Research Paper

Investigating disinfectant by-products in Harare potable water supply, Zimbabwe

Kuitakwashe Nhongo, Zvikomborero Hoko and Jameson Kugara

ABSTRACT

Formation of disinfectant by-products was investigated in the Harare water supply system from February to April 2015. Sampling sites were selected from the lake, Morton Jaffray Water Treatment Works and critical points in the distribution system. The spatial variations of trihalomethanes and selected water quality parameters were investigated for 15 sampling points in 5 sampling campaigns to assess suitability for drinking. All trihalomethane species were measured, namely chloroform, bromodichloromethane, dibromochloromethane and bromoform. Only chloroform and bromodichloromethane were detected. The study confirmed that there is trihalomethanes formation in the Harare water distribution system and that it is affected by the residence time and presence of organic matter in the system. However, the levels of trihalomethanes are generally within the levels suggested by the World Health Organization. Only bromodichloromethane presents a risk for long-term exposure as it had levels that exceeded the limit for long-term exposure suggested by the United States Environmental Protection Agency. Bromodichloromethane, turbidity and free residual chlorine levels were not suitable for drinking in some of the zones. Boosting of chlorine residuals is necessary especially in areas with free chlorine less than 0.2 mg/L. Injection of ammonia, periodic cleaning of storage reservoirs, and flushing of lines will reduce trihalomethanes formation.

Key words | bromodichloromethane, disinfection by-products, Harare, residual chlorine, trihalomethanes, water quality

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INTRODUCTION

Increased pollutant loadings on surface waters is one of the topical issues that has raised global concern. According to Hu *et al.* (2003), the addition of chlorine disinfectants and ozone can transform organic pollutants to disinfection by-products (DBPs). Trihalomethanes (THMs) are amongst the first and most common DBPs that were detected in chlorinated water (Nissinen *et al.* 2002). DBPs, that include THMs, are formed when disinfectants used in treatment of water react with organic precursors such as those from algal and wastewater sources, and inorganic precursors such as bromide, iodide and nitrite (Krasner 2009). The presence of algal organic matter has been reported as promoting formation of THMs (Liang & Singer 2003). Total Trihalomethanes (TTHMs) are made up of chloroform, bromodichloromethane (BDCM), dibromochloromethane and bromoform (Lantagne *et al.* 2008). The formation of THM compounds is dependent on raw water quality amongst other factors. Raw water quality with high levels of bromide favours the formation of brominated THMs in which the concentrations usually occur the greatest for BDCM, followed by dibromochloromethane and lastly bromoform (Wei *et al.* 2010).

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The regulation of THMs has not been part of water quality monitoring routines in many developing countries including Zimbabwe. However, in the United States and Europe, these are regulated and monitored regularly. In the Southern African Region, South Africa also regulates THMs (Matsebula 2009). Excess concentrations of THMs in drinking water have been linked to public health problems such as cancer, liver and kidney damage as well as birth defects. Weisel *et al.* (1999) concluded, from experimental animals, that exposure of rats and mice to THMs resulted in intestine, kidney and liver tumours; miscarriage; and delay in foetal development. Short-term health effects of THMs on humans were evidenced during its previous use as an inhalation anaesthetic in which it was associated with cardiac arrhythmias and abnormality of the liver and kidney (New Hampshire Department of Environmental Science (NHDES) 2006). An association was also found between human exposure to THMs and bladder cancer (World Health Organization (WHO) 2005). Chlorination of water in Peru was stopped in most potable water supplies to protect the public from exposure to THMs (Murphy & Craun 1990). However, the decision to stop chlorination of water resulted in a cholera epidemic that killed 4,000 Peruvians (Anderson 1991).

The main sources of water for the City of Harare are Lake Chivero and Manyame Dam which supply raw water to Morton Jaffray Water Treatment Works that has a design capacity of 614,000 m^3/day (Muisa *et al.* 2011). Harare also gets water from Seke and Harava Dams which supply raw water to Prince Edward Treatment Works with a design capacity of 90,000 m^3/day. The main water source for Harare, Lake Chivero, has been reported to contain high levels of nutrients and algae (Hoko & Makado 2011). There has been increased pollutant loading into the lake (Kibena *et al.* 2014). According to Gratwicke *et al.* (2003), the main sources of pollutant loadings are industries and municipal wastewater discharges from Harare and Chitungwiza. There are a number of industrial sites in Harare. Around 1996/7 industrial capacity utilization was above 85% (Saungweme & Mufandaedza 2013) but from 1998 to 2008 it declined drastically due to poor economic performance resulting in many industries closing. According to Zhou & Madhikeni (2013), capacity utilization rose from 10% in 2008 to 30–50% following dollarization of the economy in 2009. However, the manufacturing sector's recovery remained suppressed due to competition from imports, high costs of borrowing, and erratic power and water supplies (Zhou & Madhikeni 2013). Main industries include food processing, plastic, fertilizer, cement, aluminium, steel, cooking oil and tobacco. Principal water pollutants from industries are heavy metals (calcium, magnesium, aluminium copper and iron), oils and grease while nitrates and phosphates are released from sewage treatment plants (Masere *et al.* 2012; Muserere *et al.* 2014).

The main water works for Harare (Morton Jaffray) uses conventional processes which include chlorination of water at the end of the process. Thus given the poor quality of the raw water source and application of chlorine during treatment, the formation of DBPs including THMs is highly likely in the drinking water for Harare. An attempt to establish the levels of THMs in Harare's drinking water supply was made in 2003 (Kututwa 2003). The level of TTHMs was then found to be low, ranging from 0.12 to 0.33 μg/L. However, with the continued deterioration of water quality including algae formation, it is likely that the level of THMs in the water has increased.

This study was carried out from February 2015 to April 2015. The study determined the levels and the spatial variation of THMs and selected water quality parameters to assess the suitability of water for drinking.

