

Study of the variation of haloacetic acids in a simulated water distribution network

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ABSTRACT

This paper presents the analysis of the variation of haloacetic acids (HAAs) for different pipe materials in a distribution system. The work involved an experimental study on a simulated distribution system assembled in the Hydraulic Laboratory of the Engineering Institute at the National Autonomous University of Mexico (Instituto de Ingeniería UNAM). Two different scenarios were investigated based on different pipe materials, variation of temperature and initial chlorine concentrations (4.0 and 4.5 mg/L). Feed water with varying amounts of organic content was dosed with varying amounts of chlorine concentration. Water samples were collected from different locations in the distribution system and analyzed for physicochemical properties and HAAs determination. The results of this research demonstrated that the concentration of HAAs in the different segments of the distribution systems varied depending on pipe material, initial chlorine concentration, pH, residence time and the presence of natural organic matter.

Key words | chlorine concentration, haloacetic acids, natural organic matter, pipe loop, pipe material

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INTRODUCTION

Disinfection of drinking-water is essential to protect the public from outbreaks of waterborne infectious and parasitic diseases. The most serious cause of water quality deterioration in a water supply system is the loss of chlorine residual that can weaken the barrier against microbial contamination (Clark & Haught 2005). Microbiological water quality in distribution systems deteriorates for a number of reasons that includes physicochemical water quality, pipe material and water age. Maintaining high water quality in distribution systems is one of the greatest challenges for water utilities globally. This will require ensuring that the treated water quality has the highest quality, avoiding contaminant ingress from surrounding soil and ensuring that the internal structure of the pipes and accessories does not release any contaminant.

Water treatment plants commonly use free chlorine, chloramines, chlorine dioxide and ozone for disinfection. Free chlorine is the most commonly used disinfectant globally.

It is effective against bacteria and to some extent against viruses and protozoa (Golfopoulos & Nikolaou 2005). Although chlorine is a very effective disinfectant, in the presence of natural organic matter (NOM), it produces disinfection by-products such as total trihalomethanes (TTHMs) and haloacetic acids (HAAs) (Twerdok *et al.* 1997; Källén & Robert 2000; Rossmann *et al.* 2001; Rodríguez *et al.* 2004).

HAAs represent a group of disinfection by-products that include: monochloroacetic acid (MCA) ClCH_2COOH , dichloroacetic acid (DCA) Cl_2CHCOOH , trichloroacetic acid (TCA) Cl_3CCOOH , monobromoacetic acid (MBA) BrCH_2COOH and dibromoacetic acid (DBA) Br_2CHCOOH . Their combined concentration is referred to as total HAA5.

In a study conducted by Delgado (2010), links were made between exposures to HAA concentrations above the maximum contaminant level to an increased risk of cancer. The parts easily affected by over-exposure to HAAs are the kidney, liver and nervous system. Concentrations of HAAs

can vary greatly in a water distribution system depending on physicochemical parameters and treatment conditions (Nikolaou *et al.* 1999). Chlorinated Disinfection By-Products Task Group (2000) and International Programme on Chemical Safety (2000) conducted several studies in which the level of HAAs was found to be greater in treated water from surface water sources, such as rivers and lakes, compared with groundwater sources due to the variations of NOM content in the sources. One of the factors that affect water quality in distribution systems is pipe material. Mompremier *et al.* (2017) reported that characteristics of pipe material were the main factors that affect disinfection by-product formation. In a laboratory-scale distribution system study they observed that DBP concentrations were different for different pipe materials.

Nowadays, high-density polyethylene (HDPE), polypropylene (PP), galvanized steel (GS) and polyvinyl chloride (PVC) pipelines are most commonly used during the expansion and rehabilitation of existing water supply systems. Because of the special interest in using large amounts of PP and PVC pipelines by water utilities it is becoming important to investigate the impact of these materials on DBP formation. Therefore, the main objective of this study is to study the variation of HAAs in a laboratory-scale distribution system consisting of four sets of independent PVC, HDPE, PP and steel galvanized (SG) pipe loops.

MATERIALS AND METHODS

Experimental setup and preparation

The experiment setup includes a closed-loop pipe system consisting of a set of four individual PVC, SG, polypropylene (PP) and high-density polyethylene pipes 12 m in length each and 50 mm in diameter. The water supply for the distribution system comes from a 2.12 m³ water reservoir and a 450 L storage tank at elevated position for gravity flow.

