Study of the effect of pipe materials and mixing phenomenon on trihalomethanes formation and diffusion in a laboratory-scale water distribution network

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ABSTRACT

The objective of this study was to evaluate the factors that affect the formation and diffusion of disinfection by-products, especially trihalomethanes (THM), in a laboratory-scale water distribution network constructed with three different pipe materials. Sampling locations were chosen on the basis of residence time, pipe material and mixing zone. Water samples were collected and analyzed for temperature, pH, total organic carbon, turbidity, free chlorine and THM. Experiments were carried out where two different flow directions at cross junctions were studied. It was observed that for incoming flow at 90° with varying flow rate, mixing was shown to be incomplete where inflows tend to bifurcate rather than mix completely. For two incoming flows in opposing direction (180°), solute mixing has shown to be perfect due to the collision of the fluid streams. The results demonstrated how THM concentration can greatly vary in the same water distribution network due to the impact of pipe material, residence time and the outcome of mixing at cross junctions.

Key words | laboratory-scale, mixing, trihalomethanes (THM), water distribution network

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INTRODUCTION

To safeguard drinking water from disease-causing organisms or pathogens, water suppliers often add a disinfectant to drinking water, such as chlorine. Without chlorine (or some other disinfectant), millions of people would die from devastating diseases including cholera, diarrhea, malaria and others. The World Health Organization (WHO 1996) states that 'all people, whatever their stage of development and their social and economic conditions, have the right to have access to an adequate supply of safe drinking water'. To this end, WHO has developed guideline values for many contaminants in drinking water.

The addition of chlorine has been the standard in water treatment in many countries globally. However, disinfectants themselves can react with natural organic matter (NOM) which is generally measured as total organic carbon (TOC) to form disinfection by-products (DBPs) including the four primary trihalomethanes: Chloroform – $CHCl_3$, Bromodichloromethane (BDCM) – $CHCl_2Br$, Dibromochloromethane (DBCM) – $CHClBr_2$ and Bromoform – $CHBr_3$ (Rook 1974; Hood 2005; Rodríguez *et al.* 2007). Residual chlorine also reacts with the pipe material of the distribution network. Reactions with dissolved NOM and biofilms present in pipes, may form THM (Singer & Reckhow 1999). Increases in pH, water temperature, bromide concentration (Br^-), chlorine dosage (Cl_2) and residence time are also additional factors that affect DBPs formation (Croué *et al.* 1998; Lu *et al.* 2009).

In the last two decades several studies have shown that DBPs in drinking water are associated with various health risks such as cancer, kidney, liver damage and immune system dysfunction, disorders of the nervous system, hardening of the arteries, and birth defects (IARC & WHO 1991; EPA 1999; Rahman *et al.* 2010). Models have been developed based on data generated in laboratory-scale and field-scale investigations to predict the occurrence of DBPs in drinking water. In most of these models, parameters such as concentration and type of precursors, the concentration of chlorine, temperature, pH and time are taken into consideration.

Since chlorine is the parameter most difficult to predict, many kinetic models have been developed to predict chlorine concentration in different parts of the water distribution network. Chlorine concentration within a network is influenced by many factors including chlorine demand of the bulk water and pipe-wall, piping material and flow velocity (Mompremier *et al.* 2015). In order to understand how water quality parameters evolve in time and space in a drinking water distribution network, a good understanding of the mixing phenomenon at cross junctions is necessary.

