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

تأثير نوع وعمر الأنبوب على تشكل النواتج الثانوية في شبكة مياه نابلس ـ دراسه مسحيه لوجود (THM) في شبكة الشرب بمياه نابلس

Shehdeh Jodeh*, Nabeel Omar, Marwan Haddad & Laurie McNeill

شحده جودة، ونبيل عمر، ومروان حداد، وLaurie McNeill

*Department of Chemical, Faculty of Sciences, An-Najah National University, Palestine.

E-mail: sjodeh@hotmail.com.

Received: (29/11/2011), Accepted: (11/11/2012)

Abstract

Chlorination of drinking water from natural sources results in the formation of several organic compounds as disinfection by products. The most widely studied among them is a group of compounds collectively called trihalomethanes (THMs), some of which are reported to be toxic for human consumption. Consequently water supply authorities in some countries are forced to resort to costly corrective measures in order to reduce their levels below the maximum concentration limits (MCL) set by the environmental protection and health authorities. It is well established by now that the formation of such compounds is due to reactions between chlorine and some precursor organics originally present in raw water. In the City of Nablus which located in the northern West Bank- Palestinian Territory, a water system network serves about 177,000 people in Nablus and its surrounding localities, consist of, four wells, five springs, nine operating storage tanks,13 pump stations, distribution network consists of about 279 km of water pipes of different

diameter, material and ages, The treatment process used for disinfecting drinking water is chlorination, by using sodium hypochlorite, the Unaccounted for Water (UFW) is over 30% and the supply is intermittent due to water shortages, so contaminants can intrude into the pipe network and the rooftop storage tanks and react with chlorine to form disinfection by – products (DBPs), which may cause cancer and some other diseases. In this research, samples representing Nablus water system in coordination with Nablus water supply and sanitation department were taken and analyzed for content of DBPs as THM. Results shows all total trihalomethanes (TTHM) values of field survey samples were less than PSI MCL (250 ppb) and the USEPA MCL (80 ppb), except one sample from Al Qwareen Spring-trading centre at 153 ppb, which is more than the MCL set by the USEPA.

Keywords: TTHM, sanitation, drinking water, disinfection, wells.

ملخص

ان اضافة مادة الكلورين الى مياه الشرب ينتج عنها مركبات عضويه عديدة الاشكال ومن اكثرها المركبات التي تدعى (ترايهالوميثين) والتي تعتبر سامه لصحة الانسان في مدينة نابلس الواقعة شمال الضفة الغربية المحتلة نظاما مائيا يخدم حوالي ١٧٧٠٠٠ نسمة من مدينة نابلس وبعض التجمعات المحيطة بها، ويتألف من أربعة آبار وخمسة ينابيع وتسعة خزانات وثلاثة عشر محطة ضخ وشبكة مياه بطول٢٧٩ كم تقريبا من مواسير مختلفة الأقطار والأنواع والأعمار، يتم تعقيم المياه من خلال الكلورة باستخدام هيبوكلوريت الصوديوم، ومن الملاحظ وجود نسبة عالية من الفاقد مما يشير إلى وجود تسرب من الشبكة وان أي تلوث محيط بخطوط الماء التالفة يمكن أن يؤدي إلى دخول الملوثات إلى الشبكة وتلويث المياه، وان وجود الكلور وتفاعله مع الملوثات يؤدي إلى تشكل النواتج الثانوية لاستخدام الكلور في تعقيم المياه والتي أثبتت الدراسات أن وجودها في مياه الشرب يؤدي إلى الإصابة بعدد من الأمراض منها السرطان. تم من خلال هذا البحث إجراء دراسة مسحية بأخذ عينات ممثلة للنظام المائي في نابلس بالتنسيق مع دائرة المياه والصرف الصحي التابعة لبلدية نابلس وفحص نسبة النواتج الثانوية على شكل ترايهالوميثان الكلي وتبين ان كل العينات تحتوي على الترايهالوميثان الكلي ولكن بنسب ضمن المسموح به باستثناء عينة واحدة، مما يعني ضرورة أن يتم اخذ عينات بشكل دوري من النظام لمراقبة وضبط هذا المصدر بالذات وكذلك النظام المائي.

