

DETERMINATION OF TRIHALOMETHANES IN RAW AND TREATED WATER SUPPLY TO A LOCAL CITY IN ZIMBABWE

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Abstract

Concentration levels of trihalomethanes in raw and treated water for the city of Gweru were determined by solvent extraction followed by gas chromatograph detection. The trihalomethanes found were chloroform, dichlorobromomethane, dibromochloromethane and bromoform. Chloroform was the most abundant trihalomethane with concentration levels ranging from 3.70 µg/L to 45.89 µg/L. The concentration levels of trihalomethanes increased with increasing distance from the chlorination point. Total trihalomethane concentration in raw water ranged from nondetectable levels to 18.13 µg/L and in treated water ranged from 6.83 µg/L to 145.50 µg/L. A slight increase in concentration levels of trihalomethanes was shown in warmer months with the highest concentration level of 145.80 µg/L being recorded in September. Generally, the concentration levels obtained were lower than the maximum permissible limits of 460 µg/L set by World Health Organisation (WHO).

Keywords: trihalomethanes, raw water, treated water, chloroform, bromoform, dichlorobromomethane, dibromochloromethane

1. INTRODUCTION

Provision of an adequate supply of potable water is vital for human health. In providing potable water, water is treated by adding chlorine at multiple points in the disinfection process. Water from natural sources contains a number of naturally occurring organic compounds which when in contact with chlorine produce a number of disinfection by-products (DBPs) including trihalomethanes (THMs), chlorinated furones, aldehydes, halophenols, halogenated acetic acids (HAAs), haloketones and halogenated acetonitriles [1,2]. As a consequence of water treatment, DBPs have been detected in variable concentrations in different communities [3,4]. HAAs and THMs which include chloroform, dichlorobromomethane, dibromochloromethane and bromoform are predominantly formed during the water treatment process [1,5,6,7]. The concentrations of the THMs and HAAs can be used as indicators of the total loading of all chlorinated disinfections by-products, which may be found in

water [5]. These four THMs are reported possible carcinogens in humans, though there is inadequate evidence in humans and limited evidence in experimental animals [1,8]. Animals studies show links between exposure to specific THMs and liver tumors in mice rats whilst human studies suggest that there is a link between exposure to THMs and colorectal cancers [1,9]. Preliminary animal studies indicate that bromodichloromethane (BDCM) and other THMs containing bromine may be more toxic than chlorinated THMs such as chloroform. Among the four THMs, BDCM is the most potent rodent carcinogenic causing tumors than the other three compounds. Bromine substitution enhances the lipid solubility of halomethanes and consequently uptake into tissues and generally increases their chemical likelihood of biotransformation to reactive intermediate [10]. Other studies have linked the THMs to reproductive problems, including low birth weight, miscarriages, prematurity, still birth, intra-uterine growth retardation [11,4,12,13]. Beyond cancer and reproductive concerns, some researchers have found that THMs may be linked to the heart, lung, kidney, liver and central nervous system damage. The effects on the central nervous system appear soon after exposure to high doses and include sleepiness and incoordination [10,11,14].

The principal route of human exposure to THMs is the consumptions of chlorinated drinking water [9,15,16]. Trihalomethanes are volatile, they vaporize during water usage and as a result, inhalation therefore becomes an important exposure route in addition to ingestion. Upon ingestion THMs are metabolized primarily to carbon dioxide and carbon monoxide and then exhaled. However due to their lipophilicity, THMs accumulate mostly in tissues with highest lipid content in the following order: adipose tissue, brain, kidney and blood [11]. Long-term exposure will eventually result in the negative health effects. Due to the risks posed by these substances, various countries have set limits for THMs. In the United States, the Environmental Protection Agency (EPA) reduced the THMs acceptable limits in drinking water from 100 to 80 µg/L in the stage 1 disinfection by-products rule [10,6]. According to the World Health Organization (WHO) regulations, the sum of the THMs should not exceed 460 µg/L in drinking water. [17,18] There is therefore the need to monitor the presence of these compounds in drinking water supplies using reliable methods [19].