STUDY AREA

Background on Harare

Harare is the capital city of Zimbabwe and is located in the Upper Manyame Catchment. The city covers an estimated area of 890 km^2 and is surrounded by four local authorities of Chitungwiza, Norton, Ruwa and Epworth (Nhapi & Hoko 2004). The catchment area is one of the most populated and urbanized in Zimbabwe (Masere *et al.* 2012). The population of Harare Province was estimated to be 2,123,132 people out of the national total of 13,061,239 (ZimStat 2012). The city, being located upstream of Lake Chivero, its potable water source, contributes pollution to the lake (Zanamwe 1996). Figure 1 shows the location of the study area.

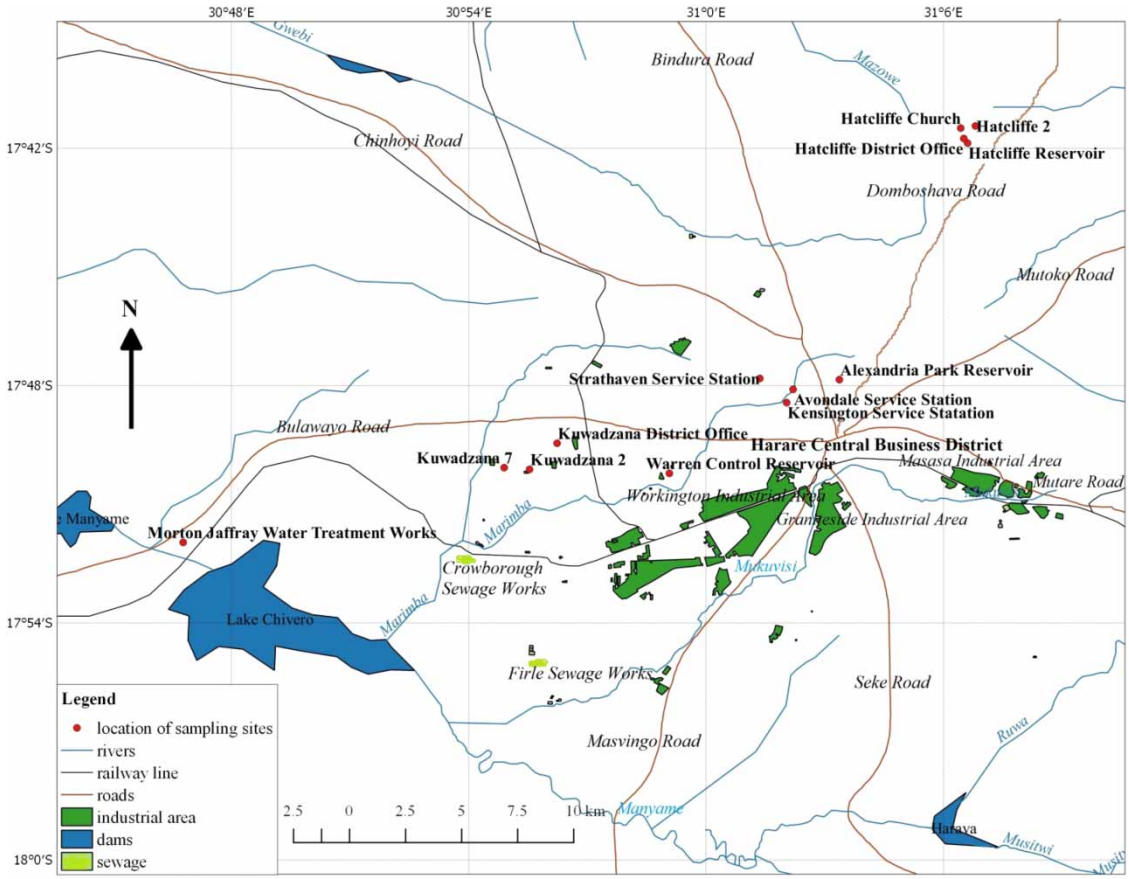

Figure 1 | City of Harare showing the location of sampling sites.

Background on water supply in Harare

The water supply system includes surface water sources, a conventional water treatment plant, transmission system, storage and distribution reservoirs and a distribution network. The main source of drinking water is Lake Chivero, located about 35 km south-west of Harare. The lake was constructed in 1952 to supply water to Harare and the surrounding farms. The lake is fed by three main rivers, namely Manyame, Mukuvisi and Marimba. These rivers are prone to pollution from industries and wastewater treatment plants in Harare and Chitungwiza that discharge poorly treated effluents (Nhapi 2009). In the late 1960s, the lake was reported to be hypereutrophic (Thornton & Nduku 1982). According to Nhapi *et al.* (2002), the eutrophic state has persisted to date due to poor wastewater management in the basin.

The Harare network is old and dilapidated and it experiences many problems. Some of the challenges include low coverage, high non-revenue water, frequent pipe leakages and bursts, intermittent water supply services and poor drinking water quality. Hove & Tirimboi (2011) reported non-revenue water of 35–40% while the current non-revenue water could be as high as 60% (Ndunguru & Hoko 2016). Poor drinking water quality was linked by Chirisa *et al.* (2015) to be one of the causes for the 2008 to 2009 cholera epidemic in Zimbabwe that claimed the lives of about 4,288 people. There has been general user rejection of the water based on poor quality perceptions and this is one factor contributing to poor revenue collection (<50% in recent years) by the City of Harare.

Background on Morton Jaffray Water Treatment Works

Morton Jaffray (MJ) Water Treatment Works is located about 35 km south-west of Harare. It was constructed in three phases. The first phase was completed in 1953 while

the second and third phases were completed in 1978 and 1996 respectively. The design capacity of the first phase is 160,000 m^3/day while the second and third phases have 227,000 m^3/day each, giving it a total of 614,000 m^3/day (Hoko & Makado 2011).

At least seven water treatment chemicals are used at the plant. Amongst the chemicals are activated carbon, sulphuric acid, algaecides, high test hypochlorite (HTH), aluminium sulphate, sodium silicate, chlorine gas and lime (Hoko & Makado 2011). Only three chemicals (aluminium sulphate, lime and chlorine) were used some years back before the current eutrophic state of the lake.

Figure 2 presents a flow chart of MJ Water Treatment Works including the two sources of raw water. However, the supply from Lake Manyame was closed during the study period due to maintenance works.