Equipment

Schematic diagrams of the laboratory-scale water distribution network are shown in Figures 1 and 2. The components of the distribution system include:

- (a) nine flow-control valves to fill and drain the system;
- (b) an online CL763 (B&C Electronics, Italy) chlorine analyzer connected in each loop, which can monitor continuously chlorine concentration in the range from 0.1 to 20 mg/L;
- (c) each chlorine analyzer equipped with a data logger (EL-USB-4, Lascar Electronics, USA) that records data over time for their analysis;
- (d) a manual mixer installed at the storage tank to get a homogeneous mixture of tap water and chemical (chlorine and NOM);
- (e) a 4HME200 centrifugal pump to transfer the water from the reservoir to the storage tank;
- (f) a 350 mercury thermometer (Lauka, USA) to measure temperature; and
- (g) an M530P (Pinnacle series, USA) unit used for pH measurement.

Experimental protocol

Prior to the experiments, pipe loops were flushed with clean water (free of chlorine) for approximately 15 minutes to ensure that no chlorine residual or other contaminants were present. Unchlorinated water was transferred from the 2.12 m³ reservoir to the elevated storage tank using a 4HME200 centrifugal pump. Five minutes later, K-Tonic solution (1.15 g/mL), which is a mix of six compounds of total nitrogen, urea nitrogen, K₂O water-soluble potassium, extract of total humic carbon, humic acid carbon and fulvic acid carbon was used as contaminant agent (1.50 mg/L in each scenario). The initial free chlorine concentrations were 4 and 4.50 mg/L for scenarios 1 and 2, respectively and the concentration decreased by 2 mg/L during the transferring and filling of the pipe-loop systems. A manual mixer was used to ensure a homogeneous mixture of tap water and chemicals (NOM and chlorine). The experiment extended for about 33 hours.

At the end of each pipe loop, a 0.18 m × 0.09 m acrylic box was installed. The first box (1) was equipped with a mini (4203, Aquakril) submersible water pump to send water samples to the chlorine analyzer (overflow cell) through a 1/4" connection. The sample ran through the potentiostatic electrode site (sensor) with a constant velocity

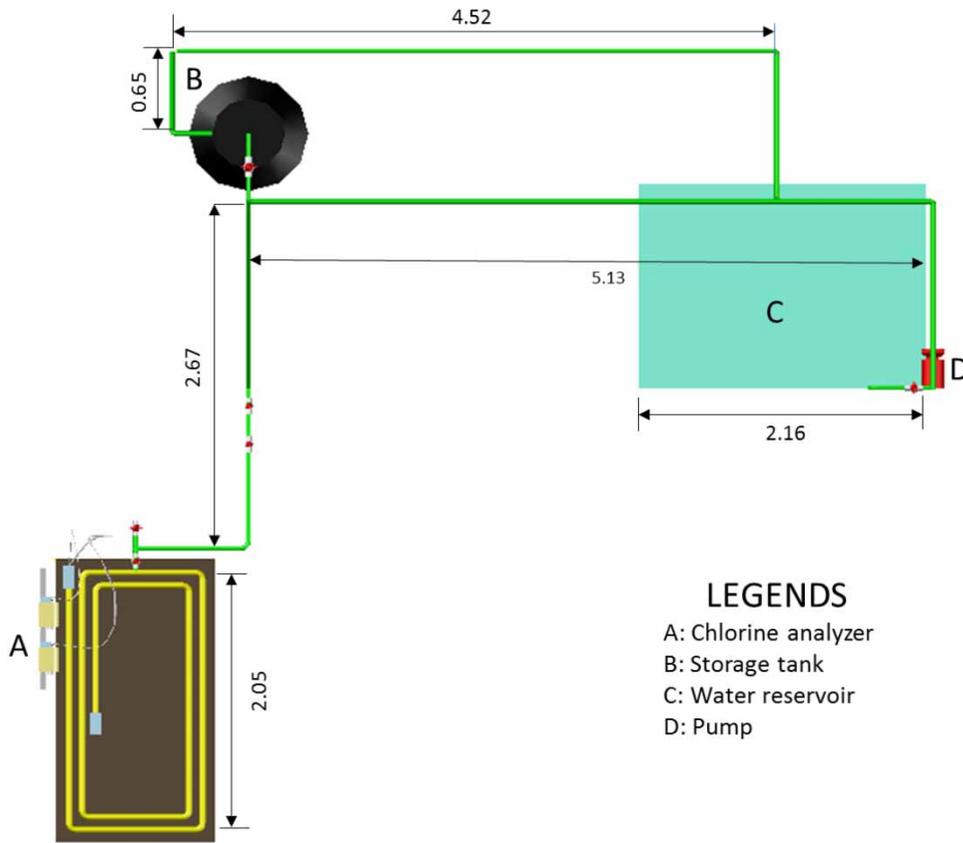


Figure 1 | Schematic diagram of the laboratory-scale water distribution network.