Trihalomethanes and other disinfection by-products can be harmful to human health and with this discovery extensive research has been undertaken to determine the origin of disinfection by-products, on their effects and on procedures to prevent formation of these products during the disinfection process [1]. In Zimbabwe, there is limited research into the occurrence and concentration of THMs in Zimbabwe National Water Authority (ZINWA) drinking water. [20] Hence, there is need to constantly monitor the concentration levels of total trihalomethanes. The main goal of this research is to determine the concentration levels of trihalomethanes in raw and treated water from selected areas in Gweru. Special attention is also given to the variations in concentration levels of trihalomethanes with increasing distance from the chlorination point and with seasons

2. MATERIALS AND METHODS

2.1 Reagents used

The reagents used were of analytical grade.

GC grade *n*-hexane and methanol (Sigma Aldrich), anhydrous sodium sulphate (Merck), activated florasil, double distilled chloroform, dichloromethane (Sigma Aldrich), bromoform (Sigma), dibromochloromethane (Sigma), concentrated sulphuric acid (Merck), chromic acid, ferroin indicator, potassium dichromate (Merck), ferrous ammonium sulphate (Sigma Aldrich), starch indicator, acetic acid, potassium iodide, sodium thiosulphate (Merck), organic-free water (obtained by boiling the water for 15 minutes)

2.2 Instrumentation

Gas Chromatograph (Perkin Elmer Claurus 500) with the following parameter settings;

Table 1: Gas chromatography analysis parameters

Parameter	Setting
Column type	Capillary elite 1701 (30m;0.53mm id)
Column temperature	220
Carrier gas	Nitrogen
Flow rate	30 ml/min
Injector type	Split/splitless
Split ratio	02:01
Detector Type	ECD Ni ⁶³
Attenuation	8
Detector Temperature	300

2.3 . Experimental

2.3.1 Sampling Procedure

The reliability of any analytical measurements is directly coupled to the uncertainties of the sampling process, sample storage, preservation and pretreatment prior to analysis [21] Water sampling was carried out periodically between June and September, 2008. Water samples were collected from the supply dam, the water works and four other sites with incremental distance from the water treatment plant once a month .Three samples were collected from each sampling area

to give a total of 72 samples. The residential areas were selected with increasing distance from the chlorination point and water samples were collected directly from taps. The water was turned on and the system allowed to flush until the temperature of the water was stabilized. The flow was adjusted to about 500 mL/min and triplicate samples were collected from the flowing stream. Water from the dam was sampled by totally immersing the sample bottle into water and slowly moving it upstream. Samples from the water works were taken from the pump outlet pump. Water samples were collected in amber colored bottles to inhibit photoreaction of halocarbons. The bottles were previously soaked in chromic acid solution and rinsed several times with double distilled water. All samples were sealed with glass stoppers and stored in the refrigerator at 4 °C before analysis.

2.3.2 Florisil and anhydrous sodium sulphate activation

Florisil was purified by soxhlet extraction using hexane and activated by baking in the oven at 200 °C for 24 hours. The anhydrous sodium sulphate dried in oven for 24 hours at 200 °C before use.

2.3.3 Extraction procedure

Sample (5 mL) was transferred into a 100 mL volumetric flask and double distilled *n*-hexane (3 mL) added. Extraction was completed by mechanically shaking the flask for 2 hours, storing for 24 hours and then transferring the organic phase into the vials.

2.3.4 The clean up procedure

To remove some organic macropollutants and elemental sulphur, which normally interfere in the GC analysis, the extract was poured into a chromatographic column containing activated florasil (7 g) and anhydrous sodium sulphate (2 g) that had been prewetted with 20 mL of double distilled *n*-hexane. The column was first eluted with 5 mL of double distilled *n*-hexane collecting the first fraction. The second elution was with 3 mL of 10% methanol in hexane. No concentration step was involved as this would result in loss of the volatile halocarbons. The extracts were kept in sample bottles for GC analysis.

2.3.5 Recovery experiments

Double distilled water was poured into a volumetric flask (100 mL) and a methanol solution of halocarbons (DBCM, DCBM, chloroform and bromoform) (5.0 µL) was transferred into the water using a microsyringe. The flask was shaken thoroughly before extraction was carried out as described above.