The first chemical added is activated carbon which is to remove odour and colour at the mixing chamber. Sulphuric acid (98%) is added to reduce the pH to a range suitable for coagulation. Pre-chlorination is done at coagulation and flocculation stages using HTH at about 0.37 mg/L to kill algae and other pathogens. Aluminium sulphate coagulant is added at levels varying from 50 to 60 mg/L and sodium silicate is added at 0.5 mg/L to enhance flocculation.

Disinfection is done at about 0.8 mg/L using chlorine gas followed by pH correction where lime is added to the treated water. Water is then channelled to the clear water storage reservoir which forms the sump for the clear water pumping station at the water works. The water is then pumped to Warren Control Reservoir (WCR) located within the supply area in Harare. Chlorine gas and ammonia are added at 1 mg/L and 0.25 mg/L respectively at WCR to maintain free chlorine within the acceptable range.

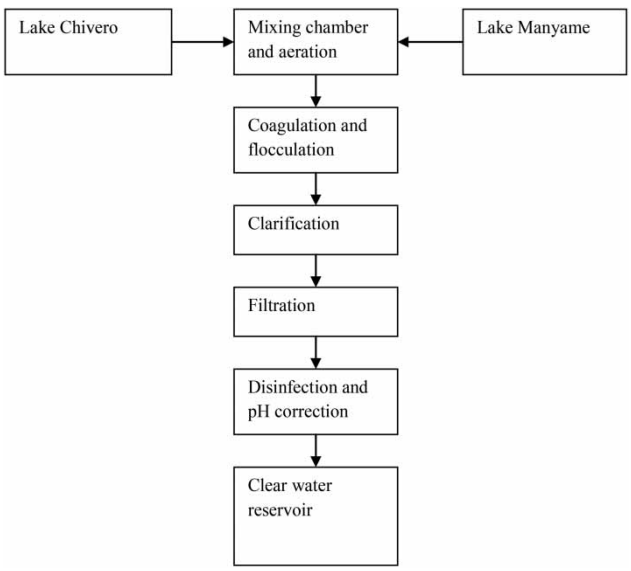

Figure 2 | Flow chart of MJ Water Treatment Works.

MATERIALS AND METHODS

Location of sampling points

A total of three zones namely Kuwadzana (that receives water first), Avondale (middle location on the selected distribution network that covers Strathaven and Kensington) and Hatcliffe (furthest location) were selected for water sampling. Figure 3 shows the schematic layout of the water supply system and location of sampling points.

Water samples were also collected from key stages of the water treatment processes at MJ, WCR, the main booster station located soon after the first zone, Alexandra Park Reservoir (ALR) that provides water to the middle zone and Hatcliffe Reservoir (HAR), located furthest. This selection allowed investigation of spatial variation and also impact of retention time in the system.

Selection of parameters that were analysed

Parameters that were analysed include free and total residual chlorine, turbidity, total solids, chemical oxygen demand (COD) and THMs. The rationale for the selection of parameters were: (a) residual chlorine reacts with organics to form DBPs (Wei *et al.* 2010); (b) THMs are the most common group of DBPs formed after chlorination of water that has organic matter (Wei *et al.* 2010); (c) turbidity is a good indicator of suspended matter in water that may be organic and is a common drinking water parameter; (d) total solids are linked to organic matter in polluted water samples as they may contain colloidal organic and inorganic matter, silt, sand, algae and aquatic planktons (APHA, AWWA, WEF 2005); and (e) COD is a common parameter used in drinking water to indicate the presence of organic matter in water samples (APHA, AWWA, WEF 2005).

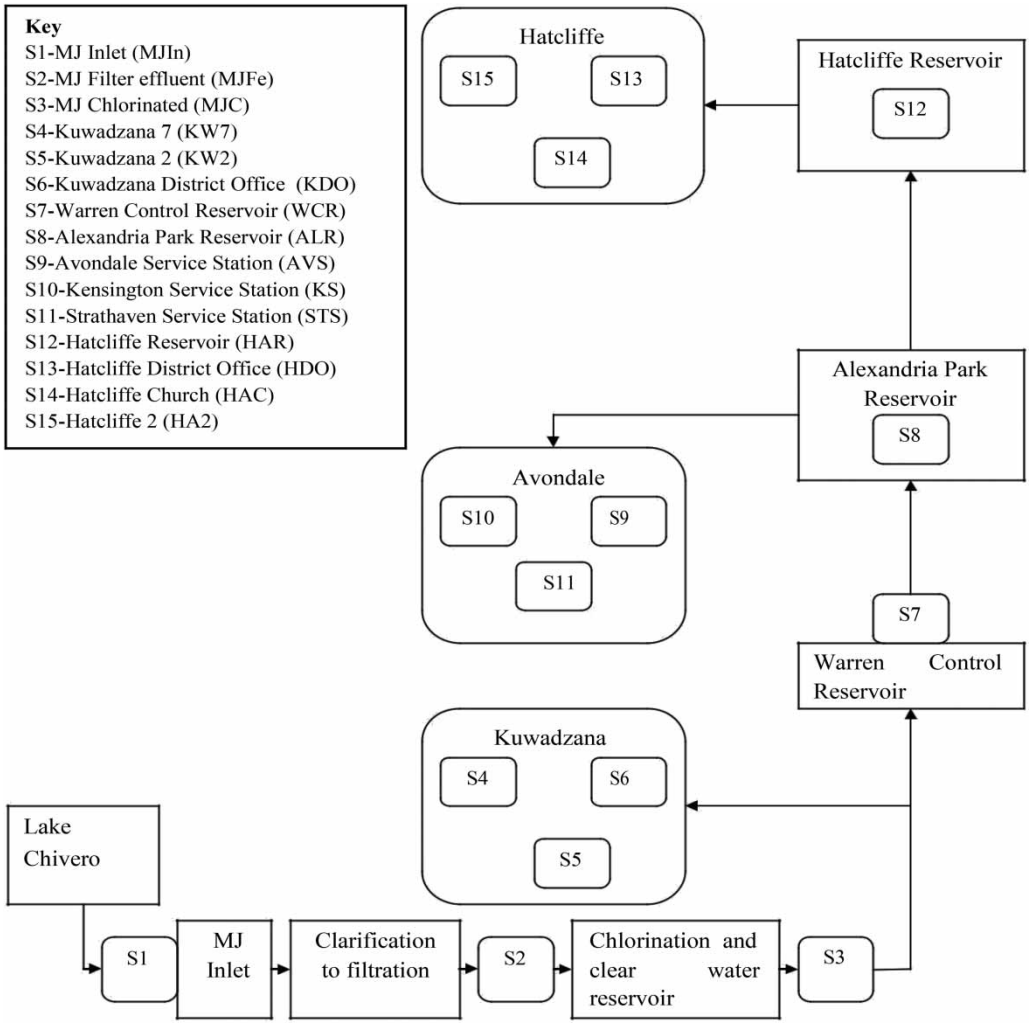

Figure 3 | Location of sampling sites.