Introduction

The City of Nablus, located in the West Bank - Palestinian Territory, has at present a water network composed of pipes of different ages and materials (steel, cast iron, galvanized steel, polypropylene (PP), and high density polyethylene (HDPE)). The water network serves about 177,000 people in Nablus and some of the surrounding localities using multiple ground water sources of varying quality. The Unaccounted for Water (UFW) reported by the Nablus municipality is over 30% and the supply is intermittent due to water shortages, so contaminants can intrude into the pipe network and the rooftop storage tanks.

Besides the fact that commonly used disinfection of drinking water has been found to be one of the biggest achievements in public health in the 20th century (Boorman et.al, 1999), the problem of a possible human health hazard resulting from the occurrence of disinfection by-products in drinking water has been considered by scientists, consumers and producers for many years (Bellar et.al, 1974).

Trihalomethanes (THM) are the main group of compounds which are formed due to water disinfection, i.e. chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), chlorodibromomethane ($CHBr_2Cl$) and bromoform ($CHBr_3$).

1. These compounds are aromatically insensible, yet their presence in water may be physiologically hazardous. Their harmful influence on organisms is presented in Table 1. At present these compounds are known to show carcinogenic properties in bioassays carried out in rodents (Dunnick et.al, 1985).

Table (1): Halomethanes.

No	Group Name	Group Compounds
1	Monosubstituted	CH_3F , CH_3Cl , CH_3Br , CH_3I
2	Disubstituted	CH_2F_2 , CH_2ClF , CH_2BrF , CH_2FI , CH_2Cl_2 , CH_2BrCl , CH_2ClI , CH_2Br_2 , CH_2BrI , CH_2I_2
3	Trisubstituted	CHF_3 , $CHClF_2$, $CHBrF_2$, CHF_2I , $CHCl_2F$, C*HBrClF , C*HClFI , $CHBr_2F$, C*HBrFI , $CHFI_2$, $CHCl_3$, $CHBrCl_2$, $CHCl_2I$, $CHBr_2Cl$, C*HBrClI , $CHClI_2$, $CHBr_3$, $CHBr_2I$, $CHBrI_2$, CHI_3
4	Tetrasubstituted	CF_4 , $CClF_3$, $CBrF_3$, CF_3I , CCl_2F_2 , $CBrClF_2$, $CClF_2I$, CBr_2F_2 , $CBrF_2I$, CF_2I_2 , CCl_3F , $CBrCl_2F$, CCl_2FI , CBr_2ClF , C*BrClFI , $CClFI_2$, CBr_3F , CBr_2FI , $CBrFI_2$, CFI_3 , CCl_4 , $CBrCl_3$, CCl_3I , CBr_2Cl_2 , $CBrCl_2I$, CCl_2I_2 , CBr_3Cl , CBr_2ClI , $CBrClI_2$, $CClI_3$, CBr_4 , CBr_3I , CBr_2I_2 , $CBrI_3$, CI_4
	* Chiral compound (molecule that is non-superposable on its mirror image).	

As the concentration of chlorine or chloramines increases, the production of disinfiction by-products (DBPs) increases. Formation reactions continue as long as precursors and disinfectant are present (Krasner, 1999 and references therein).

The treatment process used for disinfecting drinking water in Nablus City is chlorination, which is used to inactivate (or kill) pathogens (i.e., disease causing organisms) that may be found in the water supply (i.e., reservoir, ground water aquifer, or water from springs). Disinfection reduces the risk of waterborne disease and protects the public against disease. The use of chlorine creates new potential risks, because compounds known as disinfection by – products (DBPs) can be formed during the disinfection process by the reaction of disinfectants used in a

water treatment with bromide and/or natural organic matter (i.e., decaying vegetation or wastewater contamination) present in the water.

The disinfection by – products (DBPs) are formed when the disinfectant reacts with natural organic matter (NOM) and/or inorganic substances present in water. More than 250 different types of disinfection by – products (DBPs) have already been identified. (Sadiq and Rodriguez, 2004).

