Arab J Sci Eng (2014) 39:5883–5893
DOI 10.1007/s13369-014-1200-x

RESEARCH ARTICLE - CHEMICAL ENGINEERING

Model for Predicting Disinfection By-product (DBP) Formation and Occurrence in Intermittent Water Supply Systems: Palestine as a Case Study

Marwan Haddad · Laurie Mcneil · Nabeel Omar

Received: 19 December 2012 / Accepted: 31 July 2013 / Published online: 3 July 2014

Abstract A laboratory-scale experiment was conducted to investigate, evaluate, and model the formation and occurrence of disinfection by-product in Nablus water supply under various operating conditions including chlorine concentration, natural organic matter (as BOD), and incubation time of water in the distribution system. The incubation time is an important factor for Nablus water supply because of its intermittent nature. Houses and apartments in Nablus receive water once every two to three days. The results show that the extent of total trihalomethane (TTHM) formation depends not only on chlorine concentration in water but also on BOD contamination level, and the incubation period in pipes. Results were used to develop an empirical model for predicting TTHM as a function of Cl_2, BOD, and incubation period. The predictive capacity of the model was in high correlation with measured TTHM values. Results obtained and the predictive model developed provide water supply managers with TTHM prediction capability using the most important operating parameters of intermittent water supply systems.

Keywords Disinfection by-product · Chlorination · Trihalomethanes · Modeling · Water supply · Palestine

الخلاصة

تم إجراء تجربة في المختبر للتحقق وتقييم ونمذجة تكوّن وتواجد مشتقات التطهير(Disinfection By Products –DBP) في نظام إمداد المياه لمدينة نابلس تحت ظروف تشغيل مختلفة بما في ذلك تركيز الكلور المتبقي والمواد العضوية الطبيعية (ممثلة بالأكسجين الممتص حيويا) وفترة مكوث المياه في نظام إمداد المياه. إن فترة مكوث المياه تعتبر عاملاً مهماً لإمدادات المياه بنابلس بسبب طبيعتها المتقطعة حيث إن المنازل والشقق في نابلس تزود بالمياه مرة واحدة كل يومين أو ثلاثة أيام فقط. وأظهرت النتائج أن تكوين إجمالي مركبات الترايهالوميثان Trihalomethane (TTHM) في نظام إمداد المياه لا يتوقف فقط على تركيز الكلور في الماء ولكن أيضا على مستوى المواد العضوية الطبيعية وفترة مكوث الماء في الأنابيب. وقد استخدمت نتائج تجارب الأنابيب بالمختبر لوضع نموذج تجريبي للتنبؤ بتركيز مركبات الترايهالوميثان بنظام إمداد المياه بدلالة تركيز الكلور المتبقي والمواد العضوية الطبيعية وفترة مكوث المياه. وكانت قدرة التنبؤ للنموذج الذي تم الحصول عليه عالية ومثبتة بارتباط كبير بين القيم المتنبئة وتلك المقاسة بالتجربة لتراكيز الترياهالوميثا. إن النتائج التي تم الحصول عليها والنموذج المطور يوفران لمديري إمدادات المياه في البلديات ومصالح المياه القدرة على التنبؤ بتراكيز الترايهالوميثان باستخدام معاملات التشغيل المختلفة لنظم إمدادات المياه وبخاصة غير المنتظمة أو غير المتواصلة الإمداد.

1 Introduction

Palestinian water supplies have generally very good water quality at source. However, due to deterioration in water distribution systems and intermittent pumping regimes, water disinfection using chlorine either in the form of chlorine gas or hypochlorite is practiced by all municipalities and/or water suppliers as a precautionary measure. In addition to that and due to the poorly controlled disinfection process, there is a high potential of the reaction of chlorine with naturally occurring organic compounds and other materials present in the water source to occur and consequently to form disinfection by-products (DBPs) such as trihalomethanes (TTHMs)

M. Haddad (✉)
Water and Environmental Studies Institute, An-Najah National University, Nablus, Palestine
e-mail: haddadm@najah.edu

L. Mcneil
Department of Civil and Environmental Engineering, Utah State University, Logan, UT, USA

N. Omar
Beita Municipality, Engineering Department, Beita, Palestine

and haloacetic acids (HAA5) in water. These DBPs have been linked with a wide range of adverse human, animal, and environmental health effects [1–3]. As drinking water disinfection is inevitable, a fine balance should be achieved between adequate disinfection and control of DBP formation in drinking water treatment [4].

The formation, temporal, and spatial variations of DBPs in drinking water depend on the physicochemical characteristic of water (pH, temperature, BOD content, etc.) and disinfectants used (type, dose, residual concentration, etc). When Chlorine is used as disinfectant, detention time of water in the water distribution system during chlorination is another important factor to consider.

There have been no systematic measurements of DBPs made of water supplies in Palestine, and unfortunately, little is known about the occurrence and growth of DBPs in drinking water under the intermittent supply conditions experienced there. However, the results of a recent field survey of Nablus water supply system indicated the formation and occurrence of DBPs in all 21 samples collected from various locations in the system including water roof tanks and water resources. TTHM level in those samples was found to range from 6 to 153 μg/l [5].

However, there is extensive research work done on the formation and modeling of TTHM in continuous-pressurized water supply as the case of most places in the world (developed as well as developing). However, one important aspect of this research is that it tackles the formation and modeling of TTHM in intermittent water supply conditions such as those prevailing in Palestine and Jordan.

Therefore, the objectives of this research are to assess and better understand the formation and occurrence of DBPs in the Nablus water supply and to develop a relationship between DBP occurrence and chlorine dose used, organic matter level, and detention time of water in the distribution system.

2 Background

2.1 Water Supply in Palestine and Nablus

According to the Palestinian Water Authority [6], the total Palestinian water supply was 308.7 MCM/year of which 73.1 % was pumped from wells, 8.17 % from springs, and 18.73 % through the Israeli company commissioned by the Israeli occupational authorities. The total water supply for domestic purposes was 185.5 MCM/year, distributed as follows: 86.7 % via piped networks, 3.4 % from tankers, 6.7 % from rainwater harvesting, and 3.2 % by other means [7,8]. The total daily per capita water supply rates for domestic purposes in the West Bank range from 43 L/c-d (liters per capita per day) in the Jenin governorate to 162 L/c-d in the Jericho governorate (see Table 1 below).