Determination of suitability for public consumption

In order to determine the suitability of water for public consumption, water quality parameters were compared to international and national standards and guidelines. Turbidity values were compared with limits suggested by the World Health Organization (WHO) Guidelines (2011) and Standard Association of Zimbabwe (SAZ) Standard (1997). Residual free chlorine was compared with WHO Guidelines (2011). THMs were compared with United States Environmental Protection Agency (USEPA) Maximum Contamination Levels (1998) and WHO Guidelines (2011). In addition, the following THM additive toxicity ratio suggested by WHO (2004), that seeks to establish the total THM standard to account for additive toxicity, was used.

$$\frac{C_{bromoform} + C_{BDCM} + C_{DBCM} + C_{chloroform}}{GV_{bromoform} + GV_{BDCM} + GV_{DBCM} + GV_{chloroform}} \leq 1 \quad (1)$$

where C = concentration and GV = WHO Guideline value.

If the ratio is greater than 1, the water will present a health risk and will not be suitable for public consumption.

Sample collection and preservation

Grab samples were collected at selected sampling points as recommended by APHA, AWWA, WEF (2005). At taps,

water was allowed to flow for 5 minutes to allow the water temperature to stabilize before filling water in 750 mL bottles. Water samples were collected at reservoirs using a plastic sampling container tied to a string. Water was transferred from the plastic sampling container to 750 mL bottles. All sampling bottles were filled up and closed to prevent the entry of air.

Water samples were preserved for COD analysis by adding 2 mL of 99% sulphuric acid to the 750 mL bottle to reduce the pH to less than 2. Total solids were preserved by refrigeration whilst free and total residual chlorine were analysed immediately. Samples for THMs were preserved by addition of granular sodium thiosulfate to empty sampling bottles at 3 mg per 40 mL sample, followed by addition of hydrochloric acid to reduce the pH to less than 2 (USEPA 2006). To prevent glassware formation of DBPs, glassware was thoroughly cleaned in hot water with detergent and then rinsed. The glassware was then baked in an oven for 2 hours at 150 °C to eliminate any organics present. Gloves were used to handle glassware to avoid contamination. All samples were transported in a cooler box and were refrigerated at a temperature below 4 °C before analysis.

Methods of water quality analysis

Turbidity, pH, temperature, and free and total residual chlorine were measured onsite while total solids and COD were analysed at the University of Zimbabwe Water and Wastewater Laboratory. Turbidity was analysed using a potable HI 98703 Fast Tracker Turbidity Meter. Water pH was measured using an ECO Tester pH1 type potable pH meter. Free and total residual chlorine were analysed using Diethyl-p-Phenylene Diamine (DPD) tests with DPD Tablet No. 1 and 3 respectively. The oven dry method suggested by APHA, AWWA, WEF (2005) was used to analyse total solids. COD was analysed using the closed reflux, titrimetric method guidelines as recommended by APHA, AWWA, WEF (2005). THMs were analysed at the South African Bureau for Standards (SABS) laboratory using the gas chromatography mass spectrometry (GC-MS) SABS Water Laboratory Method 059. The GC column used was an Rxi (R) 5 Sil MS. The injection technique was headspace, the carrier gas was helium and the makeup gas was nitrogen. The injector temperature was 250 °C while the oven temperature was 35 °C for 1 minute, which was then increased to 90 °C at a rate of 5 °C per minute for 11 minutes and finally increased to 180 °C at a rate of 25 °C per minute for 4.6 minutes. Water sample preparation time was 5 minutes and analysis time was 16.6 minutes.

Data analysis and interpretation

Analysis of variance (ANOVA), independent t-test and coefficients of variation were used for data analysis. Tables and graphs were used for data presentation and interpretation. Measured values were compared to national and international drinking water guidelines and standards. These included the Standard Association of Zimbabwe (SAZ) Drinking Water Standards of 1997, World Health Organization (WHO) Guidelines of 2011 and United States Environmental Protection Agency (USEPA) Maximum Contamination Levels of 1998.

RESULTS AND DISCUSSION

Spatial variation of total solids

Table 1 shows total solids that were measured at selected sampling points whilst Figure 4 shows the average values.

Total solids for raw water was higher than other sampling points except for sampling points in Hatcliffe.

Table 1 | Total solids measured from February to April 2015

Parameter	MJInlet (mg/L)	MJFilter (mg/L)	MJChlorinated (mg/L)	Kuwadzana (mg/L)	Avondale (mg/L)	Hatcliffe residents (mg/L)
Total solids ($n = 75$)	220–2,096 (710 ± 490)	158–2,058 (630 ± 472)	142–524 (276 ± 134)	180–1,590 (483 ± 453)	164–2,198 (568 ± 609)	312–4,194 (1,193 ± 1,315)