The main objective of this work was divided in two parts:

The first part was to develop, evaluate and improve a simple rapid and sensitive method for extraction and determination of THMs in drinking water by solid phase microextraction (SPME) combined with gas chromatography – mass spectrometry (GC-MS).

The second objective was to identify the effects of pipe materials and ages on the formation of DBPs. Pipe segments of different materials and ages were installed at the Water Environment and Studies Institute (WESI) laboratory and filled with water at different chlorine doses, contamination loads and different incubation periods applied to the different segments, The results of this part of study will be published at different article.

Experimental

Water Sources

The water sources of Nablus are four wells: a well west of the city (Deir Sharaf well) and three other wells east of the city (Audala, Al-Badan, Al Far'a), and five springs (Ein Beit El Ma, Al-Qaryon, Ras Al-Ein, Ein Al-Assal, Ein Dafna).

The capacities of the four wells and the five springs are given in the following Table 2.

Table (2): The water sources of Nablus and its capacity.

No	Source	Average Yield (m^3/day)
1	Audala Well	4500
2	Al-Badan Well	4300
3	Al Far'a Well	6000
4	Deir Sharaf well	3500
5	Ein Beit El Ma spring	1574
6	Al-Qaryon spring	1447
7	Ras Al-Ein spring	1169
8	Ein Al-Assal spring	457
9	Ein Dafna spring	340

Water Quality

The treatment process used for disinfecting drinking water in Nablus City is chlorination, by using sodium hypochlorite, which is manufactured as bleach under the brand name Clorox. Sodium hypochlorite reacts in water as follows as a disinfectant:

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

Sodium hypochlorite is produced in a clear liquid form and is completely soluble in water. The municipality obtains this disinfectant from a sub-contractor (Helen Factory for chemicals) who gets the chlorine from an Israeli factory (Makhtasheem) in Beir Al Sabea' in 250 kg containers, with a concentration of 12 percent by weight. The dose used is 1 kg of chlorine per 200 m^3 of water (personal communication, Ali Qarqash, responsible for the disinfection process in Nablus Water Supply and Sanitation Department, 2009)

Field survey Plan

The field survey is aimed at evaluating the occurrence of disinfection by – products (DBPs) in the Nablus water supply system. The field survey consisted of the following steps:

- Defining preliminary sampling locations in coordination with Nablus water supply and sanitation department
- Samples cover different water sources, roof tanks and water pipe network with different materials and ages
- Collected samples were analyzed for content of disinfection by – products (DBPs) as THM. Samples were prepared and analysis was conducted in the Chemical, Biological and Drugs Analysis Center (CBDAC) at An-Najah National University according to Standard Methods for the Examination of Water and Wastewater (1996)

Sampling Locations

To cover the water system of Nablus City, and in coordination with Nablus water supply and sanitation department the following locations were defined in Table 4.

Sampling Procedure

The following steps were followed:

1. Sampling vials (glass bottles of 1 liter volume) were obtained.
2. Each sample vial was labeled including sample ID, sample location, sample date and time.
3. The water tap which represents the sampling location (water network, water tank, reservoir, source) was opened about 3-5 minutes and the system allowed to flush until the water temperature has stabilized to ensure the sample does not represent stagnant water that has set for a long time in the water line or reservoir.
4. Bottles were rinsed with water from the sampling location before sampling.
5. Samples were capped and taken to the lab and preserved in a refrigerator at 4°C until analysis.

Sample Analysis

Sample Collection

Finished drinking water samples (1000 cm^3) were collected for analysis from both 21 field survey samples (see Table 4). The samples were taken in a standard way after running a few liters of water from the tap for the field samples. A 0.l g of sodium thiosulfate ($Na_2S_2O_3 \bullet 5H_2O$ analytical grade POCH SA, Gliwice) was added to each sample to quench any remaining chlorine residual and stop formation of THMs.

The containers had teflon-lined screw caps. The water samples were kept no longer than three days at + 4°C.