The average rate of unaccounted water (UFW) in urban water supply systems was estimated at 42 % of total water supply (it varies between 25 and 55 %); therefore, the average per capita domestic water consumption in these areas is much less than that listed above [9].

The City of Nablus is located in the northern West Bank—Palestinian Territory. The Nablus water supply system started in 1934 with partial service (50 % of the population). Now, the system serves 99 % of the 30.58 km^2 service areas, which includes the city itself and several surrounding communities, with a total of approximately 177,000 people. The water sources of Nablus include five wells and five springs

Table 1 Quantity of water supply for domestic sector in the West Bank, 2010

Governorate	Water supply for domestic sector (MCM)	Population midyear	Water consumed (MCM)	Total losses (MCM)	Daily allocation per Capita (liter/capita/day)
West Bank[a]	85.0	2,275,982	60.3	24.7	73.0
Jenin	6.0	274,001	4.3	1.7	43.0
Tubas	1.7	54,765	1.2	0.5	60.0
Tulkarm	4.6	165,791	2.8	1.8	46.0
Nablus	11.2	340,117	7.9	3.3	64.0
Qalqiliya	4.0	97,447	3.1	0.9	87.0
Salfit	2.6	63,148	2.0	0.6	87.0
Ramallah and Al-Bireh	16.2	301,296	11.9	4.3	108.0
Jericho and Al-Aghwar	3.6	45,433	2.7	0.9	162.0
Jerusalem[a]	4.6	144,740	2.8	1.8	53.0
Bethlehem	10.7	188,880	7.0	3.7	102.0
Hebron	19.8	600,364	14.6	5.2	67.0

[a] Data exclude those parts of Jerusalem, which were annexed by Israel in 1967. *Source*: PCBS 2010 and PWA, 2011 [7,10]

Table 2 Capacity of Nablus water sources

No.	Source	Average yield (m^3/day)
1	Audala well	5,280
2	Al-Badan well	4,800
3	Al Far'a well	4,320
4	Deir Sharaf well	4,320
5	Sabastia well	8,160
6	Ein Beit El Ma spring	1,574
7	Al-Qaryon spring	1,447
8	Ras Al-Ein spring	1,169
9	Ein Al-Assal spring	457
10	Ein Dafna spring	340
	Total	31,867

Data Source: WSD, 2010 [11]

Table 3 Average annual water quality for sources used in Nablus water supply

Parameter	Concentration	Parameter	Concentration
pH (U)	7.22–7.40	Ca (mg/L)	52–80
Turbidity (NTU)	0.21–0.28	Mg (mg/L)	12–22
NO3 (mg/L)	16–41	Na (mg/L)	12–27
SO4 (mg/L)	6.5–11	K (mg/L)	1–2
PO4 (mg/L)	0	Fe (mg/L)	0
F (mg/L)	0.21–0.25	Zn (mg/L)	0
TDS (mg/L)	247–420	Pb (mg/L)	0
Total alkalinity (mg/L) as CaCO3	160–240	Cr (mg/L)	0
Total Hardness (mg/L) as CaCO3	190–290	Cd (mg/L)	0
		Cu (mg/L)	0
		Br (mg/L)	0.02–0.025

Data Source: Authors

(Table 2), with a total yield of nearly 32,000 m^3/d in 2010. The actual average water consumption in the year 2010 was 72 l/c-d, and the UFW rate was 29 % [11].

Water quality of Nablus water supply is good and comply with Palestinian drinking water quality standards. Table 3 includes average annual water quality measurements for 10 groundwater sources (wells and springs) used in Nablus water supply.

The distribution network consists of 13 storage tanks, 13 pump stations, and about 304 km of water pipes ranging in diameter from 2 to 12 in. The existing system consists of a variety of pipe types: steel (254 km), polypropylene (24 km), ductile iron (14 km), and high-density polyethylene (12 km) pipes, and there is a range of pipe ages. While some of the network is more than 60 years old, most of the pipes (about 224 km) were installed in the last 15 years [11].

The Nablus water system is divided into nine individual service zones, but some interconnections exist between these zones. The Municipality supplies the zones intermittently by opening and closing various valves as necessary, with typical pumping duration of 8–16 h. For example, in January, water is pumped to each zone every third or fourth day. In the high-demand season of summer, water may be pumped only once every 5–7 days [11]. During the periods of no supply, the pipes in that zone are drained, which increases the chance of contaminant intrusion into the pipe network. Due to this intermittent supply system, most residences are equipped with roof storage tanks with capacity of up to several cubic meters.

The only treatment practiced in Nablus water supply is chlorination using sodium hypochlorite solution. Chlorine is dosed at each of the storage tanks in the system. A typical dose is 1 kg of 12 % solution per 200 m^3 of water, which yields a dose of approximately 0.6 mg/L as Cl_2. Monitoring indicates that detectable chlorine residual is maintained throughout most of the system. For example, in 2009, 127 of 130 samples had a detectable (>0.1 mg/L) chlorine residual (range = 0.1–1 mg/L, mean = 0.43 mg/L, median = 0.4 mg/L) [12].

2.2 Disinfectants and Disinfection By-products Formation and Operational Challenge

There are many known organic and inorganic DBPs, as well as possibly as yet unidentified DBPs formed in disinfected water. Total trihalomethanes (TTHM—chloroform ($CHC1_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHBrCl_2$), and dibromochloromethane($CHBr_2Cl$) and haloacetic acids (HAA5—monochloro-, dichloro-, trichloro-, monobromo-, dibromo-) are widely occurring classes of DBPs formed during disinfection with chlorine and chloramine. These DBPs generally form at much lower levels when chloramine is used instead of chlorine. The amount of trihalomethanes and haloacetic acids in drinking water from one water system can change from day to day, depending on the season, water temperature, amount of chlorine added, the amount of plant material in the water, and a variety of other factors. The four THMs (TTHM) and five HAAs (HAA5) measured and regulated in the Stage 2 DBPR act as indicators for DBP occurrence. There are many other known DBPs, in addition to the possibility of unidentified DBPs present in disinfected water [13]. Total organic carbon and bromate are the two major compounds reacting with chlorine to form TTHM. In general, all types of disinfectants produce and form a variety of oxidation and disinfection by-products [3,14,15]. For example, Chlorine and hypochlorite can form halogenated by-products such as trihalomethanes and haloacetic acids; ozone can form bromate and chlorite; chlorine dioxide can form chlorite and chlorate; chloramines can form genotoxic

iodo-acid DBP; and non-aromatic compounds may be significant sources of DBP precursors

Other chlorination DBPs include chloral hydrate, haloacetonitriles, halopropanones, and chloropicrin. Cyanogen chloride is a unique DBP in chloraminated waters. Aldehydes, ketoacids, and carboxylic acids are organic by-products commonly detected in ozonated waters.