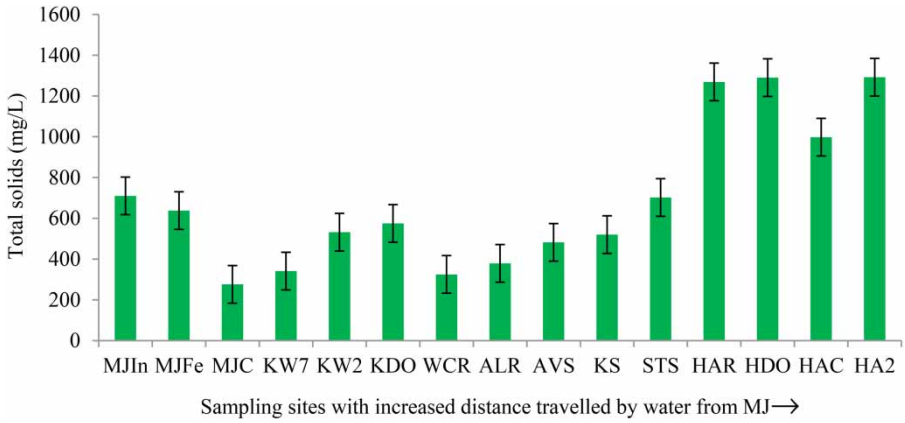

Figure 4 | Average total solids measured from February to April 2015 (MJIn = MJ inlet; MJFE = MJ Final effluent; MJC = MJ after chlorination; KW7 = Kuwadzana 7; KW2 = Kuwadzana 2; KDO = Kuwadzana District Office; WCR = Warren Control Reservoir; ALR = Alexander Park Reservoir; AVS = Avondale Service Station; KS = Kenington Service station; STS = Strathaven Service Station; HAR = Hatcliffe Reservoir; HDO = Hatcliffe District Office; HAC = Hatcliffe Church; HA2 = Hatcliffe 2).

Total solids were reduced by the conventional water treatment process at MJ resulting in lower levels after treatment. There was spatial variation of total solids between the study zones and this generally showed an increasing trend from the water works towards the furthest point. However this was not significant as variation of average values between zones had an ANOVA p value of 0.06. The increase could be caused by regrowth of algae and entry of solids through ingress of groundwater into the distribution system due to changes in pressure resulting from intermittent water supply. Insufficient pressure in a pipeline, which is often due to intermittent supply of water, is a common cause of distribution system contamination worldwide (Lee & Schwab 2005). In a system experiencing intermittent water supply, pressure drops significantly when supply is cut resulting in a vacuum effect in the pipe, which can then draw in contaminants through leaks in the pipe including through joints especially for old networks (Lee & Schwab 2005). Harare's water supply system is generally very old and has been experiencing high water losses with non-revenue water reported to be around 60% (Ndunguru & Hoko 2016). The contamination of water in intermittent supply systems by groundwater ingress is more pronounced during rainy seasons when the water table is high compared to the dry season (Kumpel & Nelson 2013). Thus, when the water level is above the pipe there is higher pressure in the ground compared to that in the pipe when supplies are cut, resulting in movement of water into the pipe through cracked sections and joints. This study was carried out during the rainy season and thus the possibility of groundwater ingress into the pipeline was high.

The water supply in Harare in most parts has been intermittent due to the water rationing programme. This, coupled with the old age of the pipes which now experience many leaks and bursts, creates the opportunity for groundwater to enter the pipelines when pressure is low in the system. This appears to be serious in Hatcliffe, an area that was supplied with water for 2 to 3 days per week. The ingress of particles and groundwater, often of poor quality, through leaking joints creates a public health risk.

Spatial variation of turbidity

A summary of turbidity results is presented in Table 2. Results were compared to WHO Guidelines (2011) and SAZ Standard (1997). Figure 5 shows the spatial variation of average values of turbidity.

The coefficients of variation of turbidity in each of the zones were 23, 20 and 143% in Kuwadzana, Avondale and Hatcliffe, respectively. There were significant differences in mean turbidity levels between Kuwadzana and Hatcliffe; and Avondale and Hatcliffe. Mean levels were within SAZ (1997) Standard of 1 NTU in Kuwadzana and Avondale but far above this limit in Hatcliffe. The average turbidity of 5.8 NTU for raw water was higher than in the distribution system. The level of turbidity was reduced during water treatment. The average

Table 2 | Turbidity measured from February to April 2015

Parameter	MJ inlet (NTU)	MJ filter effluent (NTU)	MJ after chlorination (NTU)	Kuwadzana (NTU)	Avondale (NTU)	Hatcliffe residents (NTU)
Turbidity ($n = 75$)	3.62–6.70 (5.81 ± 0.89)	0.49–0.68 (0.56 ± 0.07)	0.57–1.09 (0.83 ± 0.26)	0.55–1.14 (0.84 ± 0.19)	0.42–1.12 (0.83 ± 0.17)	0.58–18.10 (4.34 ± 6.21)
WHO (2011) Guideline	5	5	5	5	5	5
SAZ (1997) Standard Recommended	1	1	1	1	1	1
SAZ (1997) Standard Maximum limit	5	5	5	5	5	5

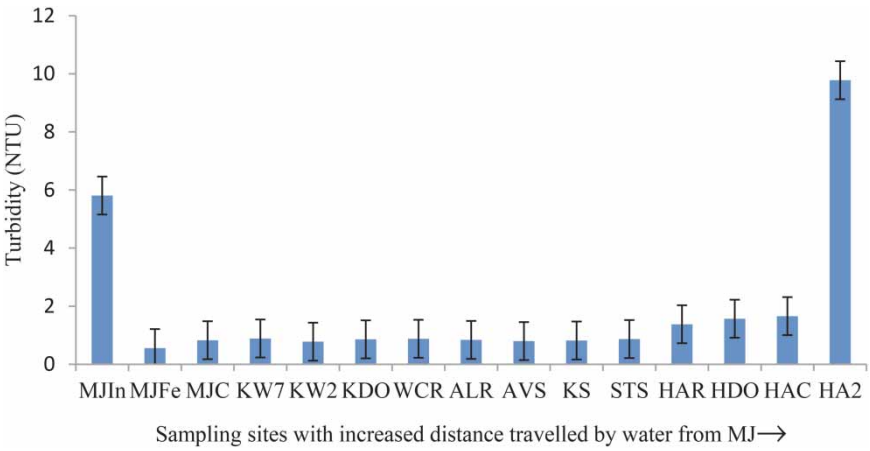

Figure 5 | Spatial variation of average turbidity for February to April 2015.

turbidity level of 0.6 NTU measured at MJ filter effluent suggests that the plant was performing well.