Austin *et al.* (2008) studied mixing phenomenon at cross junctions; in their study, the Reynolds number ranged from 10,000 to 42,000. These findings indicated that mixing at cross junction was incomplete. Song *et al.* (2009) also studied the same phenomenon based on a series of tracer experiments in a pressurized 5×5 network model with 9 cross junctions. Results showed on the one hand how the perfect mixing assumption could lead to an overestimation of dilution at cross junctions. On the other hand, it also showed that an incomplete mixing model can improve the prediction of solute transport in water distribution systems that have multiple cross junctions. Mompremier *et al.* (2015) reported the impact of mixing phenomenon in the prediction of chlorine residuals in municipal water distribution systems, showing that free chlorine concentration could vary within the network depending on the flow direction at cross junctions and
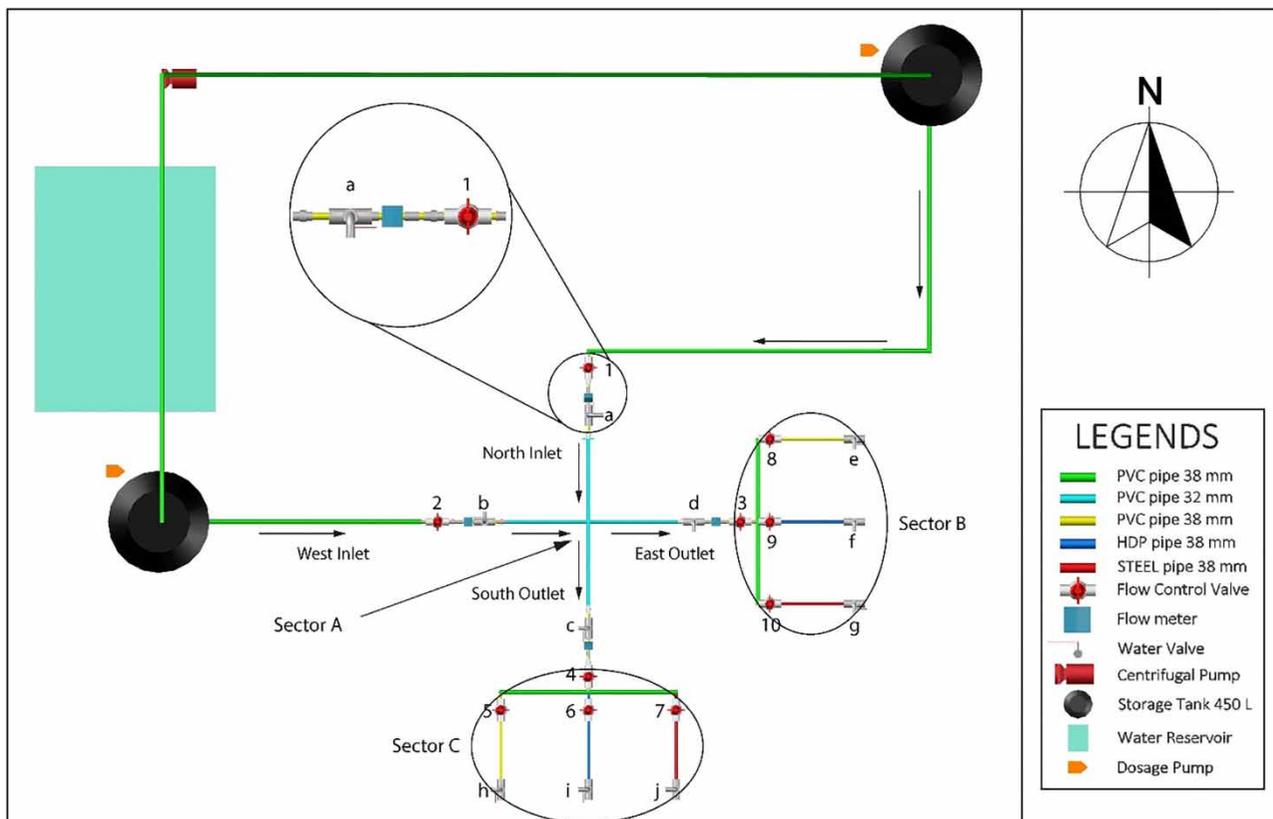

Figure 1 │ Schematic description of the experimental distribution network for scenario 1 [sector A inflows at 90˚].

identifying a larger vulnerability zone due to the impact of incomplete mixing in some cross junctions. Such hydraulic conditions have an impact on water quality parameter within a network and to the best of our knowledge, no previous studies have investigated the impact of flow conditions at cross junctions on THM formation and diffusion.

Therefore, the current study was initiated with two objectives: (i) to study the impact of mixing phenomenon on THM formation and diffusion in a water distribution system; and (ii) to identify the main factors affecting THM formation in a water distribution system.

