E-6
5	0.0018	365	70	75	25550	2	0.079	3.8E-6
6	0.0016	365	70	75	25550	2	0.079	3.4E-6
z 7	0.0015	365	70	75	25550	2	0.079	3.2E-6
8	0.0017	365	70	75	25550	2	0.079	3.6E-6
9	0.0019	365	70	75	25550	2	0.079	4.0E-6
10	0.0016	365	70	75	25550	2	0.079	3.4E-6
Control	0.06	365	70	75	25550	2	0.084	134.4E-6

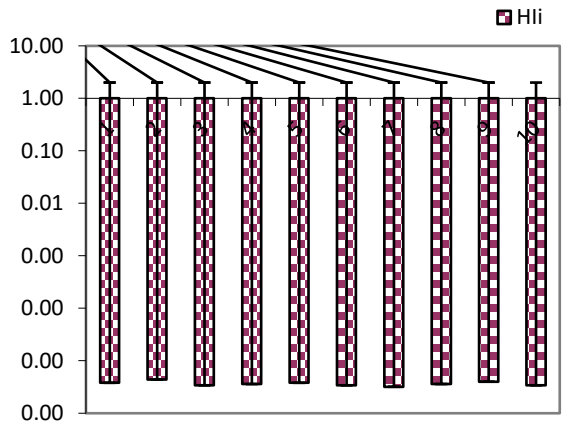

Figure 8. BF risk assessment in Mousl City

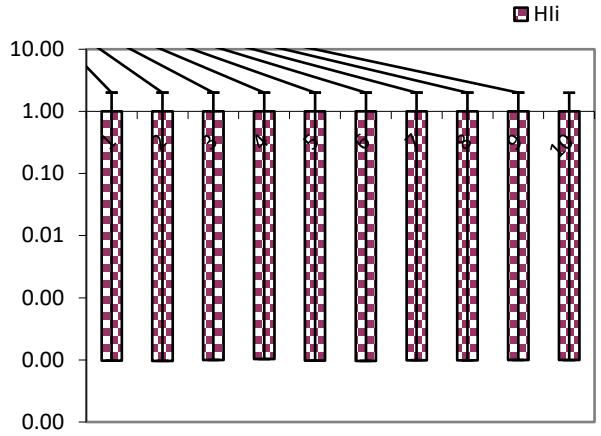

Figure 9. THMs risk assessment in Mousl City

3.9 THMs

The carcinogenic risk for THMs is shown in Figure 9. The mean calculated value of hazard cancer risk for trihalomethanes due to treated water uptake is in the acceptable low risk (165.3 x 10^{-6}). The risk assessment of THMs (HIi) ranged from 96.4 x 10^{-6} to 103.2 x 10^{-6} with average value 9.87 x 10^{-6}, as shown in Figure 9.

Table 9. THMs risk assessment

Site	C_{ai}	EF	ED	BW	AT	IR_a	RfD_i	HI_i
1	0.059	365	70	75	25550	2	0.062	97.5E-6
2	0.0584	365	70	75	25550	2	0.062	96.6E-6
3	0.0603	365	70	75	25550	2	0.062	99.7E-6
4	0.0624	365	70	75	25550	2	0.062	103.2E-6
5	0.0591	365	70	75	25550	2	0.062	97.7E-6
6	0.0583	365	70	75	25550	2	0.062	96.4E-6
7	0.0599	365	70	75	25550	2	0.062	99.0E-6
8	0.0593	365	70	75	25550	2	0.062	98.0E-6
9	0.0601	365	70	75	25550	2	0.062	99.4E-6
10	0.06	365	70	75	25550	2	0.062	99.2E-6
Control	0.1	365	70	75	25550	2	0.062	165.3E-6

From the observation of THMs and its compounds, the calculation of IWHO risk index was 0.45 and less than 1.0, thus ensures that the drinking water in Mousl was safe and have low risks according to WHO index.

BDCM > DBCM > bromoform > chloroform. This observation was complying with the WHO guidelines and THMs (Stalter et al. 2016). The minimum level of chloroform risk was less than 10−6 (negligible risk), that could be because of the presence of brominated THMs compounds over-chlorinated ones in water samples. While, with another researches, chloroform have the lower

4. Conclusions

The present study summarized the following points of conclusions;

•The values of THMs and its species are complying with the WHO and USEPA standards.

•The observation of THMs showed that, the values of CF is the highest value, and BF is the lowest value and nearly not detected.

•The parameters that cause high formation of THMs should be reduced by coagulation-flocculation, AC, and RO technology.

•To control the health hazard of THMs, so the break point chlorination dose of chlorine should be applied, and the THMs, should be investigated and recorded in water networks.

•The USEPA toxicity of THMs concentrations of CF, BDCM, DBCM and BF in the water networks are not

exceeded than WHO guideline values for the investigated sites, and so it's have low adverse toxic and non-carcinogenic risks in health impacts, but THMs concentrations are within the WHO guidelines.

•The lifetime cancer risk for the THMs components via multi pathway exposure routes are 1.03×10^{-6}which was slightly higher than the 1.0×10^{-6} that recommended by the USEPA.

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Conflict of interest

The authors declare no conflicts of interest regarding the current research.

Author Contribution

For example:

Z.A. Alshrefy: proposed the research problem, developed the theory, verified the analytical methods, and discussed the results and writing the paper.

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