The health impacts resulting from ingesting DBPs are important, of concern, and a big challenge due to the fact that the majority of people drink water from public water supply. A convincing proof suggests that DBPs have already begun to cause large-scale damage to the health of humans, animals, and wildlife [16,17]. Reports indicate that DBPs when ingested will react with human body's internal parts content and may result in various health impacts such as liver, pancreas, and kidney tumors [18–22]; red blood cells decrease [23,24]; cancer to bladder, colon, rectum, and urinary track [1,2,25–35]; cardiovascular diseases [36,37]; growth retardation [38–43]; birth defects; pregnancy failure; and abortion [44–49] and other (immune suppression and cancer, breast cancer, cognitive/behavioral deficits, and wildlife).

Although these impacts are not yet fully confirmed and still under evaluation and discussion by scientists, governments, and researchers, the long-term impacts of DBPs should be taken into consideration.

The levels of certain DBPs formed from chlorine are strictly regulated because of their known potential as mutagens or carcinogens [21,35].

It was reported that as of 2009, there have been more than 48 scientific publications reporting 118 models to predict DBP formation in drinking waters [50]. However, this abundance of research work and data was generated for medium and large continuous supply systems, and very little was done on modeling DBP formation in small intermittent water distribution systems.

2.3 Regulating and Modeling DBP Exposure Concentrations

Because of their high occurrences in drinking water and potential health risks, DBPs are regulated in drinking water by the US EPA. The Total Trihalomethane Rule established a maximum contaminant level (MCL) of 100 mg/L for four THMs in finished water [51]. The Stage 1 Disinfectants and Disinfection By-products Rule established MCLs at 80 mg/L for four THMs, 60 mg/L for five HAAs, 10 mg/L for bromate, and 1 mg/L for chlorite [15,41].

3 Methods and Materials

This study included a field study and a laboratory study. The field campaign measured TTHM concentrations at 21 locations within the Nablus water network, while the laboratory study evaluated TTHM formation in pipes under a variety of controlled conditions. The field survey results were reported by Jodeh et al. [5]. The laboratory experiment results will be presented and discussed in this article.

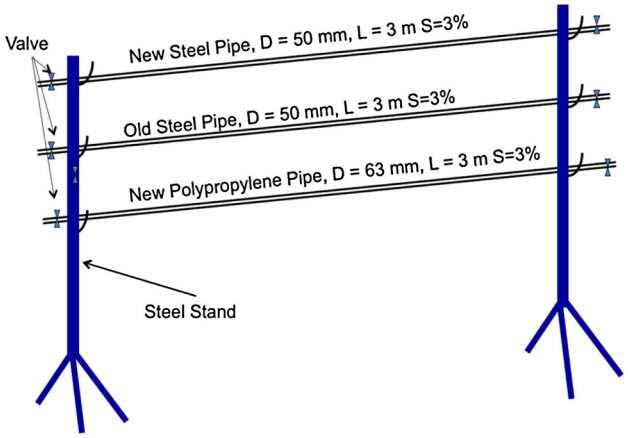

Fig. 1 Schematic diagram of experimental setup

3.1 Experimental Setup: Laboratory Pipe Study

A laboratory-scale pipe experiment was conducted at the Water and Environmental Studies Institute (WESI) laboratory at An-Najah National University in Nablus. The laboratory was kept at a constant temperature of 26 °C for the duration of the experiment.

Three pipe materials were studied: old steel, new steel, and new polypropylene. Old steel pipes (15–20 years old) were obtained when the Nablus Municipality Water Department removed pipes from their existing network. New steel and polypropylene pipes were obtained from a local supplier. Triplicate 3-m sections of each pipe material were mounted on steel stands with a 3 % slope, for a total of nine pipes studied. Each pipe had a valve at each end (Fig. 1).

Some variables were not tested such as pH and temperature because of their values in the system are constant (pH of water around 7 most of the year) or difficult to control (temperature).

A total of six testing rounds (R) were conducted with the nine pipes, for an overall number of 54 samples (Table 4). The nine pipe segments were filled with water of varying quality as follows:

- For each pipe material, pipes were filled with Nablus tap water, supplemented with chlorine doses of 0.3, 0.6, and 0.9 mg/L. These values are typical of free chlorine residual levels reported in the Nablus water system over 16 years of monitoring.

Table 4 Description of experimental program

Pipe type	Diameter (mm)	Length (m)	Number of pipes	Incubation period 1 = 72 h		Incubation period 2 = 120 h	
				CL_2 doses (mg/L)	BOD level (mg/L)	CL_2 doses (mg/L)	BOD level (mg/L)
New steel (NS)	50	3	3	R1—0.3	0	R4—0.3	0
					10		10
					30		30
				R2—0.6	0	R5—0.6	0
					10		10
					30		30
				R3—0.9	0	R6—0.9	0
					10		10
					30		30
Old steel (OS)	50	3	3	R1—0.3	0	R4—0.3	0
					10		10
					30		30
				R2—0.6	0	R5—0.6	0
					10		10
					30		30
				R3—0.9	0	R6—0.9	0
					10		10
					30		30
Polypropylene (P)	63	3	3	R1—0.3	0	R4—0.3	0
					10		10
					30		30
				R2—0.6	0	R5—0.6	0
					10		10
					30		30
				R3—0.9	0	R6—0.9	0
					10		10
					30		30

R = Testing round

- For each pipe segment filled with each chlorine dose, the water was mixed in separate rounds with three BOD contamination levels: 0, 10, and 30 mg/L (maximum level of BOD ever found in Nablus water supply).
- Two incubation periods were applied for water in the pipes: 72 and 120 h (the same periods used in Nablus water supply system for intermittent pumping).