MATERIALS AND METHODS

Experimental setup and preparation

In order to study the impact of mixing phenomenon, residence time and pipe material on the formation and diffusion of THM, a series of experiments were carried out in a laboratory network system. The experimental setup was divided into three sectors:

1. Sector A consisted of a cross junction pipe system with two inlets and two outlets:
   Scenario 1: Inlets – North and West; outlets South and East (Figure 1)
   Scenario 2: Inlets – North and South; outlets East and West (Figure 2).
2. Sector B consisted of three different pipe materials (supplied from East outlet of sector A in scenarios 1 and 2).
3. Sector C also consisted of three different pipe materials (supplied from South outlet in scenario 1, and West outlet in scenario 2).

Three pipe materials were used: steel galvanized, polyvinyl chloride (PVC) and high-density polyethylene (HDPE) with diameters of 32 and 38 mm.
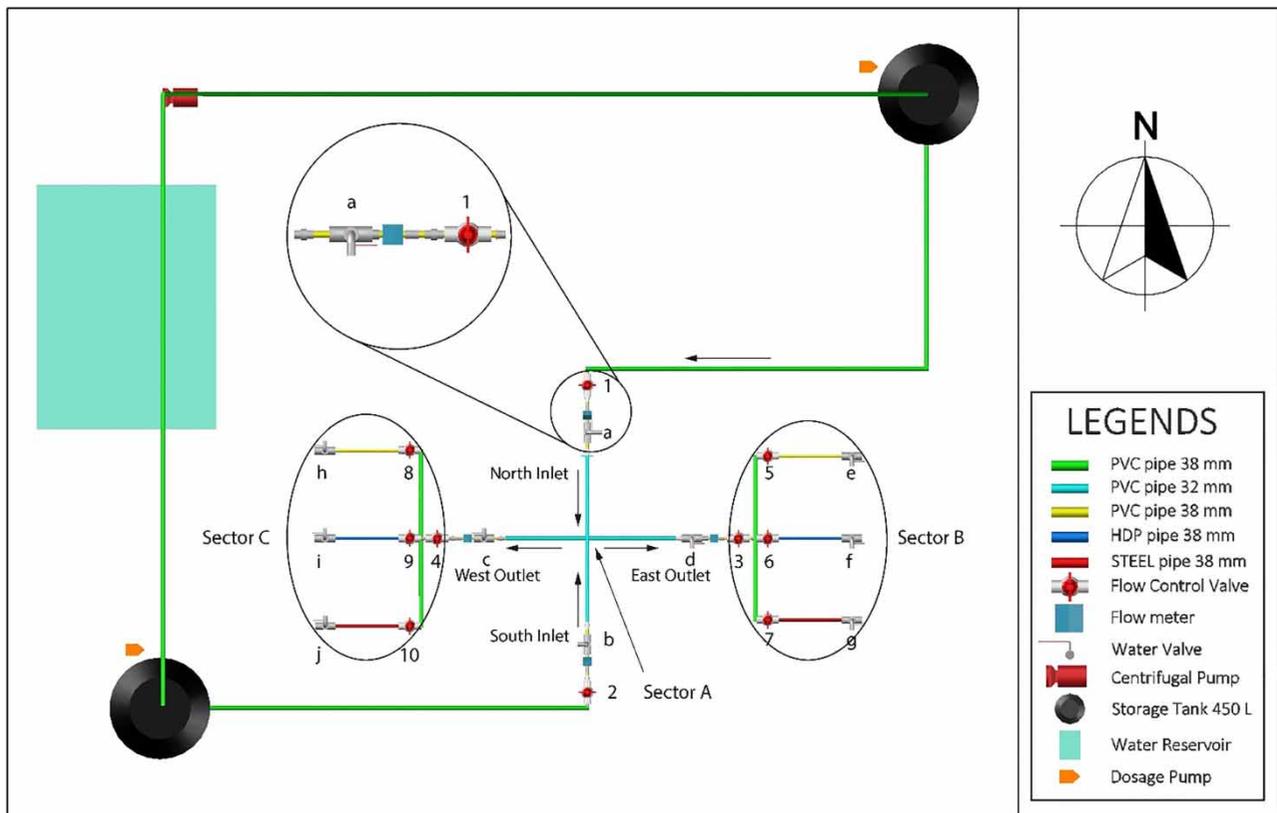

Figure 2 │ Schematic description of the experimental distribution network for scenario 2 [sector A inflows at 180°].