2.3.6 Preparation of composite standard

10 mL of each trihalomethane standard were taken from individual stock solutions of concentration 1×10^{-3} g/mL into a 100 mL volumetric flask. The standards were dissolved by shaking and sonicating in hexane and then made up to the mark with hexane to give a solution with a concentration of 1×10^{-4} g/mL. These

stock solutions were diluted and mixed to produce working standards with the following concentrations:

Table 2: Concentration of working standards

Standard	Standard Concentration g/mL	Working Standards Concentration g/mL
Chloroform	1×10^{-4}	2×10^{-6}
Bromoform	1×10^{-4}	1×10^{-6}
Dibromochloromethane	1×10^{-4}	0.5×10^{-6}
Bromodichloromethane	1×10^{-4}	0.5×10^{-6}

2.3.7 Gas chromatograph analysis

Determination of the halocarbons was done using GC with a microprocessor, a split/splitless capillary injector and Ni-63 electron capture detector. The retention times of the trihalomethanes were determined by running standards. Each trihalomethane was identified in the sample chromatogram by comparing the retention of the suspect peak against that of the standard. The concentration of each trihalomethane was calculated by comparing the peak areas of the samples to those of the standards.

2.3.8 Determination of chemical oxygen demand (COD)

Sample (100 mL) was placed in a round-bottomed flask and dichromate solution (25 mL) was added. Concentrated

sulphuric acid (75 mL) was then added carefully and the mixture was mixed after each addition. Glass beads were added to the reflux mixture to prevent bumping. After refluxing for 2 hrs, the condenser was cooled and then washed with deionised water (25 mL). The refluxed mixture was transferred to a 500 mL Erlenmeyer flask, and the reflux flask was washed 4 times with deionised water. The sample was diluted to 350 mL and the excess dichromate was titrated with standard ferrous ammonium sulfate. A blank sample consisting of 50 mL deionised water and reagents was refluxed in the same manner.

2.3.9 Determination of residual chlorine

Sodium sulfate (25 g) was dissolved in 1 litre of distilled water and this was standardized against potassium dichromate. Water sample (100 mL) was placed into a conical flask and an excess of potassium iodide crystal was added to the sample. The mixture was heated whilst stirring to completely dissolve the potassium iodide crystals. The mixture was cooled and titrated with sodium thiosulphate using starch as an indicator.

2.3.10 Determination of pH

pH was determined using a pH meter. The pH meter was calibrated using pH 4 and 7 buffers. After calibration, the glass pH electrode was immersed into the water samples and the pH was recorded.

Table 3: Concentration levels of THMs per sampling area for the month of June

Site	BDCM $\mu\text{g/L}$	DBCM $\mu\text{g/L}$	Chloroform $\mu\text{g/L}$	Bromoform $\mu\text{g/L}$	TTHMs $\mu\text{g/L}$
1	ND	0.003 ± 0.006	3.938 ± 0.058	0.003 ± 0.006	3.773 ± 0.055
2	0.763 ± 0.040	2.127 ± 0.162	4.717 ± 0.162	6.703 ± 0.127	14.31 ± 0.33
3	3.567 ± 0.208	6.310 ± 0.122	7.803 ± 0.038	ND	17.68 ± 0.157
4	8.257 ± 0.055	8.227 ± 0.032	10.290 ± 0.507	9.170 ± 0.060	35.993 ± 0.414
5	4.590 ± 0.408	9.180 ± 0.070	15.647 ± 0.159	11.763 ± 0.129	41.18 ± 0.447
6	7.137 ± 0.021	9.397 ± 0.110	31.126 ± 0.811	28.247 ± 0.110	76.037 ± 0.768

Table 4: Concentration levels of THMs per sampling area for the month of July

Site	BDCM $\mu\text{g/L}$	DBCM $\mu\text{g/L}$	Chloroform $\mu\text{g/L}$	Bromoform $\mu\text{g/L}$	TTHMs $\mu\text{g/L}$
1	2.683 ± 0.047	1.970 ± 0.020	3.770 ± 0.058	0.003 ± 0.006	8.243 ± 0.090
2	1.983 ± 0.070	ND	4.850 ± 0.065	ND	6.787 ± 0.116
3	3.993 ± 0.021	2.803 ± 0.025	5.180 ± 0.020	8.107 ± 0.025	20.083 ± 0.051
4	7.813 ± 0.032	4.223 ± 0.015	10.07 ± 0.076	12.770 ± 0.025	34.887 ± 0.092
5	10.23 ± 0.066	12.800 ± 0.010	18.80 ± 0.010	18.800 ± 0.006	60.627 ± 0.072
6	10.88 ± 0.042	14.750 ± 0.070	40.59 ± 0.662	19.800 ± 0.040	86.020 ± 0.650