For chlorine dosing, the residual chlorine of the tap water was first measured using a Hach colorimetric test. Then, the appropriate amount of chlorine was added (using sodium hypochlorite solution) as required to achieve the required dose. The residual chlorine was measured again after chlorine addition to ensure the proper value was achieved.

Because a total organic carbon analyzer was not available, organic content was monitored using biochemical oxygen demand (BOD). To add organic matter, solid waste was obtained from a chicken farm in Nablus City, dried in sunlight, and ground to the size of a sesame seed (approximately 1 mm). One gram of waste was soaked in 1 L of water for 2 days; the BOD measured after five days was 100 mg/L. This solution was then diluted with tap water to the appropriate BOD concentration. Initial BOD in tap water was measured prior to adding organic matter and was zero for all samples.

Samples were collected at the end of each experimental round in 1-L glass bottles with Teflon-lined screw caps. The sample bottles were filled to the rim from the water valve at the lower end of each pipe segment and 0.1 g of sodium thiosulfate ($Na_2S_2O_3\ 5H_2O$ analytical grade POCH SA, Gliwice) was added to each sample to quench any remaining chlorine residual and stop the formation of THMs. Bottles were then capped and preserved in a refrigerator at 4 °C until analysis, with a maximum holding time of 3 days.

3.2 Analytical Methods

For each sample Cl_2, BOD, pH, temperature, and DBPs were analyzed according to the standard methods for the examination of water and wastewater [52].

3.2.1 TTHM Extraction

The DBP compounds were separated from the water samples by SPME technique and as described by Luks-Betlej and Bodzek [53].

A micro-extraction time of 8 min and mixing the sample at 400 rpm achieved equilibrium conditions. After the set time of the micro-extraction, the fibers were immediately inserted into the injector of GC/MS of PerkinElmer Clarus 500 Gas Chromatograph–Mass Spectrometer, where the desorption took place within 2 min at 170 °C. The time of thermal desorption was verified by fiber purity control by blank test; moreover, the fibers were cleaned at 250 °C, before each extraction. Two hundred extractions were performed with the PDMS fibers.

3.2.2 TTHM Analysis

A PerkinElmer Claurus 500 GC/MS was used for TTHM analysis. The chromatograph was equipped with 560D MS detector and a column of Elite 5MS with poly(dimethylsiloxane) phase (30 m × 0.25 mm × 0.25 μm film thickness). The parameters of chromatographic analysis were as follows:

- Stock solutions of 5,000 μg/mL of each chemical dissolved in methanol were made. The solutions were kept refrigerated in amber-colored vials.
- Temperatures: split/splitless injector 170 °C, detector 250 °C; program: 30 °C (5 min), 30–120 °C (9 °C min), 120 °C (10 min). Carrier gas He: 20 cm/s; desorption time from the fibers: 2 min.
- To make calibration curves, aliquots dissolved in methanol with concentration of 5,000 μg/mL of all standards were applied. The solutions were kept refrigerated in amber-colored vials. The basic aliquots were dissolved with methanol in order to prepare spiked water solutions for making calibration curves.
- Calibration curves for chloroform ($CHC1_3$) were made for the concentration range 5–30 μg/L, for bromodichloromethane ($CHBrCl_2$) 0.25–4 μg/L, dibromochloromethane ($CHBr_2Cl$) 0.5–5 μg/L, bromoform ($CHBr_3$) 0.05–0.1 μg/L, respectively. Calibration curve details are shown in Table 5.

Calibration curves for four THMs determined by the SPME-GC/MS method were estimated. Each of the four compounds was measured individually, and the TTHM was calculated as the sum of the four concentrations.

Table 5 Calibration curves correlation coefficients

Compound	b^a	a^a	r^2	RSD %	Detection limit ppb
$CHBrCl_2$	145.7	1,212.3	0.998	6–10	2.1
$CHBr_2Cl$	414.7	1,220.8	1	3–5	3.1
$CHBr_3$	−10.36	782.4	0.999	3–12	3.2
$CHC1_3$	−22.82	308.9	0.999	3–10	2.5

[a] Linear regression constants $y = ax + b$

4 Results and Discussion

Results obtained for the TTHM formation in water pipes under various test conditions are summarized in Tables 6 and 7 and Figs. 2 and 3.

4.1 Effect of BOD in Water on TTHM Formation

In the presence of soluble organics in water (measured as BOD) for all types of pipe material, the TTHM concentration increased in water as both the chlorine concentration increased and incubation period in pipes increased. This increase was highest in old steel pipes, then new steel pipes, and the least was in polypropylene pipes (see Tables 6, 7; Figs. 2, 3). This result is in agreement with the work of Stuart et al. [54]. For zero addition of BOD and for the three types of pipes, there was an increase in TTHM concentrations for chlorine dose (Cl 0.36–0.62) and then there was a decrease for the second chlorine dose (Cl 0.62–0.90). This decrease probably due to decay of one or more of the four TTHM compounds (see Tables 6, 7; Figs. 2, 3).

TTHM Data shown in Tables 6 and 7 indicated that

- In the absence of BOD and for under all test conditions, TTHM was formed and occurred.
- The TTHM rate was decreasing as initial chlorine concentration in water was increasing. This decrease was the highest in old steel pipes and with longer incubation period.
- In general, there was no TTHM rate trend for initial BOD concentration and incubation period change.
- The TTHM rate for the 120-h incubation period was decreasing with increasing initial BOD and chlorine concentration. This decrease might be attributed to that with longer incubation periods, TTHM concentration start to decompose.
- The TTHM rate as a function of increasing initial chlorine and BOD concentration was higher for polypropylene pipes than old and new steel pipes.