The system also included the following:

(a) A water reservoir (2.12 m^3 of capacity).
(b) Two storage tanks (450 L of capacity each) at elevated position for gravity flow.
(c) Four flow meters (CZ300s model Contazara S.A, Spain) located at each inlet and outlet of the cross junction (sector A) to measure instantaneous flow rate in the system.
(d) Ten flow control valves (labelled 1–10). One valve at each inlet and outlet of sector A and three valves at the entrance of sectors B and C were used to change the operating condition of the system.
(e) Ten water valves (labelled a–j). One at each inlet and outlet of sector A and three at the exit of sector B and C were used to collect water samples.
(f) Two dosing pumps (BL3-12, HANNA instrument, Mexico) were used to control the chlorine concentration released from the storage tank.
(g) An advanced chlorine measurement system (CL763, B&C electronics, Italy) that detects chlorine concentration in the range from 0.1 to 20 mg/L was installed in sector A (at inlets and outlets). This equipment is designed for inflow continuous measurement of residual chlorine. In sectors B and C a different chlorine measurement method was used.
(h) A data logger (El-USB-4, Lascar electronics, USA) connected to each controller and a PC for analysis. Schematic diagrams of the experimental distribution network for scenario 1 and scenario 2 are shown in Figures 1 and 2, respectively.

In order to get a homogeneous mixture of tap water and chemicals (NOM and chlorine), a manual mixer was installed at each storage tank (see Figure 3).

Experimental procedure

To carry out the experiments, clean water from the 2.13 m^3 reservoir was pumped to the elevated storage tanks using a 4HME200 centrifugal pump. K-Tonic solution (1.15 g/mL) which is a mix of six compounds such as total nitrogen, urea nitrogen, K_2O water-soluble potassium, extract of total humic carbon, humic acid carbon and fulvic acid carbon was used as contaminant agent. Descriptions of the scenarios in term of residence time, chlorine and NOM concentrations in storage tanks are presented in Table 1.
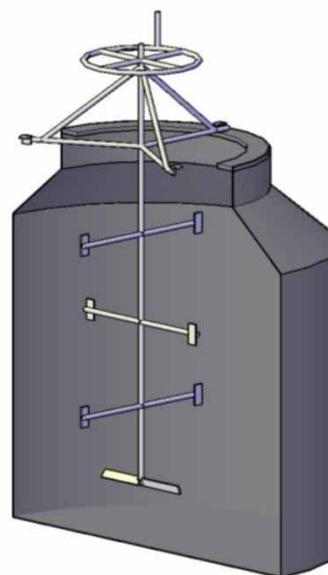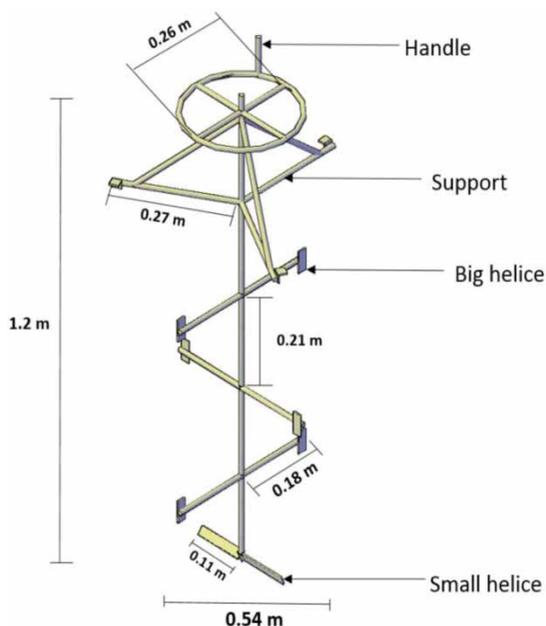

Figure 3 | Schematic drawing of a manual mixer.