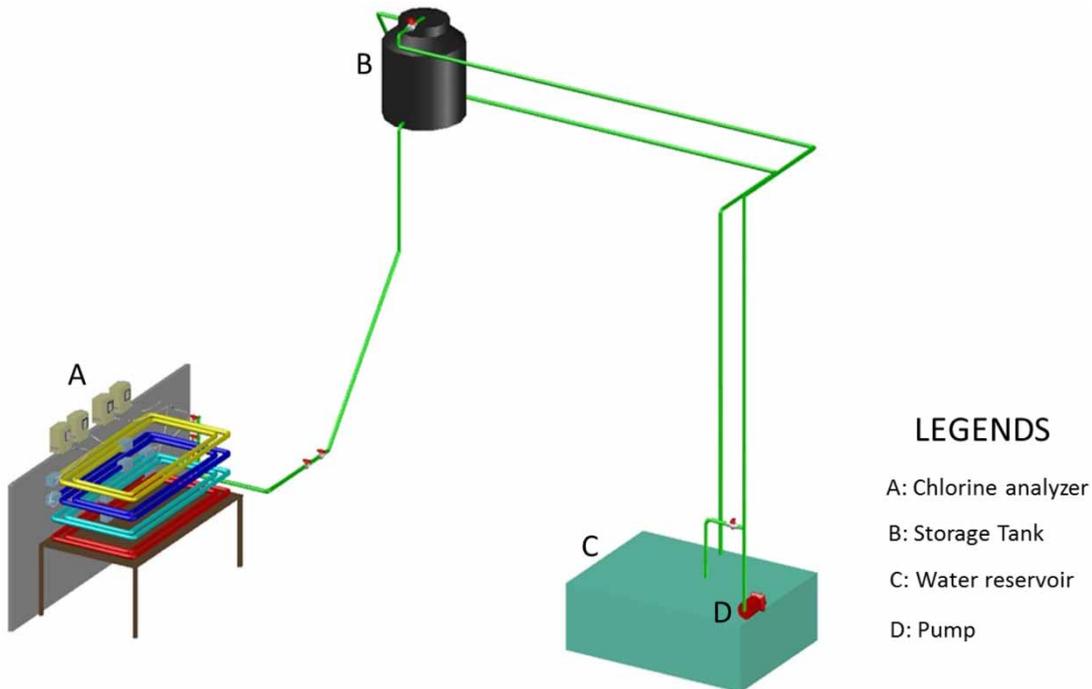


Figure 2 | 3D view of the schematic diagram of the laboratory-scale water distribution network.

then exited through 10 × 14 mm tubing to the second acrylic box located in the other end of the loop. Thus, chlorine concentration was continuously monitored in the simulated distribution system. The experiments were performed at a constant velocity of 0.0061 m/s.

CHEMICAL ANALYSIS

Haloacetic acid determination

Materials

A stirring hotplate (CIMANEC) was used for the water baths. A 10 mm × 3 mm magnetic stir bar was placed within the sample to mix the solution. A mercury thermometer (Lauka, USA) with 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 dose of sodium thiosulfate in the samples, some tuberculin mini-glass syringes of 100 and 500 µL were used. Finally, carboxen/polydimethylsiloxane (carboxen/PDMS 75 µm) provided by SUPELCO was used for the extraction of the volatile compounds.

Sample collection

Water samples were collected in 50 mL glass bottles with Teflon-lined screw closure. An amount of 0.1 g of sodium thiosulfate (Na₂S₂O₅·5H₂O) was added to each sample to quench any remaining chlorine residual and stop further chlorination by-product formation. Samples were sealed and transported to the laboratory, and stored in a refrigerator at 4 °C away from light until analysis with a maximum holding time of 1 day.