The average turbidity level measured after the point of chlorination was slightly higher than that of filter effluent, and the increase could be caused by the addition of chlorine gas and lime. Turbidity levels increased significantly in Hatcliffe and this can be attributed to an increase in suspended matter in the distribution system. This increase, like for solids, could be linked to ingress of dirty water due to intermittent supply and re-growth of algae. Higher turbidity levels can be linked to high organic matter that can react with residual chlorine to yield DBPs. The turbidity of water in Hatcliffe was highest and far exceeded that of treated water at MJ.

Spatial variation of chemical oxygen demand

A summary of COD levels measured at selected sampling sites is presented in Table 3. Measured values were not compared to international drinking water quality standards because there is no standard and guideline value in current documents. The average values of COD are presented in Figure 6.

Table 3 | Chemical Oxygen Demand measured from February to April 2015

Parameter	MJ inlet (mg/L)	MJ filter effluent (mg/L)	MJ chlorinated (mg/L)	Kuwadzana (mg/L)	Avondale (mg/L)	Hatcliffe residents (mg/L)
COD ($n = 75$)	3.52–12.76 (9.27 ± 3.49)	2.64–4.84 (3.46 ± 0.88)	0.44–4.40 (2.00 ± 1.56)	0.44–5.28 (3.26 ± 1.17)	0.88–11.44 (4.72 ± 3.07)	2.64–10.56 (6.04 ± 2.47)

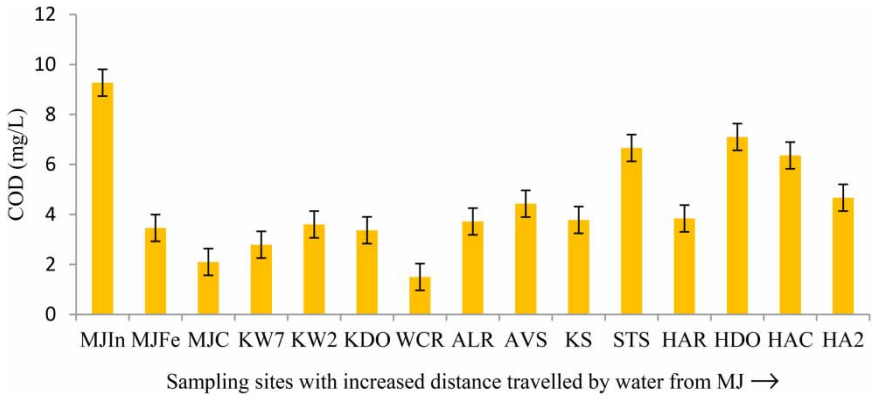

Figure 6 | Average chemical oxygen demand for February to April 2015.

The coefficients of variation in each of the zones were 36, 65 and 41% in Kuwadzana, Avondale and Hatcliffe, respectively. ANOVA results showed significant differences in mean levels of COD between Kuwadzana and Hatcliffe zones ($p = 0.01$). The average of 3.46 ± 0.88 mg/L measured at filter effluent suggests potential presence of organic matter components that may react with chlorine to form THMs. The level measured after the point of chlorination was lower than that for filter effluent. This could be caused by the addition of chlorine, an oxidizing agent, which can oxidize organics as well as ammonia to chloramines resulting in reduction in COD (USEPA 1999).

COD generally showed an increasing trend with distance from the water works. The reduction in COD at WCR is due to the addition of chlorine at the site. Chlorine levels are boosted at WCR. The increase in COD levels with distance from the water works could be caused by accumulation and re-growth of microorganisms and entry of dirty water due to leaks and intermittent supply in the distribution network that may increase the oxygen demand of water. The levels of solids and turbidity influence COD. The results of turbidity and solids also show an increasing trend with distance from the water works. The levels of COD in Hatcliffe were higher than the levels recorded in Avondale. This could be resulting from an increased amount of oxidizable organic material in the system due to ingress of dirty groundwater into the network owing to intermittent water supply for Hatcliffe. This is evidenced by higher levels of total solids and turbidity recorded in Hatcliffe than Avondale and other areas studied. However, the levels of COD in Avondale area were generally higher than those in Kuwadzana and at Warren Control. Thus, the trend suggests increasing COD with increasing retention time in the system which tends to increase contamination of the water in the old water supply systems (like that for Harare) that are prone to leakage and interrupted water supply. Higher levels of COD in Hatcliffe were comparable to the levels for raw water. Hatcliffe is the furthest zone on the network among the areas studied and also had the worst service in terms of water supply receiving water some 2 to 3 days in a week. Thus the impact of retention time of water and intermittent supply was more severe in Hatcliffe.

Spatial variation of free and total residual chlorine

Table 4 below shows a summary of results for chlorine for the selected sampling sites. Measured values were compared against WHO (2011) Guidelines. Figure 7 shows the spatial variation of average values of free residual chlorine.

The coefficients of variation for free residual chlorine in each zone were 73, 76 and 60% in Kuwadzana, Avondale and Hatcliffe, respectively, whilst they were 85, 59 and 50% for total chlorine residuals. High coefficients of variation values obtained imply higher deviation of treated water quality suggesting variations in dosages of chlorine. Of the three selected zones, the mean levels of free and total residual chlorine were significantly different ($p < 0.05$) between Avondale and Hatcliffe. Some 54% of water samples were below the lower limit recommended by WHO (2011) of 0.2 mg/L for free residual chlorine, suggesting underdosage of chlorine and decay due to reactions with organic matter in the bulk phase. Free and total residual chlorine

Table 4 | Residual chlorine results for February to April 2015

Parameter	MJ after chlorination (mg/L)	Kuwadzana (mg/L)	Avondale (mg/L)	Hatcliffe residents (mg/L)	WHO (mg/L)
Free residual chlorine ($n = 75$)	0.12–0.46 0.30 ± 0.17	0.05–0.42 (0.15 ± 0.11)	0.06–0.70 (0.25 ± 0.19)	0–0.11 (0.05 ± 0.03)	0.20–0.50
Total residual chlorine ($n = 75$)	0.25–0.95 0.60 ± 0.350	0.10–1.06 (0.34 ± 0.29)	0.15–1.31 (0.57 ± 0.34)	0.01–0.21 (0.10 ± 0.05)	–