Table 6 Summary of TTHM formation in water pipes under various test conditions

BOD (mg/L)	$T(h)$	Cl_2= 0.36 mg/L		Cl_2= 0.62 mg/L		Cl_2= 0.9 mg/L	
		Sample no.	TTHM (μg/L)	Sample no.	TTHM (μg/L)	Sample no.	TTHM (μg/L)
0	72	OS1/1	111	OS3/1	118	OS2/1	123
0	120	OS1/2	131	OS3/2	211	OS2/2	169
10	72	OS1/3	121	OS3/3	160	OS2/3	188
10	120	OS1/4	148	OS3/4	215	OS2/4	298
30	72	OS1/5	176	OS3/5	288	OS2/5	326
30	120	OS1/6	193	OS3/6	298	OS2/6	357
0	72	NS1/1	88	NS3/1	89	NS2/1	94
0	120	NS1/2	92	NS3/2	187	NS2/2	114
10	72	NS1/3	93	NS3/3	151	NS2/3	162
10	120	NS1/4	136	NS3/4	201	NS2/4	276
30	72	NS1/5	156	NS3/5	262	NS2/5	302
30	120	NS1/6	171	NS3/6	281	NS2/6	319
0	72	PP1/1	63	PP3/1	81	PP2/1	72
0	120	PP1/2	74	PP3/2	163	PP2/2	89
10	72	PP1/3	74	PP3/3	138	PP2/3	157
10	120	PP1/4	111	PP3/4	193	PP2/4	259
30	72	PP1/5	141	PP3/5	238	PP2/5	287
30	120	PP1/6	159	PP3/6	273	PP2/6	307

OS Old steel pipe, *NS* new steel pipe, *PP* polypropylene

Table 7 Percent change in TTHM under various test conditions

Pipe concentration	Percent increase in TTHM					
	Initial BOD = 0 mg/L		Initial BOD = 10 mg/L		Initial BOD = 30 mg/L	
	t = 72 h	t = 120 h	t = 72 h	t = 120 h	t = 72 h	t = 120 h
Old steel pipe						
Cl 0.36–0.62	6	38	24	31	39	35
Cl 0.62–0.90	4	−20	15	28	12	17
New steel pipe						
Cl 0.36–0.62	1	51	38	32	40	39
Cl 0.62–0.90	5	−39	7	27	13	12
Polypropylene Cl						
0.36–0.62	22	55	46	43	41	42
Cl 0.62–0.90	11	−45	12	26	17	11

It is important to note that the formation and occurrence of TTHM in water with initial zero or no BOD presence probably due to chlorine reaction with other compounds found in the water other than BOD. In this regard, it was reported by Cooke and Kennedy [55] that the formation and occurrence of DBP in drinking water could start before the water treatment plant (chlorine addition) due to the presence of taste and odor-causing matters and algae and/or the emergence of chemical solvents and refrigerants to water sources from industrial sources [56–58]. Further studies are needed to explore this point and decide on the source of TTHM (DBPs) reaction when no initial BOD or soluble organics present in water.

4.2 Effect of Chlorine Presence in Water on TTHM Formation

The presence of chlorine in water and in all pipe material has resulted in direct positive increase in TTHM formation regardless of soluble organics presence. The levels of TTHM

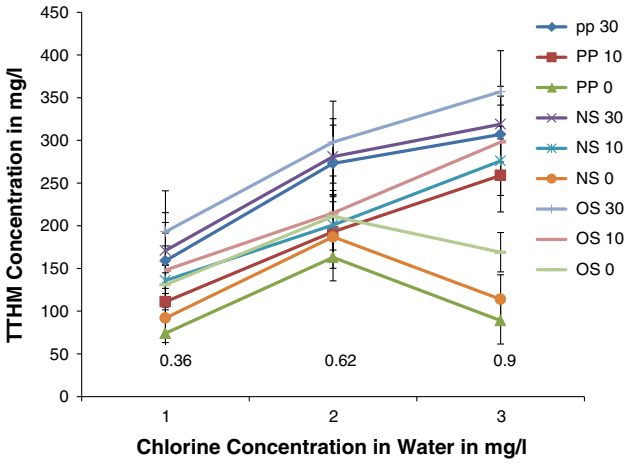

Fig. 2 TTHM pipe experiment results for $t = 120$ h

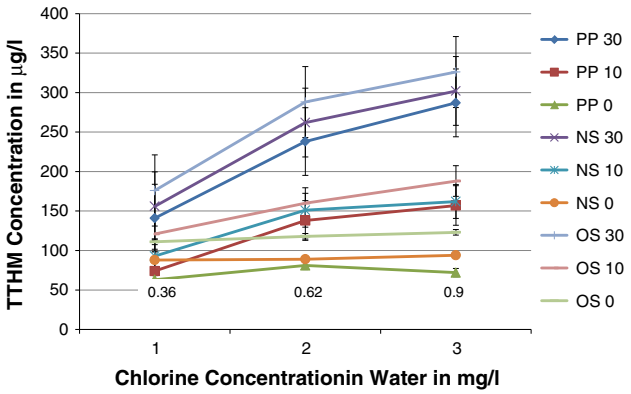

Fig. 3 TTHM pipe experiment results for $t = 72$ h

formed for chlorine concentration equal or less than 0.9 mg/L were within accepted USEPA [42] and Palestinian standards of 80 and 250 mg/L, respectively. Results indicate that with chlorine concentration in water up to 1.0 mg/L, incubation period of 72 h, and BOD up to 10 mg/L, TTHM formation was under or within Palestinian drinking water standards [59]. However, these TTHM concentrations do exceed and in some cases over double USEPA standards. A result that clearly question the effectiveness and safety of Palestinian TTHM standards. As chlorine concentration and the incubation period increased, TTHM exceeded both Palestinian and USEPA standards.

4.3 Effect of Incubation Period on TTHM Formation

Results obtained indicated the direct positive effect of the incubation period of water in pipes on TTHM formation except at high chlorine dose and incubation period of 120 h decrease was observed due to decomposition of TTHM.

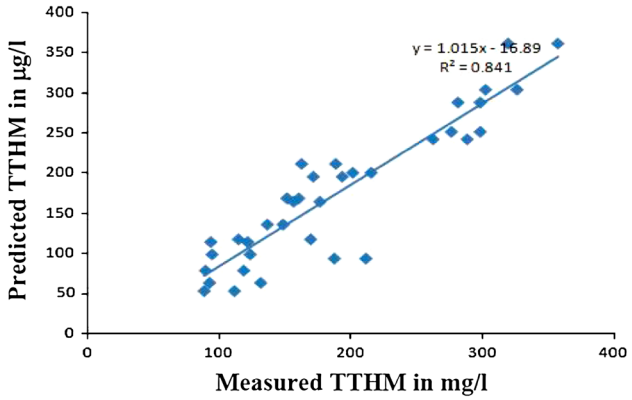

Fig. 4 Relation between measured and predicted TTHM

4.4 Effect of Pipe Material on TTHM Formation

It is clear from the obtained results that in regard to TTHM formation in water pipes, the propylene pipes and under all conducted test conditions were with minimum and less TTHM formation in water incubated than in other pipes and accordingly represent the best pipe material among the three tested pipe types to be used in the conditions tested under this research.