Table 5: Concentration levels of THMs per sampling area for the month of August

Area	BDCM µg/L	DCBM µg/L	Chloroform µg/L	Bromoform µg/L	TTHMs µg/L
1	ND	1.093±0.015	ND	6.520±0.010	7.613±0.012
2	ND	1.787±0.015	4.800±0.010	9.217±0.015	15.803±0.015
3	5.883±0.505	10.100±0.015	8.103±0.006	7.023±0.021	31.107±0.049
4	9.203±0.025	11.300±1.010	13.123±0.015	18.030±0.015	51.653±0.015
5	6.317±0.015	17.010±0.015	27.530±0.075	16.210±0.021	67.067±0.100
6	12.23±0.036	22.130±0.015	44.387±1.358	44.387±1.358	109.030±1.370

Table 6: Concentration levels of THMs per sampling area for the month of September

Area	BDCM µg/L	DCBM µg/L	Chloroform µg/L	Bromoform µg/L	TTHMs µg/L
1	18.130±0.208	ND	ND	ND	18.033±0.208
2	26.530±0.551	18.400±0.100	27.033±0.153	18.000±0.100	89.800±10.520
3	29.900±0.557	4.067±0.153	20.267±0.153	25.200±0.300	79.433±1.026
4	40.230±0.351	26.270±0.321	27.500±0.100	36.170±0.306	130.167±0.924
5	50.500±0.265	29.970±0.321	35.267±0.351	30.030±0.208	145.767±0.635
6	25.170±0.252	40.170±0.493	43.400±1.002	36.770±0.551	145.133±2.272

Table 7: Percentage recoveries at three spiking levels

Spiking level (µg/L)	Chloroform			Bromoform			DCBM			DCBM		
	5	10	20	5	10	20	5	10	20	5	10	20
Mean TTHMs (µg/L)	3.89	7.56	16.29	3.89	7.56	16.29	4.26	7.84	17.9	4.6	8.87	15.57
Recovery (%)	77.8	75.6	81.5	77.8	75.6	81.5	85.2	78.4	89.4	92	88.7	77.9

3. RESULTS AND DISCUSSION

Figures 1-5 and tables 3-6 show that the trihalomethanes are present in both raw and treated water. The raw water from Gwenoro dam contained mainly chloroform (Tables 3-6). Levels of chloroform, the most common THM, are generally high in chlorinated water originating from surface water, because of higher organic matter present [22].

The trihalomethanes are liquids at room temperature. They are extremely volatile, with vapour pressures at 25 °C ranging from 0.80 kPa for bromoform to 23.33 kPa for chloroform. The THMs are only slightly soluble in water, with solubilities less than 1 mg/ml at 25 °C. Their log octanol–water partition coefficients range from 1.97 (chloroform) to 2.38 (bromoform) [23]. Hence, the low concentrations obtained (Tables 3-6) can be attributed to evaporation of the THMs whilst in the lake. Levels of THMs increase as the chlorinated water moves from the water treatment plant through the distribution system, because of the continued presence of residual chlorine. Figures 1-4 show the properties of the water analysed. The pH of the water remained fairly constant throughout the water samples. The pH for raw water was

lower than the rest of the sampling sites. This could be because the treatment process controls the pH within acceptable limits. COD decreases as THM concentrations increase. This indicates that the dissolved organic matter is consumed as the THMs are being formed [24]. This was evident in all samples collected for the different months (Figs 1-4).

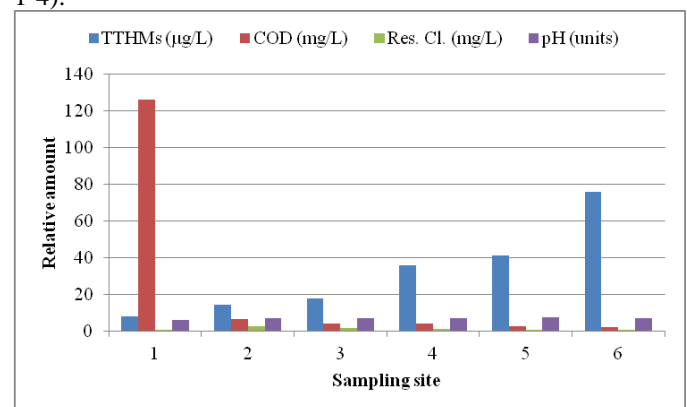


Fig 1: Variation of concentration levels of TTHMs with pH, COD and residual chlorine for the month of June.