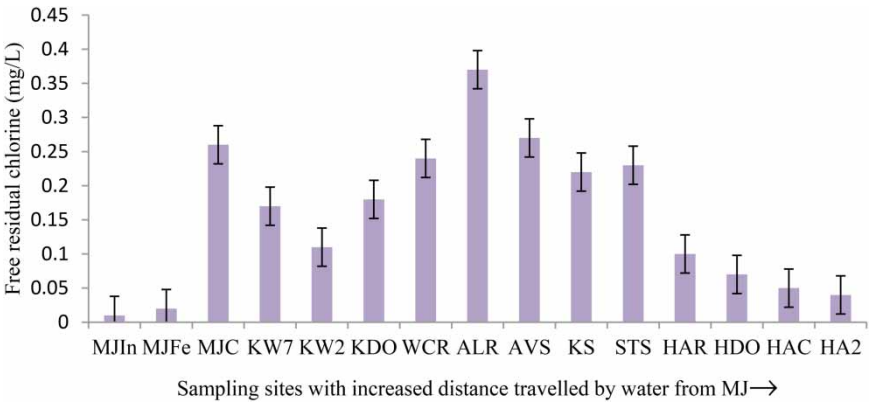

Figure 7 | Spatial variation of average free chlorine residual for February to April 2015.

were higher after chlorination at MJ and boosting at WCR compared to the sites in the distribution system. The concentration levels at ALR were higher than in Avondale because water is pumped from WCR to ALR first before being gravitated back to Avondale. As such due to decay with time the levels are lower in Avondale when compared to ALR. Alexander Park Reservoir surprisingly had higher levels of chlorine than Warren Control. The cause of this could not be established. The council confirmed that there is no further chlorine dosage beyond WCR hence the increase in chlorine in the reservoir could be due to accumulation of chorine in the sediments. The council reported that it has not been desludging or cleaning the reservoirs for some time. The decrease in residual chlorine in the distribution system after addition of chlorine at MJ and WCR could be caused by bulk phase reactions with organic matter. These reactions lead to the formation of DBPs (Al-Jasser 2007). Generally chlorine levels show a decreasing trend with distance beyond the points of chlorine addition. Results for solids, turbidity and COD, on the other hand, show an increasing trend with distance from MJ. Thus the reduction in free residual chlorine is also linked to increasing organic content in the water distribution system that reacts with chlorine and reduces its concentration.

In the distribution system, the average free residual chlorine was within the acceptable range of 0.20–0.50 mg/L recommended by WHO (2011) only in Avondale. Kuwadzana and Hatcliffe had levels below the lower limit of 0.20 mg/L. The recurrent outbreaks of cholera and typhoid in Harare have been linked to poor urban water and sanitation management (Chirisa *et al.* 2015). Another study on the 2008–9 cholera outbreak in Zimbabwe by Mason (2009) also concluded that the breakdown in water supply and sewerage disposal in high density urban areas was undoubtedly a main factor in the emergence and rapid spread of infections. Thus, the low levels of chlorine in the distribution system create a risk of contamination of the drinking water and transmission of pathogens from water to man, given the poor state of the sewerage system and intermittent water supply.

Spatial variation of trihalomethanes

Table 5 below shows measured THM values. Out of the four THM species measured, only chloroform and

Table 5 | Measured trihalomethanes for February to April 2015

Parameter	MJ water treatment	Kuwadzana (μg/L)	Avondale (μg/L)	Hatcliffe (μg/L)	USEPA (μg/L)	WHO (μg/L)
Chloroform ($n = 75$)	Not detected	5.00–8.00 (6.60 ± 0.80)	7.00–12.00 (9.00 ± 1.30)	19.00–23.00 (20.00 ± 0.90)	70.00[a]	300[b]
BDCM ($n = 75$)	Not detected	1.00–2.00 (1.00 ± 0.40)	1.00–3.00 (2.00 ± 0.50)	3.00–5.00 (4.00 ± 0.50)	0.60[a]	60[b]
TTHMs ($n = 75$)	Not detected	5.00–10.00 (7.60 ± 1.20)	9.00–14.00 (11.00 ± 1.20)	23.00–28.00 (24.00 ± 1.20)	80.00[c]	–

[a]USEPA maximum contamination goals (MCGLs).
[b]WHO Guidelines (WHO 2011).
[c]USEPA maximum contamination levels (MCLs) (USEPA 1998).

bromodichloromethane (BDCM) were detected at all sampling points except at MJ. Thus only chloroform and BDCM are presented and TTHMs in this study comprise of the sum of these two.

Results were compared to USEPA (1998) and WHO (2011). All values of chloroform and TTHMs were within the acceptable limits by USEPA Standard (USEPA 1998) and WHO Guidelines (WHO 2011). All BDCM values were within the acceptable limit suggested by WHO (2011). However, all values of BDCM were above maximum contamination levels (MCLs) of 0.6 μg/L for long-term exposure set by USEPA (1998). Thus at present only BDCM could be of major concern when considering the MCLs as it was above the acceptable limit of 0.6 μg/L for long-term exposure proposed by USEPA (1998). Lake Chivero, Harare's main water supply source was eutrophic by the mid-1960s (Magadza 2008). Other studies (Nhapi *et al.* 2002) have confirmed that the eutrophic state has persisted and shown a trend of deterioration of water quality in the lake due to poor wastewater management in the basin. Thus, Harare's potable water has been prone to formation of THMs for over 50 years leading to a risk of long-term exposure.

The calculated WHO THM additive toxicity ratios for selected zones based on Equation (1) are shown in Table 6. Ratios obtained in the three zones which ranged from 0.04 in Kuwadzana to 0.13 in Hatcliffe were far less than the WHO THM ratio limit of 1 suggested in WHO (2004).

Table 6 | Calculated THM additive toxicity ratios for February to April 2015

	Kuwadzana	Avondale	Hatcliffe	WHO Ratio Limit
Calculated WHO ratio	0.04	0.06	0.13	≤1

Figures 8 and 9 show the spatial variation of chloroform and BDCM, respectively.