Table 1 | Description of scenarios in terms of chlorine concentration, NOM level and residence time in storage tanks in different scenarios

	North storage Tank	West storage Tank
SCENARIO 1		
Chlorine concentration [mg/L]	1.77	1.35
K-tonic solution [mg/L]	1.00	0.50
Residence time [hour]	6.00	6.00
SCENARIO 2		
Chlorine concentration [mg/L]	1.94	1.24
K-tonic solution [mg/L]	2.00	1.50
Residence time [hour]	6.00	6.00

ANALYTICAL METHODS

Temperature and pH measurement

A 350 mercury thermometer (Laura, USA) was used to measure water temperature and a M530P (Pinnacle series, USA) unit was used for pH measurement.

Free chlorine measurement

Two methods were used for free chlorine measurement. Since water samples were collected directly from inlets and outlets while entering sector A (cross junction) free chlorine measurement was made using an advanced system (CL763, B&C electronics, Italy) that can detect concentration in the range from 0.1 to 20 mg/L. The collected signals were transferred to a data logger (El-USB-4, Lascar electronics, USA) connected to each controller and a PC for analysis.

Samples were collected from pipe segments to measure chlorine concentration in sectors B and C after 18 hours of residence time. In these sectors, however, chlorine concentration was measured by employing the Iodometric titration method based on using $Na_2S_2O_3$ for titration. Equation (1) was used to calculate the chlorine concentration.

$$mg\, Cl = \frac{(A \pm B) \times N \times 35450}{mL\, sample} \tag{1}$$

where:

$A =$ mL titration for sample
$B =$ mL titration for blank
$N =$ normality of $Na_2S_2O_3$

Turbidity and TOC determination

Turbidity was measured using a turbidimeter (2100A, HACH, Mexico). TOC analysis was carried out based on catalytic combustion at 720°C using a TOC-L CSH (Shimadzu Corporation, Germany).

Trihalomethanes determination

Materials

A stirring hotplate (CIMANEC) was used for water baths. A 10 mm × 3 mm magnetic stir bar was placed within the sample to provide the stirring action. A mercury thermometer (Laura, USA) with a range from −20 to 110°C was employed to measure sample temperature. For the measurement of the mass of the reagents, an analytical balance (Explorer Ohaus) with range from 10 mg to 130 g was used. For administration of precise low volume doses of sodium thiosulfate to the samples, tuberculin mini glass syringes of 100 and 500 μL were used. Finally, two Carboxen/polydimethylsiloxane (carboxen/PDMS 75 μm) (SUPELCO) fibres were used for the extraction of the volatile compounds (THM).

Sampling protocol

Triplicate 60 mL water samples were collected in glass bottles with Teflon-lined screw closure. Then, 0.1 g of sodium thiosulfate ($Na_2S_2O_3·5H_2O$) was added to each sample to quench any remaining chlorine residual and stop the formation of THMs, then sealed and stored in a refrigerator at 4 degrees until analysis with a maximum holding time of one day.

THM extraction

The THMs compounds were extracted from the samples by the solid-phase micro extraction technique (Luks-Betlej &

Bodzek 2000; Haddad *et al.* 2014). Solutions of 2,000 μg/mL of each chemical dissolved in methanol were made. Instrumental configuration and analysis conditions are presented in Table 2.

RESULTS AND DISCUSSION

Scenario 1 (sector A)

The first goal of the experiments was to study the hydraulic behavior of the flow at the inlets (North and West). This scenario provided varying inflows, varying chlorine and NOM concentrations. It was observed that the flow at the North inlet was blocked by the incoming water from the west, which had greater flow rate. This forced some of the flow (from the North inlet) to get pushed across the junction and exit through the East outlet with an incomplete mixing (Chávez *et al.* 2005; Ho *et al.* 2007; Austin *et al.* 2008; Ho & O'Rear 2009). This had an impact on water quality parameters at outlets.