Since THMs are as a result of the reaction between organic matter in water and chlorine used for the disinfection, chlorine is consumed whilst the concentration of TTHMs increases (Figs. 1-4). Thus the graph indicated that for an increase in the concentration of total THMs, there is a decrease in concentration levels of residual chlorine. The same general trend was observed in the samples collected for the different months (Figs 2-4). There is also an increase in levels of TTHMs from sampling area 1 to 6 for the four months (June-September) (Figs 1-4). Chloroform has the highest concentration levels of the four trihalomethanes (Tables 3-6) since it is the most common trihalomethane.

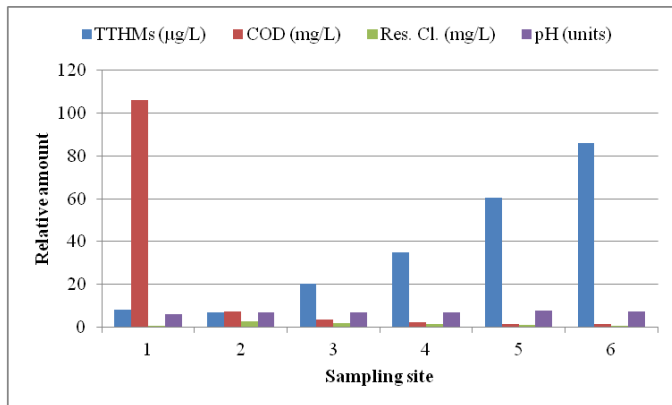


Fig. 2: Variation of concentration levels of TTHMs with pH, COD and residual chlorine for the month of July.

The organic matter in raw water is high as shown by the high values for chemical oxygen demand values obtained (Figs. 1-4). In treated water, the organic matter was generally low but enough to interact with chlorine to form trihalomethanes. The low values of the chemical oxygen demand in treated water is because of the treatment processes carried out at Works Plant which include coagulation, flocculation and sedimentation. The concentration levels of total THMs in raw water are low (Figs. 1-4). Although disinfected sewage effluent is discharged into the water source, minute quantities of the TTHMs were obtained because the THMs are highly volatile and they escape into the atmosphere whilst in the dam.

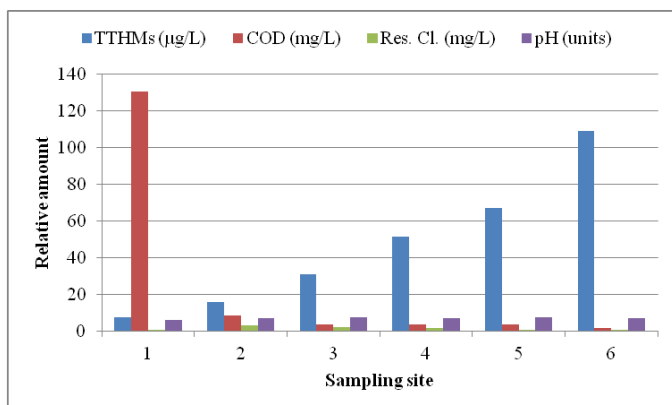


Fig. 3: Variation of concentration levels of TTHMs with pH, COD and residual chlorine for the month of August.

No relationship between pH and concentration levels of trihalomethanes could be established. This is because the pH of water remained fairly constant at all the sampling sites. However, at high pH, more hypochlorite ions are formed, causing the effectivity of chlorine disinfection to decrease and more trihalomethanes are formed [20]. The maximum EPA allowable pH levels range from 6.0 to 9.0. All the pH levels for the water samples collected ranged between 6.02 and 7.73 (Figs 1-4) and hence were within acceptable levels.