Sample preparation and HAAs extraction

Water samples were placed in a 50 mL vial and the following reagents were added: 200 µL of concentrated sulphuric acid, 3 mL of methyl tert-butyl ether (MTBE). The flask was sealed, vortexed, mixed for 3 min, then 2 mL of the

extract (MTBE) was transferred into a 3 mL screw-capped septum vial and evaporated to dryness under a gentle stream of nitrogen for approximately 5 min. Then, 50 µL of sulphuric acid and 70 µL of ethanol were added to the vial, which was sealed with a 20 mm PTFE/silicone septum. The solution was mixed with a magnetic stirrer (200 rpm) then placed into a thermostatic bath at 55 °C for 10 min to derivatize the HAAs. Finally, haloacetates were extracted from the samples by the headspace solid-phase micro extraction (HS-SPME) technique. The 75 µm carboxen/polydimethylsiloxane (CAR/PDMS) fibre was exposed to the headspace above the aqueous solution for 20 min. Then the corresponding haloacetates were desorbed after 10 min in the injector port of the gas chromatograph at 250 °C. Instrumental configuration and analysis conditions are presented in Table 1.

Turbidity was measured using a turbidimeter (2100A, HACH, Mexico), temperature was measured using a 350 mercury thermometer (Lauka, USA). An M530P (Pinnacle series, USA) unit was used for pH measurement.

RESULTS

Scenario 1

Experiments in scenario 1 were conducted over a period of 32 hours. An amount of 150 mL of water samples was taken from different pipes after 3, 6, 9, 12, 24, 27, 30 and 33 h for physicochemical analysis and HAAs determination. Triplicate analyses were performed on each sample. HAAs concentrations for scenario 1 are presented in Figure 3.

HAAs concentrations were found to be at very low levels (0.005 to 0.035 ppm) in all pipes. The formation was known to be related to various parameters such as: chlorine dose, chemical reactions, characteristics of pipe material, pH level, NOM and residence time.

Many studies have proven that reaction time of the precursors and disinfectant was the main factor affecting HAAs formation (Singer 2002; Qi et al. 2004; Chang et al. 2010). The formation of HAAs increased with time. Experiments started with the same amount of HAAs (0.014 mg/L) in the system, HAAs levels were found to be greater

Table 1 | Instrumental configuration and analysis conditions

Chromatographic system	
Gas chromatograph	Agilent Model 6890 N
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	250 °C
Injection volume	1 µL
Injection mode	splitless
Purge time	2.00 min
Purge flow	50 mL/2.00 min
Carrier gas	He
Flow velocity	23.3 mL/min
Oven temperature	40 °C, 5 min initial, 20 °C/min to 280 °C
Detector temperature	270 °C
Desorption time	10 min
Micro-extraction time	20 min
The m/z fragment	
<i>monochloroacetic acid (MCAA)</i>	77 as 100%, 29 as 53% and 49 as 41%
<i>monobromoacetic acid (MBAA)</i>	123 as 100%, 121 as 88% and 29 as 29%
<i>dichloroacetic acid (DCAA)</i>	83 as 100%, 29 as 70% and 85 as 68%
<i>trichloroacetic acid (TCAA)</i>	117 as 100%, 119 as 98% and 29 as 55%
<i>bromochloroacetic acid (BCAA)</i>	129 as 100%, 29 as 54% and 109 as 36%
<i>dibromoacetic acid (DBAA)</i>	173 as 100%, 174 as 98% and 29 as 41%
The % recovery retention time calibration curve/concentration range	
Mix compounds	99.98% 6.10–10.7 min 20–220 µg/L

3 hours later. However, the results of this scenario showed the impact of pipe material on the variation of HAAs concentration. Since HAAs levels were similar among all the pipe loop systems (HDPE = PVC = PP = SG) at the beginning of the experiment, the same concentrations were expected in samples collected 3 hours later in the whole system. However, HAAs levels were different in the four pipe loops in this order: HDPE > PP > PVC > SG.

Li et al. (2008) also studied the influence of pipe material on the formation of HAAs. Experiments were conducted using copper and glass pipe. Their results showed that the formation of HAAs in copper pipe and in glass pipe both increased with time. However, a higher formation of

HAAs species was observed in copper pipe than in glass pipe.