4.5 Development of Predictive Model for TTHM Formation

In order to predict the occurrence of TTHM in drinking water, nonlinear regression analysis using SPSS [60] was used to develop a predictive model. The model expresses total trihalomethane (TTHM) concentration in terms of BOD, Cl_2 concentration, and incubation time.

The proposed model is

$$\mathrm{TTHM} = 24.758 \times \mathrm{BOD}^{0.3292} \times \mathrm{Cl2}^{0.5579} \times t^{0.3386}$$

where TTHM, Trihalomethane in mg/L; BOD, Biological oxygen demand in mg/L; Cl_2, chlorine concentration in mg/L; $t$incubation period in hours.

The model indicates that chlorine presence in water has a higher impact on TTHM formation than BOD or incubation period. The plot of predicted TTHM values by the model versus the measured ones indicates good correlation (Fig. 4).

A comparison of model predicted TTHMs with actual measurements for 21 field samples taken from Nablus water supply system (see Fig. 5 below) indicates a fair agreement between the two, although the correlation coefficient was low ($r = 0.55$).

4.6 Potential Application of the Model

Applying the developed model to various Cl_2 concentrations, BOD water contamination levels and incubation periods of water in pipes point toward the following:

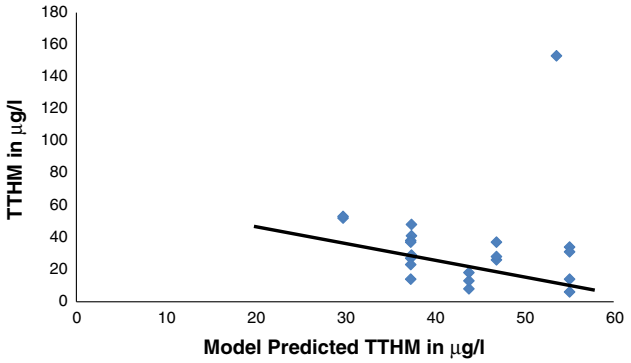

Fig. 5 Relation between measured and predicted TTHM (Field Data)

In case of fixed BOD in water at 10 mg/L and incubation period in pipes at 72 h and variable chlorine concentration in water, the maximum allowable Cl_2 concentration in water to fulfill Palestinian Standards is 1.2 mg/L and with EPA standards is 0.2 mg/L. The predicted TTHM by the model indicates that the permissible TTHM by USEPA standards of 80 TTHM seems very practical and safe, while the permissible TTHM by the Palestinian standard of 250 TTHM is the opposite.

In case of fixed chlorine concentration in water of 0.62 mg/L and incubation period in pipes at 72 h and variable BOD concentration in water, the maximum allowable BOD concentration in water to fulfill Palestinian Standards is 30 mg/L and with EPA standards is 4 mg/L. Again, and in this case, the predicted TTHM by the model indicates that the USEPA standards seem very practical and safe, while the Palestinian standard is the opposite.

In case of fixed chlorine concentration in water of 0.62 and 10 mg/L BOD concentration in water, and variable incubation period in pipes, the maximum allowable incubation period in pipes to fulfill Palestinian Standards is 238 h and with EPA standards is 8 h. Again, and in this case, the predicted TTHM by the model indicates that the USEPA standards seem very practical and safe, while the Palestinian standard is the opposite.

As shown above, the developed model effectively and reasonably predicts TTHM concentrations at various conditions.

5 Conclusions

The data obtained from the pipe segments experiment indicate that

- TTHM formation in water is influenced not only by chlorine concentration in water but also pipe material, BOD contamination level, and incubation time of water in the pipe.
- Results obtained were used to develop an empirical model for TTHM prediction as a function of chlorine concentration in water, BOD contamination level in water, and incubation time in pipes.
- The presence of chlorine in water and in all pipe material resulted in direct increase in TTHM formation regardless of soluble organics presence or extent.
- TTHM formation under all test conditions was highest in old steel pipes, then in new steel pipes and the least in polypropylene pipes.
- At average operating conditions, as the incubation period of water in pipes increased, TTHM formation in water also increased
- TTHM concentration in water increased as both the BOD concentration and the chlorine concentration in water increased.
- The developed model effectively and reasonably predicts TTHM concentrations at various conditions.
- Further studies are needed to explore this point and decide on the source of TTHM (DBPs) reaction when no initial BOD or soluble organics present in water.

References

1. Alavanja, M.; Goldstein, I.; Susser, M.: Case–control study of gastrointestinal and urinary tract cancer mortality and drinking water chlorination. In: Jolley, R.L.; Gorchev, H.; Hamilton, D.H. (eds.) Water Chlorination: Environmental Impact and Health Effects. Ann Arbor, Michigan, Ann Arbor Science Publishers, **2**, 395–409 (1978)
2. Hildesheim, M.E.; Cantor, K.P.; Lynch, C.F.; Dosemeci, M.; Lubin, J.; Alavanja, M.; Craun, G.: Drinking water source and chlorination byproducts: risk of colon and rectal cancers. Epidemiology **9**(1), 28–36 (1998)
3. International Program on Chemical Safety, IPCS: Environmental Health Criteria 216: Disinfectants and Disinfectant By-products. A report published November 30, 2004, jointly by: United Nations Environment Program (UNDP), International Labor Organization (ILO), and World Health Organization (WHO). http://www.who.int/ipcs/publications/ehc/ehc_216/en/ (2004). Accessed Oct 2011
4. Manivannan, G., editor: Disinfection and Decontamination: Principles, Applications, and Related Issues. Published by 2008 by Taylor & Francis Group, LLC, pp 43–44 (2008)
5. Joudeh, S.; Nabeel, O.; Haddad, M.; McNeil, L.: The effects of pipe material and age on the formation of disinfection by-products (DBP) in Nablus Water Network—survey study of the occurrence of trihalomethanes in Nablus drinking water. An-Najah J. Res. Natl. Sci. **27**, 1–14 (2013)
6. PWA,Palestinian Water Authority: Water Database. Ramallah—Palestine (2009)
7. PCBS, Palestinian Central Bureau of Statistics: Quantity of Water Supply for Domestic Sector and Water Consumed and Total Losses and Population and Daily Allocation per Capita in the West Bank by Governorate, 2010. http://www.pcbs.gov.ps/Portals/_Rainbow/Documents/water/Water_Tabel_E_tab7.htm (2010). Accessed Oct 2012.