Generally the values obtained for the COD test are high because the method represents a more complete oxidation. Due to the extremely strong oxidizing conditions, the COD represents the oxidation of most organic and inorganic compounds. High organic matter was detected in raw water with concentrations being above 100mg/L. This is due to the discharge of sewage effluent into the dam as well as run off water containing organic matter. In treated water, the concentration of organic matter was greatly reduced. This is because of the water treatment processes at the water works plant, before chlorination, which eliminates some of the organic matter. There was also a decline in the organic matter along the distribution system. This can be attributed to the consumption of organic matter in the formation of trihalomethanes. In some instances, more organic matter was detected along the distribution system [11]. This could have been because of burst pipes, which allowed organic matter to dissolve into the water. Burst pipes are frequent in the city.

The data obtained indicate that chloroform is the most abundant of the four trihalomethanes (Tables 3-6). Chlorine is also more reactive than bromine, hence chlorine substitution is more likely to occur, and thus chloroform is in higher concentration.

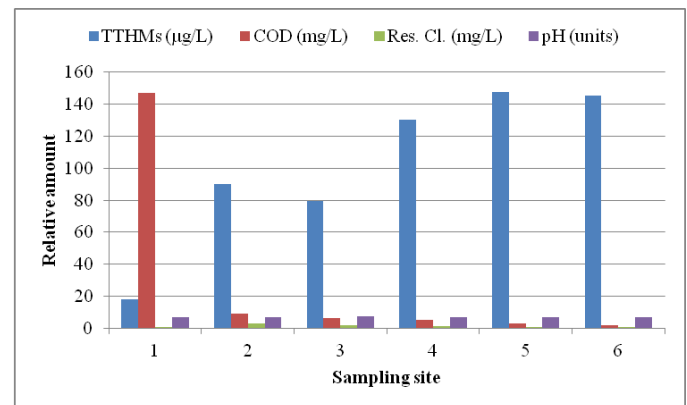


Fig. 4: Variation of concentration levels of TTHMs with pH, COD and residual chlorine for the month of September.

Statistical treatment of the results obtained using the correlation analysis test indicates that there is a negative correlation between trihalomethane concentration and the chemical oxygen demand. In the analysis there are two hypotheses, null hypothesis (H_0) and the alternate hypothesis

(Hi). Null hypothesis (Ho): the chemical oxygen demand does not affect the concentration levels of total trihalomethanes. Alternate hypothesis (Hi): chemical oxygen demand affects the concentration levels of total trihalomethanes.

The correlation is significant at the 0.01 level since the p-value is 0.00, which is less than 0.05, thus the null hypothesis is rejected whilst the alternative hypothesis is accepted.

There is also negative correlation between the trihalomethane concentration levels and the residual chlorine. The p-value obtained (0.00) is less than 0.05. There is a significant correlation at the 0.01% significance level. The null hypothesis is rejected whilst the alternative hypothesis is accepted.

Chlorine residue in water is maintained whilst it is in the distribution system. This ensures that the re-growth of microorganisms is prevented, thus keeping the water safe. Minute quantities of chlorine residue were detected in raw water, which could have been due to chlorine residue used in sewage and wastewater treatment.

Water samples collected from the treatment plant had TTHMs concentrations ranging from 3.773 $\mu\text{g/L}$ to 18.130 $\mu\text{g/L}$. These concentration levels are lower than those obtained in the residential areas which range from 6.833 $\mu\text{g/L}$ to 145.500 $\mu\text{g/L}$. There is a general increase in concentration of TTHMs with distance from the treatment plant (Figs. 1-4). The reaction between chlorine and organic matter is not instantaneous. The formation of trihalomethanes is dependant on the contact time between chlorine and organic matter. The greater the distance from the chlorination point the greater the time for the reaction between chlorine and dissolved organic carbon.

The total trihalomethanes studied did not exceed the maximum permissible concentration levels of 460 $\mu\text{g/L}$ set by the World Health Organization. The trihalomethane concentrations recorded were generally lower than the set standards of chloroform (200 $\mu\text{g/L}$), bromoform and dibromochloromethane (100 $\mu\text{g/L}$) and dichlorobromomethane (60 $\mu\text{g/L}$). [18] In the samples analysed, none exceeded these individual trihalomethane set standards. However, maximum permissible limits set by the EPA and Germany were regularly exceeded, for example the highest concentration levels of TTHMs for the months of August and September were 109.000 $\mu\text{g/L}$ and 145.800 $\mu\text{g/L}$ respectively. These concentration levels are above the 80 $\mu\text{g/L}$ set by these countries [20]. The lower concentration levels obtained could be due to the ever-increasing demand for portable water. The population of Gweru is increasing thus the demand for potable water is high as compared to the water supplied by the City Council. Therefore water spends less time in the distribution system and the contact time is reduced. The formation of trihalomethanes is also reduced.