Results of scenario 1 showed that chlorine reacts differently with pipe material. Figure 4 shows the variation of chlorine concentration within the pipe loop system. SG pipe loop showed higher chlorine decay rate followed by HDPE, PVC and PP pipe loop during the first four sampling campaigns. However, chlorine decay rate was found to be higher in GS followed by PP, HDPE and PVC at 33 h.

A decrease was noticed of 13.79%, 30% and 37% in water samples collected from HDPE, PVC and PP pipe within 6 h. However, an increase of 33% was observed in the GS pipe loop. Three hours later, HAAs levels measured

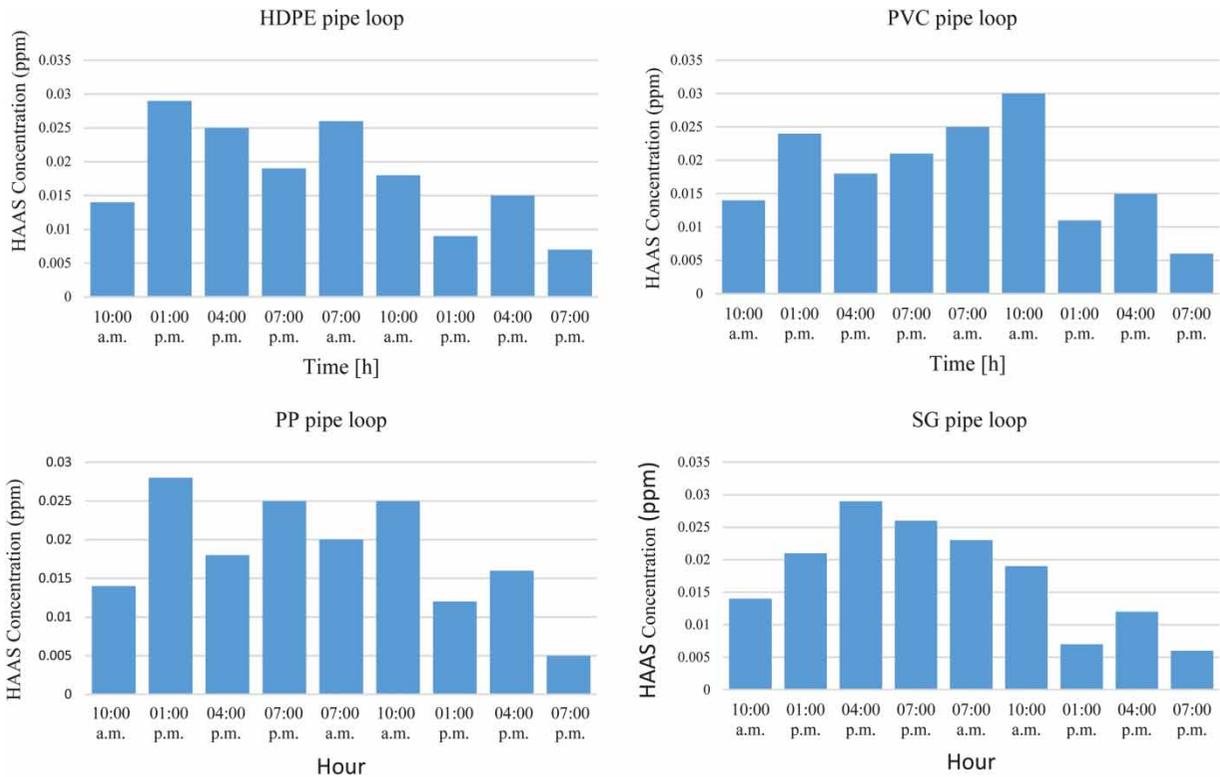


Figure 3 | HAA concentration in the pipe loop system for scenario 1.