Because of the incomplete mixing, physicochemical water quality parameters varied from one outlet to another in the same experimental setup. In the case of sector A, water quality parameters such as free chlorine, TOC, and turbidity had

Table 2 | Instrumental configuration and analysis conditions

Chromatographic system			
Gas chromatograph	Agilent Model 6890N		
Inlet	Split/splitless		
Detector	Agilent 5973 MSD		
Column	30 m × 0.25 mm × 0.25 μm		
Fibre	Carboxen/polydimethylsiloxane (carboxen/PDMS 75 μm, SUPELCO		
Experimental conditions			
Inlet temperature	310 °C		
Injection volume	1 μL		
Injection mode	splitless		
Purge time	0.75 min		
Purge flow	60 mL/min		
Carrier gas	He		
Flow velocity	1 mL/min		
Oven temperature	40 °C, 4 min initial, 16 °C/2 min to 120 °C		
Detector temperature	270°		
Desorption time	5 min		
Micro-extraction time	8 min		
The m/z fragment			
Chloroform ($CHCl_3$)	83 as 100%, 85 as 75% and 87 as 20%		
Bromoform ($CHBr_3$)	173 as 100%, 171 as 50% and 173 as 49%.		
Bromodichloromethane ($CHBrCl_2$)	83 as 100%, 85 as 75% and 47 as 25%;		
Dibromochloromethane ($CHBr_2Cl$)	129 as 100%, 127 as 80% and 131 as 25%		
	The % recovery	Retention time	Calibration curve/concentration range
Chloroform ($CHCl_3$)	99.45%	2.17 min	2–100 μg/L
Bromoform ($CHBr_3$)	99.81%	7.02 min	40–200 μg/L
Bromodichloromethane ($CHBrCl_2$)	99.68%	5.26 min	40–200 μg/L
Dibromochloromethane ($CHBr_2Cl$)	99.24%	3.43 min	20–100 μg/L

higher values in the East outlet. In the case of THM level, the North inlet had higher concentration than the West inlet. It could be seen that the South outlet which contained mostly water from the West inlet and only a slight mix from the North inlet had a lower level of THM (under the limit of quanti-fication). Flow rates and water quality parameters at inlets and outlets of sector A for scenario 1 are presented in Table 3.

Results for scenario 1 (sectors B and C)

Results from sectors B and C clearly showed the impact of the mixing phenomenon, pipe materials and residence time on THMs formation and diffusion in a water distri-bution network. Inflows to these sectors come from the East and South outlets of sector A which had varied physico-chemical characteristics due to the incomplete mixing that occurred at the junctions. Results of physicochemical analy-sis of the samples collected after a residence time of 18 hours in three different pipe materials of both sectors are presented in Tables 4–7. The results indicate that THMs levels increased in HDPE and PVC pipe materials as the incubation period in pipes increased (18 hours). These find-ings corroborated those obtained by Saidan *et al.* (2013) which observed that THMs levels increase as the residence

time extended. The ranking of THMs formation rates in the experiments was as follows: polyethylene > PVC > steel pipe. However, the low THMs rate in the steel pipe might be attributed to many factors such as longer incubation period (Haddad *et al.* 2014); reactions of the flow with other compounds in the pipe, the increase of TOC and the absence of chlorine could be other factors. Water quality parameters for samples from the different materials for sector B are shown in Table 4, while a statistical analysis of the THMs concentration is presented in Table 5.

Results in Table 5 show a good correlation between the THMs rates obtained in the three sample measurements.

In sector C, the observation was similar to that of sector B, however a lower THMs concentration was measured, and can be attributed to the water coming out of the South outlet of sector A which contained lower chemical compounds such as chlorine and TOC levels. Results for this scenario are presented in Tables 6 and 7.

Results for scenario 2 (sector A)

In scenario 2, a different combination of flows was investigated to assess mixing phenomena at cross junctions and its impact on THMs occurrence and diffusion. It could be seen that

Table 3 | Flow and water quality parameters at inlets and outlets of sector A [scenario 1]

Sampling points	Flow rates [L/s]	Chlorine [mg/L]	pH	Temperature [˚C]	Turbidity [NTU]	Residence time [min]	TOC [mg/L]	Total trihalomethanes [μg/L]
North inlet	0.50	0.70	7	19.3	1.2	10	0.57	2.34
West inlet	1.14	0.35	7	18.9	0.9	10	0.40	<LOQ
South outlet	0.72	0.37	7	18.6	1.0	10	0.43	<LOQ
East outlet	0.92	0.53	7	18.6	1.1	10	0.52	2.66

LOQ, Limit of quantification.