The coefficients of variation in each of the zones were 12, 14 and 6% in Kuwadzana, Avondale and Hatcliffe, for chloroform. The coefficients were 10, 25 and 13% for BDCM and 16, 11 and 5% for TTHMs. Lower coefficient of variation values obtained indicates lower variation of levels of THMs which could be linked to the slow rate of formation of THMs. There were statistically significant differences ($p < 0.05$) in mean levels of chloroform, BDCM and TTHMs between all successive zones. Beyond the water works, Kuwadzana which is the first area to receive water from the plant had the lowest level of TTHMS while Hatcliffe, which is furthest from the plant, had the highest TTHM levels. Results of COD also show a similar pattern where the highest levels were found in the furthest zone. Thus THM formation appears to be linked to residence time of the water in the system and presence of organic matter as inferred from COD values. Algae has been reported as a problem in Harare's drinking water (Hoko & Makado 2011). As such there is the possibility of algae re-growth in the distribution system that could be increasing the formation of chloroform. Reactions between chlorine and organics to form THMs is time dependent (Liang & Singer 2003). Long residence time increases THMs in storage tanks and piping. In systems with long water ages like the Harare system, estimated around 8 days on average, flushing of the distribution system is one of the measures

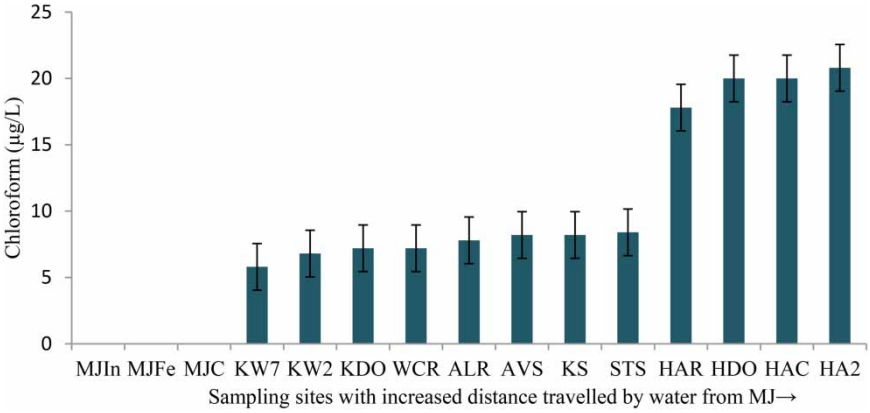

Figure 8 | Spatial variation of average chloroform for February to April 2015.

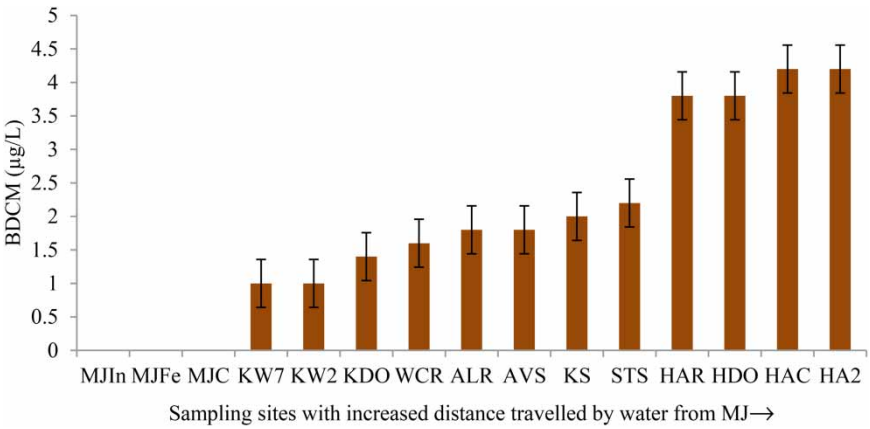

Figure 9 | Spatial variation of average BDCM for February to April 2015.

suggested for reduction of THM formation (Boccelli *et al.* 1998). The injection of ammonia tends to reduce the formation of THMs (Diehl *et al.* 2000). Ammonia is injected at the central reservoirs for the Harare Water Distribution at WCR. This could be helping to reduce THM formation.

The levels of TTHMs measured in the Harare Water Distribution System (up to 28 µg/L) are comparable to 9.8 to 38.7 µg/L obtained by Liang & Singer (2003) in the USA. Values of 14.5 ± 9.9 µg/L were obtained by Wei *et al.* (2010) in China. Health effects of bladder and renal cancer, and reproductive and developmental effects in people exposed to THMs in chlorinated water were reported by Bove *et al.* (1995) in the USA. Although this was not studied, the risks of these health effects are high in Harare.

At present the THM levels are generally within recommended limits and THM ratios are below the maximum of 1 suggested by WHO (2004). However, BDCM exceeded the USEPA limit for long-term exposure. THM formation varied with distance and residence time and was affected by increasing levels of COD.

CONCLUSIONS

The study confirmed that there is THM formation in the Harare water distribution system and that it is affected by the residence time of the water in the system and presence of organic material inferred from increasing COD. The highest levels of THMs and COD were obtained at the points in the distribution system furthest from the water works

(Hatcliffe). However, the levels of THMs are generally within the levels suggested by the World Health Organization. Only BDCM presents a risk for long-term exposure as it had levels that exceeded the limit for long-term exposure suggested by USEPA. When considering all parameters, levels increased with distance from the water works (turbidity, solids, COD and THMs) and reduced with distance for chlorine. Thus, water quality deteriorated with distance from the treatment plant and was poorest at the furthest point. BDCM, turbidity and free residual chlorine levels were not acceptable in some of the zones thus presenting health risks. Boosting of chlorine residuals is necessary especially in areas where free chlorine was less than 0.2 mg/L. However, it should be accompanied by injection of ammonia, periodic cleaning of storage reservoirs, flushing of the distribution network and replacement of old pipes to minimize formation of THMs. There is the need for research on the feasibility of other alternative disinfectants that do not result in formation of THMs.

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