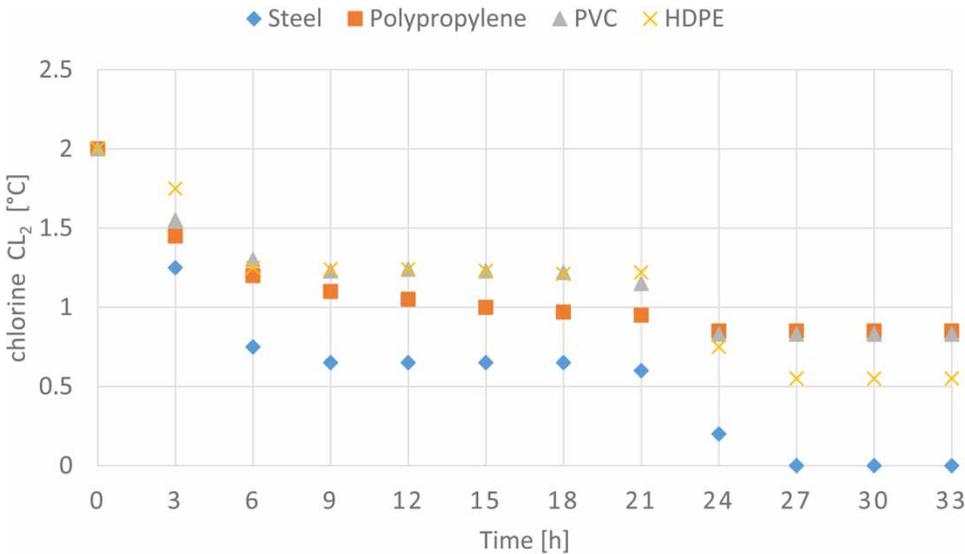


Figure 4 | Variation of chlorine concentration in the pipe loop systems.

in the GS and HDPE pipe loops decreased, while an increase of 16% and 39% was observed in HAAs concentrations in water samples collected from PVC and PP pipe loops respectively.

HAAs concentrations in the HDPE and PVC pipe loops were approximately 37% and 19% greater in the next 21 h, which may be due to day and night temperature variations in the system (Figure 5).

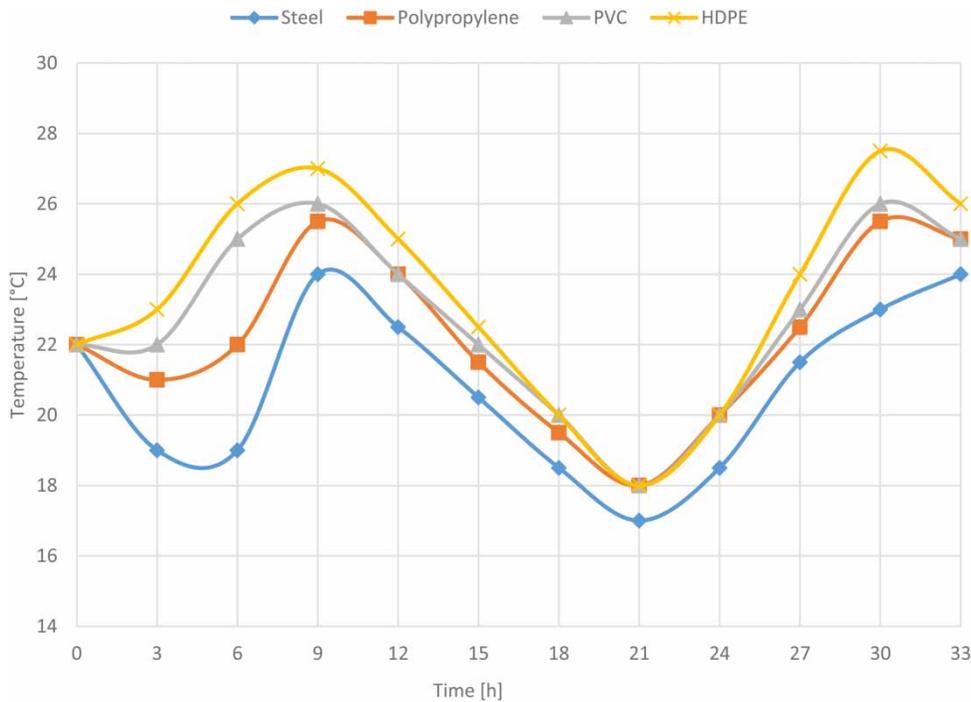


Figure 5 | Variation of water temperature in the pipe loop system for scenario 1.

Table 2 | Comparisons between final Cl_2 and HAAs levels for scenario 1

	HDPE pipe loop	PVC pipe loop	PP pipe loop	SG pipe loop
Cl_2 [mg/L]	0.89	0.89	0.53	0
HAAS [mg/L]	0.007	0.006	0.005	0.006

Comparisons between final Cl_2 concentration and HAAs level are shown in Table 2. A slight difference in HAAs level was observed in all the pipes. However, complete chlorine residual loss was observed only in the GS pipe loop, leading to a decrease of HAAs level. These findings corroborated those obtained by Singer (2002) and Williams & Williams (1998) which reported that HAAs species are subject to biodegradation in the absence of disinfectant residuals.