Table 4 | Water quality parameters for samples from different pipe materials in sector B [scenario 1]

Sampling points	Chlorine [mg/L]	pH	Temperature [˚C]	Turbidity [NTU]	Residence time [hr]	TOC [mg/L]	Total trihalomethanes [μg/L]
Initial water quality parameters of sector B							
Sector B	0.53	7	18.6	1.1	N/A	0.52	2.66
Final water quality parameters of sector B							
PVC pipe	0.00	7	18.3	1.1	18.00	1.04	12.1
HDP pipe	0.27	7	19.0	1.1	18.00	2.40	15.1
Steel pipe	0.00	7	18.5	1.2	18.00	1.35	0.86

Table 5 | Statistical analysis (THM values) for sector B [scenario 1]

Sampling points	THM [μg/L] Sample 1	THM [μg/L] Sample 2	THM [μg/L] Sample 3	Final concentration THM μg/L [mean]	Standard deviation
Final THM concentration in sector B					
PVC pipe	12.3	13	11	12.1	1.04
HDP pipe	15.3	17	13	15.1	2.00
Steel pipe	0.83	0.9	0.87	0.86	0.03

incoming water entered the junction from the North and South inlet pipes where the incoming flows struck against each other and exited through the West and East outlets (Figure 2). This flow regime resulted in a perfect mixing condition (Mompremier *et al.* 2015) where the resultant water quality parameters in each outlet was almost similar (Table 8).

Contrary to the case of the first scenario, levels of THMs measured in both outlets were uniform (with a slight difference) due to the perfect mixing of the flows.

Results for scenario 2 (sectors B and C)

The flow in these sectors comes from the East and South outlets of sector A. Contrary to scenario 1 where the level of THMs varied from sectors B and C, results in this

Table 6 | Statistical analysis (THM values) for sector C [scenario 1]

Sampling points	THM [μg/L] Sample 1	THM [μg/L] Sample 2	THM [μg/L] Sample 3	Final concentration THM μg/L [mean]	Standard deviation
Final THM concentration in sector C					
PVC pipe	8.52	8.30	9.50	8.77	0.63
HDP pipe	13.0	15.0	12.0	13.33	1.52
Steel pipe	0.35	0.44	0.30	0.36	0.07

scenario indicated that physiochemical water quality parameters were uniform in both sectors. Consequently, THMs analysis provided similar results in both sectors due to perfect mixing in sector A (see Tables 9–12). The same ranking of THM rate observed in scenario 1 was also observed in this scenario.

As shown in Tables 9 and 11, these values represented the highest level of THMs rate throughout the experimental study and might be attributed to the increase of the physicochemical parameters of water, especially the chlorine and TOC (0.88 mg/L). As in the case of scenario 1, chemical analysis in sectors B and C resulted in a low level of THMs in steel pipes compared to HDPE and PVC pipes. However, the THMs rate in steel pipes (in this scenario) are 10 times higher than that measured in scenario 1. This could be explained by the fact that chlorine residuals were lost more quickly in these pipes (in scenario 1) due to the lower level of TOC and chlorine compared to their levels in scenario 2.