8. Haddad, M.: Existing and Future Water Status in Palestine. Paper prepared for Strategic Foresight Group, Nablus Palestine, February 2010 (2010)
9. PWA, Palestinian Water Authority: Water Supply in the West Bank 2005. Report prepared by the Directorate General for Staregic Planning, Ramallah, Palestine (2005)
10. Palestinian Water Authority: Water Information System. Ramallah—Palestine (2011)
11. WSD, Water and Sanitation Department: Personal Communication with Eng. Arij Kitaneh, Head of IT and Data Center at WSD, Nablus Municipality, September 2010
12. Omar, N.: The Effects of Pipe Material and Age on the Formation of Disinfection By-products (DBP) in Nablus Water Network. Master Thesis, An-Najah National University, Nablus, Palestine, December 2010
13. EPA-United States Environmental Protection Agency: Fact Sheet: Stage 2 Disinfectants and Disinfection Byproducts Rule. Published by Office of Water (4607M) EPA 815-F-05-003 December 2005. http://www.epa.gov/safewater/disinfection/stage2/pdfs/fs_st2_finalrule.pdf (2005). Listed December 2005, accessed June 2013
14. Castellon, C.; Disinfection Byproduct (DBP) Precursors in Central MA Watershed and DBP Occurence in MA Water Supplies. http://scholarworks.umass.edu/cee_ewre/15/ (2005). Listed September 2008, accessed Oct 2012 (2008)
15. Yuefeng, X.: Disinfection Byproducts in Drinking Water: Formation, Analysis, and Control . A book published 2004 by CRC Press LLC (2004)
16. Thornton, J.: Pandora's Poison: Chlorine, Health, and a New Environmental Strategy. Published by MIT Press, pp: 105–106 (2000)
17. United States Environmental Protection Agency: What is Our Drinking Water?: Identification of New Chemical Disinfection By Products (DBPs). http://www.epa.gov/athens/research/process/drinkingwater.htm (2012). Listed January 2012, accessed Oct 2012
18. Ade, P.; Guastadisegni, C.; Testai, E.; Vittozzi, L.: Multipleactivation of chloroform in kidney microsomes from male and female DBA/2J mice. J. Biochem. Toxicol. **9**, 289–295 (1994)
19. Ijsselmuiden, C.B.; Gaydos, C.; Feighner, B.; Novakoski, W.L.; Serwadda, D.; Caris, V.; Comstock, G.W.: Cancer of the pancreas and drinking water: a population-based case–control study in Washington County, ML. Am. J. Epidemiol. **136**, 836–842 (1992)
20. Fox, T.R.; Schumann, A.M.; Watanabe, P.G.; Yano, B.L.; Maher, V.M.; McCormick J.J.: Mutational analysis of the H-ras oncogene in spontaneous C57BL/6 × C3H/He mouse liver tumors and tumors induced with genotoxic and nongenotoxic hepatocarcinogens. Cancer Res. **50**, 4014–4019 (1990)
21. Woodruff, N.W.; Durant, J.L.; Donhoffner, L.L.; Penman, B.W.; Crespi, C.L.: Human cell mutagenicity of chlorinated and unchlorinated water and the disinfection byproduct 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX). Mutat. Res. **495**, 157 (2001)
22. Knecht, K.T.; Mason, R.P.: The detection of halocarbon-derived radical adducts in bile and liver of rats. Drug Metab. Dispos. **19**, 325–331 (1991)
23. Koivusalo, M.; Vartiainen, T.; Hakulinen, S.; Pukkala, E.; Jaakkola, JJ.: Drinking water mutagenicity and leukemia, lymphomas, and cancers of the liver, pancreas and soft tissue. Arch. Environ. Health **50**, 269–276 (1995)
24. Abdel-Rahman, M.S.; Couri, D.; Bull, R.J.: Kinetics of ClO2 and effects of ClO2, ClO2−, and ClO3− in drinking water on blood glutathione and hemolysis in rat and chicken. J. Environ. Pathol. Toxicol. **3**, 431–449 (1980)
25. Bielmeier, S.R.; Best, D.S.; Guidici, D.L.; Narotsky, M.G: Pregnancy loss in the rat caused by bromodichloromethane. Toxicol. Sci **59**, 309–315 (2001)
26. Cantor, K.P.; Lynch, C.F.; Hildesheim, M: Chlorinated drinking water and risk of bladder, colon, and rectal cancers: A case–control study in Iowa. In: Disinfection By-products in Drinking Water: Critical Issues in Health Effects Research. Washington, DC, International Life Sciences Institute, p 133 (1995)
27. Koivusalo, M; Jaakkola, JJ; Vartiainen, T; Hakulinen, S: Drinking water mutagenicity and gastrointestinal and urinary tract cancers: An ecological study in Finland. Am. J. Public Health. **84**, 1223–1228 (1994)
28. Risch, H.A.; Burch, J.D.; Miller, A.B.; Hill, G.B.; Steele, R.; Howe, G.R.: Dietary factors and the incidence of cancer of the urinary bladder. Am. J. Epidemiol. **127**(6), 1179–1191 (1988)
29. Savin, J.E.; Cohn, P.D.: Comparison of bladder and rectal cancer incidence with trihalomethanes in drinking water. Epidemiology 7(Suppl 4), S63 (1996)
30. So, B.J.; Bull, R.J.; Dibromoacetate (DBA) acts as a promoter of abnormal crypt foci in the colon of F344 rats. Toxicologist **15**, 1242 (1995)
31. IARC, International Agency for Research On Cancer: Monograph on the Evaluation of Carcinogenic Risk to Humans: Chlorinated Drinking Water, Chlorination Byproducts, Some Other Halogenated Compounds; Cobalt and Cobalt Compounds, 52 Lyon IARC, 1991 (1991)
32. Keegar, T.; Whitaker, H.; Nieuwenhuijsen, M.J.; Toledano, M.B.; Elliott, P.; Fawell, J.; Wilkinson, M.; Best, N.: Use of routinely collected data on trihalomethane in drinking water for epidemiological purposes. Occup. Environ. Med. **58**, 447–452 (2001)
33. Morris, R.D.; Audet, A.M.; Angelillo, I.F.; Chalmers, T.C.; Mosteller, F.: Chlorination, chlorination by-products, and cancer—a meta analysis. Am. J. Public Health **82**, 955–963 (1992)
34. Cragle, D.L.; Shy, C.M.; Struba, R.J.; Stiff, E.J.: A case–control study of colon cancer and water chlorination in North Carolina. In: Jolley, R.L.; Bull, R.J.; Davis, W.P. (eds.) Water Chlorination: Chemistry, Environmental Impact, and Health Effects. Chelsea, Michigan, Lewis Publishers, Inc., vol. 5, pp 153–159 (1985)
35. Komulainen, H.: Experimental cancer studies of chlorinated by-products. Toxicology **198**, 239 (2004)
36. Penn, A.; Lu, M.X.; Parkes, J.L.: Ingestion of chlorinated water has no effect upon indicators of cardiovascular disease in pigeons. Toxicology **63**(3), 301–313 (1990)
37. Nordenberg, A.; Delisle, G.; Izukawa, T.: Cardiac arrhythmia in a child due to chloral hydrate ingestion. Pediatrics **47**, 134–135 (1971)
38. Borzelleca, J.F.; Carchman, R.A.; Effects of selected organic drinking water contaminants on male reproduction. Research Triangle Park, North Carolina, US Environmental Protection Agency (EPA 600/1-82-009; NTIS PB82-259847) (1982)
39. Carlton, B.D.; Basaran, A.H.; Mezza ,L.E.; George, E.L.; Smith, M.K.: Reproductive effects in Long-Evans rats exposed to chlorine dioxide. Environ. Res. **56**, 170–177 (1991)
40. EPA-United States Environmental Protection Agency: Draft Drinking Water Health Criteria Document for Chloramines. Office of Science and Technology, Office of Water, Washington,DC (1994)
41. EPA-United States Environmental Protection Agency: National Primary Drinking Water Regulations; Disinfectants and Disinfection Byproducts, Final Rule, Federal Register, 63, 69392, (1998)
42. EPA-United States Environmental Protection Agency: Panel Report and Recommendation for conducting Epidemiological Research on Possible Reproductive and Developmental Effects of Exposure to Disinfected Drinking Water. Office of Research and Development, Washington, DC (1998)
43. EPA-United States Environmental Protection Agency: Integrated Risk Information System. Office of Research and Development, Office of Health and Environmental Assessment, Cincinnati, OH (1998)