The results indicated that pipe material and residence time were the main factors that affect HAAs level. However, variation of water temperature in the pipe should be considered as the main factor that affected HAAs instability.

Scenario 2

For scenario 2 the experiment was performed over a 33-hour period and samples were collected after 8, 23 and 33 h. Triplicate analyses were performed on each sample. HAA concentrations for scenario 2 are presented in Figure 6.

HAAs concentration was reported to be 21% greater at the beginning of the experiment. This increase could be directly associated with the chlorine concentration, which was shown to be 12.5% greater than that encountered in scenario 1. The same observation was made in scenario 2, however.

The available results of this finding showed a wide variation in the concentration levels of HAAs throughout the period of investigation, which illustrated different trends within the pipe loop system. This complexity resulted in greater difficulty in establishing a general trend of HAAs. However, the current study provides some useful information and allows the description of relationships between observed HAAs and variables such as: pipe material, chlorine dose, temperature and presence of natural organic matter. This is in agreement with the data

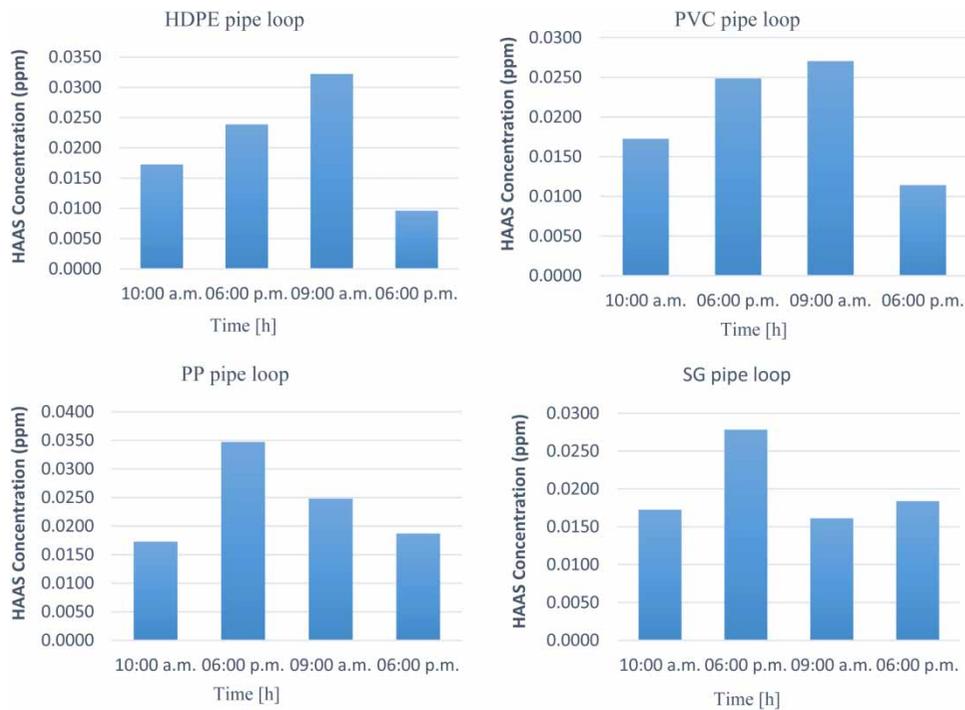


Figure 6 | HAAs concentrations in the pipe loop system scenario 2.

shown in studies performed by *Chang et al. (2010)* and *Rodriguez et al. (2007)*.

CONCLUSIONS

The study collected water samples from an experimental setup assembled in the hydraulic laboratory of the Engineering Institute at the National Autonomous University of Mexico. HAAs formation was associated with residence time, initial chlorine concentration and pipe material. However, it was observed that HAA level increased rapidly within the first 3 h of the experiments and was found to be unstable during the experiments. This instability could be associated with the variation of water temperature in the pipe loop system in the range of 17 and 37 °C. HAAs levels in the experimental setup also varied considerably according to the pipe material. These findings showed that HAAs species are subject to biodegradation in the absence of disinfectant residuals. HAAs levels were found to be lower at the end of the experiments due to the low level of chlorine concentrations measured in the samples and the impact of pipe materials.

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