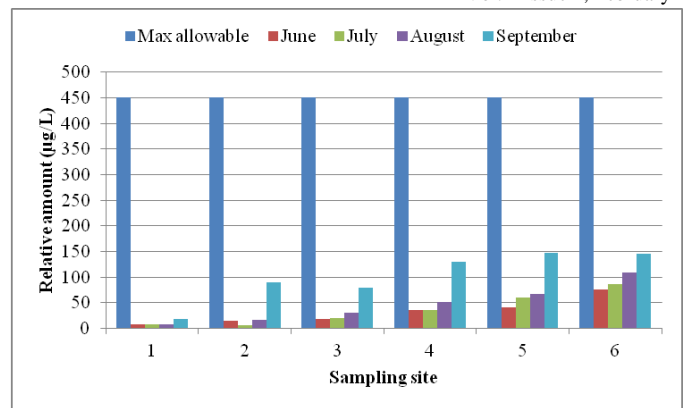


Fig. 5: Comparison of maximum allowable concentration levels and observed concentration levels of TTHMs.

The level of trihalomethanes detected depends upon a number of variables. Firstly, the status of the raw water prior to the treatment influence the levels detected. The process of coagulation, flocculation, sedimentation and filtration in the water treatment plant do not totally eliminate the dissolved organic matter. The chemical oxygen demand tests carried out on water sampled at the treatment plant indicate that some organic matter remained after treatment. The remaining organic matter at the plant ranged from 6.69 mg/L to 9.43 mg/L from June to September. There was a slight increase in the organic matter from the colder months to the warmer months. This increase could be due to the increase in the decomposition rate of materials as a result of increased reaction rates due to higher temperatures. Decomposition rates proceed faster at higher temperatures than at lower temperatures. When the dose and residual of the disinfectant are higher, more disinfection by-products are formed. When temperature increases, reaction take place faster causing higher chlorine concentration required for proper disinfection. This causes more halogenic by products to be formed. [1] The shortages of chemicals could be another contributing factor as to why the total elimination of organic matter cannot be achieved. The Sunday Mail reported that the responsible authorities had run out of funds to purchase chemicals [25].

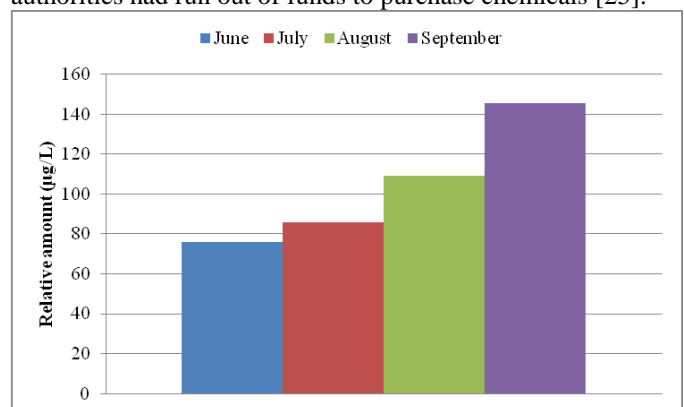


Fig. 6: Variation of TTHMs with sampling month.

There is a seasonal variation in formation of TTHMs (Fig 6). During the warmer months, there are high levels of THMs in comparison to colder months [20]. It has been postulated that this is linked to algae blooms. During summer months, algae growth is at its peak. THM levels are high due to contribution of extra cellular material from algae (increased concentration of soluble organic content)[20].

4. CONCLUSION AND FUTURE WORK

4.1 Conclusion

Trihalomethanes were determined present in raw and treated water. However, minute quantities were detected in raw water. The most abundant trihalomethane is chloroform with concentration levels ranging from 3.70 µg/L to 45.89 µg/L. There is an increase in concentration levels of trihalomethanes with increasing distance from the chlorination point. There is also a slight increase in the concentration of TTHMs in the warmer months, with the highest concentration levels increasing from 60.43 µg/L to 145.80µg/L.

4.2 Future work

Further study should be conducted covering a larger area of the city and also a study can be carried out for a large city and results can be compared.

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