44. Bove, F.J.; Fulcomer, M.C.; Klotz, J.B.; Esmart, J.; Dufficy, E.M.; Savrin, J.E.: Public drinking water contamination and birth outcomes. Am. J. Epidemiol. **141**(9), 850–862 (1995)
45. Aschengrau, A.; Zierler, S.; Cohen, A.: Quality of community drinking water and the occurrence of spontaneous abortions. Arch. Environ. Health **44**(5), 283–290 (1989)
46. Aschengrau, A.; Zierler, S.; Cohen, A.: Quality of community drinking water and the occurrence of late adverse pregnancy outcomes. Arch. Environ. Health **48**(2), 105–114 (1993)
47. Bove, F.J.; Fulcomer, M.C.; Koltz, J.B.; Esmart, J.; Dufficy, E.M.; Zagraniski, R.T.: Report on Phase IV-A: Public Drinking Water Contamination and Birthweight Fetal Deaths, and Birth Defects, a Cross-Sectional Study. New Jersey Department of Health, Trenton, NJ (1992)
48. Bove, F.J.; Fulcomer, M.C.; Koltz, J.B.; Esmart, J.; Dufficy, E.M.; Zagraniski, R.T.; Savrin, J.E.: Report on Phase IV-B: Public Drinking Water Contamination and Birthweight and Selected Birth Defects, a Case–Control Study. New Jersey Department of Health, Trenton, NJ (1992)
49. Fisher, J.W.; Whittaker, T.A.; Taylor, D.H.; Clewell, H.J.; Andersen, M.E.: Physiologically-based pharmacokinetic modeling of the pregnant rat: A multiroute exposure model for trichloroethylene and its metabolite, trichloroacetic acid. Toxicol. Appl. Pharmacol. **99**, 395–414 (1989)
50. Chowdhury, S.; Champagne, P.; McLellan, J.: Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review Review Article. Sci. Total Environ. **407**(14), 4189–4206 (2009)
51. EPA-United States Environmental Protection Agency: National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water, Federal Register, 44, 68624, (1979)
52. American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF): Standard Methods for the Examination of Water and Wastewater (1996)
53. Luks-Betlej, K; Bodzek, D.: Determination of tri,-tetrachloromethanes and trichloroethane by using microextraction with GC-ECD detection. Chem. Anal. **45**, 45–51 (2000)
54. Stuart, M.; Gooddy, D.; Kinniburgh, Klinck, B.: Trihalomethane formation potential: a tool for detecting non-specific organic groundwater contamination. Urban Water **3**, 173–184 (2001)
55. PSI, Palestinian Standards Institute: Drinking Water Standards. http://www.psi.gov.ps/Article.aspx?id=93&PageID=93 (2010). Accessed Oct 2011
56. Cooke, G.D.; Kennedy, R.H.: Lake Reserv. Manag. **17**(3), 157–174 (2001)
57. Wikipedia: Trihalomethane. http://en.wikipedia.org/wiki/Trihalomethane (2012). Accessed Oct 2012
58. United States Environmental Protection Agency, EPA: Fact Sheet: Stage 2 Disinfectants and Disinfection Byproducts Rule. Published by Office of Water (4607M), EPA 815-F-05-003, December 2005. http://www.epa.gov/safewater/disinfection/stage2/pdfs/fs_st2_finalrule.pdf (2005). Accessed Oct 2011
59. Cook, D.; Drikas, M.: Impact Of Water Quality And Treatment On Disinfection By-Product Formation. In: Proceedings of the 74th Annual Water Industry Engineers and Operators' Conference, Australian Water Quality Centre, 6 to 8 September, 2011, pp 56–63 (2011)
60. SPSS: IBM SPSS Statistics 15. SPSS Inc. 233 South Wacker Drive, 11th Floor, Chicago, IL 60606-6412, USA (2006)