CONCLUSIONS

The data obtained from the experimental research indicated the following:

In scenario 1, since the West inlet flow rate was 2.28 times greater than the North inlet flow rate, bifurcation of the North inlet into the East inlet was clearly observed with only a slight mixing. A heterogeneous distribution of contaminants was observed in the sector A outlets. Therefore, THMs analysis provided the highest concentration in sector B since it (sector B) was supplied by the East

Table 7 | Water quality parameters for samples from different pipe materials in sector C [scenario 1]

Sampling point	Chlorine [mg/L]	pH	Temperature [°C]	Turbidity [NTU]	Residence time [hr]	TOC [mg/L]	Total trihalomethanes [μg/L]
Initial water quality parameters of sector C							
Sector C	0.37	7	18.6	1.0	N/A	0.43	<LOQ
Final water quality parameters of sector C							
PVC pipe	0.0	7	18.3	1.1	18	0.80	8.77
HDP pipe	0.1	7	18.3	1.0	18	1.75	13.33
STEEL pipe	0.0	7	18.1	1.1	18	1.01	0.36

Table 8 | Results for sector A [scenario 2]

Sampling points	Flow rates [L/s]	Chlorine [mg/L]	pH	Temperature [°C]	Turbidity [NTU]	Residence time [hr]	TOC [mg/L]	Total trihalomethanes [µg/L]
North inlet	0.84	1.05	7	19.8	1.6	6.0	0.87	10.00
South inlet	0.50	0.60	7	18.1	1.1	6.0	0.76	4.00
West outlet	0.68	0.88	7	17.3	1.2	6.0	0.81	7.89
East outlet	0.66	0.88	7	17.5	1.2	6.0	0.78	7.98

Table 9 | Water quality parameters for samples from different pipe materials in sector B [scenario 2]

Sampling point	Chlorine [mg/L]	pH	Temperature [°C]	Turbidity [NTU]	Residence time [hr]	TOC [mg/L]	Total trihalomethanes [µg/L]
Initial water quality parameters in sector B							
Sector B	0.88	7	17.5	1.2	0.0	0.81	7.98
Final water quality parameters of sector B							
PVC pipe	0.25	7	18.8	1.2	18	1.04	28.56
HDP pipe	0.34	7	19.0	1.3	18	3.29	43.73
STEEL pipe	0.00	7	18.9	1.5	18	1.08	8.93

outlet which contained mostly water from the North inlet with only a slight mix from the West inlet.

In scenario 2, flow entering at the North and South inlets (180°) struck against each other and exited through adjacent outlets. Water quality parameters in both outlets were similar since effluents exiting them were composed of a perfect mixing of both inflows. THMs levels were equal in both outlets, hence in sectors B and C.

Table 10 | | Statistical Analysis for sector B [scenario 2]

Sampling points	THM [µg/L] Sample 1	THM [µg/L] Sample 2	THM [µg/L] Sample 3	Final concentration THM µg/L [mean]	Standard deviation
Initial THM concentration in sector B = 7.98					
Final THM concentration in sector B					
PVC pipe	28.64	30.6	26.46	28.56	2.07
HDP pipe	43.8	41.6	45.8	43.73	2.10
Steel pipe	9.9	8.9	8	8.93	0.95

Table 12 | Statistical analysis for sector C [scenario 2]

Sampling points	THM [µg/L] Sample 1	THM [µg/L] Sample 2	THM [µg/L] Sample 3	Final concentration THM µg/L [mean]	Standard deviation
PVC pipe	28.40	26.80	30.2	28.47	1.70
HDP pipe	43.64	45	42.3	43.64	1.35
Steel pipe	9.00	9.60	7.90	8.84	0.86

Table 11 | Water quality parameters for samples from different pipe materials in sector C [scenario 2]

Sampling point	Chlorine [mg/L]	pH	Temperature [°C]	Turbidity [NTU]	Residence time [hr]	TOC [mg/L]	Total trihalomethanes [µg/L]
Initial water quality parameters in sector C							
Sector C	0.88	7	17.5	1.2	N/A	0.78	7.89
Final water quality parameters of sector C							
PVC pipe	0.24	7	18.8	1.2	18	0.98	28.47
HDP pipe	0.36	7	19.0	1.3	18	3.20	43.64
STEEL pipe	0.00	7	18.9	1.5	18	1.06	8.84

The results also indicated that pipe material and residence time were the main factors that affect THMs increase. It was shown that THMs concentration increased as residence time increased. However, different level of THMs were recorded in the different sectors due to the effect of pipe material. Results from this study are useful in understanding the effect of pipe material and its configurations in distribution systems, and help develop a better mathematical model to predict the occurrence and formation of THMs in water distribution systems.

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