A stock solution of a THM mixture of chloroform ($CHC1_3$), bromodichloromethane, ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$) (each 5000 µg/mL in MeOH) were purchased from J.T. Baker were used. The suitable solutions of the standards were prepared in methanol (Suprasolv, Merck) by dilution in volumetric flasks in the range of 1-100 µg/L for each analyte together.

Solid-Phase Microextraction (SPME)

The compounds were extracted from the water samples by SPME technique (Luks-Betlej and Bodzek, 2000). The extraction was carried out in 3 ml screw cap vials fitted with silicone/PTFE septa, (Supelco Corp.) to which the sample was being poured underneath the seal. The microextractor fibers coated with 100 µm film of poly(dimethylsiloxane) (PDMS, 100 µm) from Supelco Corp. The standard solutions were prepared by spiking amount of working standard solution. Micro extraction conditions were selected experimentally, based on previous studies (Luks-Betlej and Bodzek, 2000). 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 Perkin Elmer Clarus 500 Gas Chromatograph-Mass Spectrometer, where the desorption took place within 2 min at 230°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.

Quantitative Analysis

GC/MS analysis was performed in the gas chromatograph of Perkin Elmer Claurus 500 type. The chromatograph was equipped with 560D MS detector, and a column of Elite 5MS with poly(dimethylsiloxane) phase (30 m x 0.25 mm x 0.25 μm film thickness) dimensions. The parameters of chromatographic analysis were as follows:

The injector was used in splitless mode for 5 min and held isothermally at 230°C. The detector temperature was 250°C. The oven temperature program was 50°C (5 min), 30-230°C ramping at 10°C min, 230°C held for 10 min. The carrier gas was helium at a flow rate of 2 mL/min. The calibration curve was made for 5 different concentrations as mentioned before. There are a lot of factors controlled the quality of results including fiber thickness, extraction time, temperatures and the salt added to the solutions. Depending on previous studies (Bahri and Driss, 2010), we used the best parameters for the experiment and the results are shown in Table 3.

Table (3): Summarized the results of the calibration curve for standards of 1-100μg/l and n=5 using SPME-GC/MS.

Compound	Retention Time(min)	R^2	LOD(ng/L)
CHCl3	8.76	0.99315	1.2
$CHCl_2Br$	11.17	0.99572	5.8
$CHClBr_2$	13.14	0.99158	2.9
$CHBr_3$	15.87	0.99376	4.3

Where R^2 represents the correlation coefficients for the compounds, the limits of detection (LODs) defined as the concentration of analytes in the sample which causes the peak with a signal-to-noise ratio of 3 were also calculated usin a spike of less than 0.2 μg/L in water.

Results

The results were measured separately for each single compound, then added together as a total THM. The following Table 4 and Figure 1. show the field survey sample locations and results.

Table (4): Field survey sample locations and results.

Sample No	Sample Location		TTHM (ng/L)
1	Reservoir	Alhaj Nimer Reservoir	14
2	Network	Al Watani Hospital	26
3	Network	Amman Street	27
4	Source	Dafna spring	6
5	Reservoir	Ein Dafna Old Reservoir	8
6	Reservoir	Ein Beit Elma New Reservoir	34
7	Reservoir	Ein El Asal spring Reservoir	13
8	Reservoir	Ras El Ein Spring Reservoir	14
9	Reservoir	Ein Beit Elma Old Reservoir	18
10	Reservoir	Qaryon spring Reservoir	31
11	Roof Tanks	Askar Camp- plastic roof tank	52
12	Roof Tanks	Askar Camp-steel roof tank	41
13	Network	Old City	53
14	Roof Tanks	Old City- plastic roof tank	48
15	Network	Rafidia Al Balad- plastic	38
16	Roof Tanks	Rafidia Al Balad- plastic	29
17	Network	Sayel Fuel Station- Alquds street – steel	37
18	roof tank	Sayel Fuel Station- Alquds street –plastic	28
19	network	AlQatoni Taxi- Almaajeen- steel	23
20	roof tank	AlQatoni Taxi- Almaajeen- plastic	37
21	Source	Al Qwareen Spring-trading centre	153

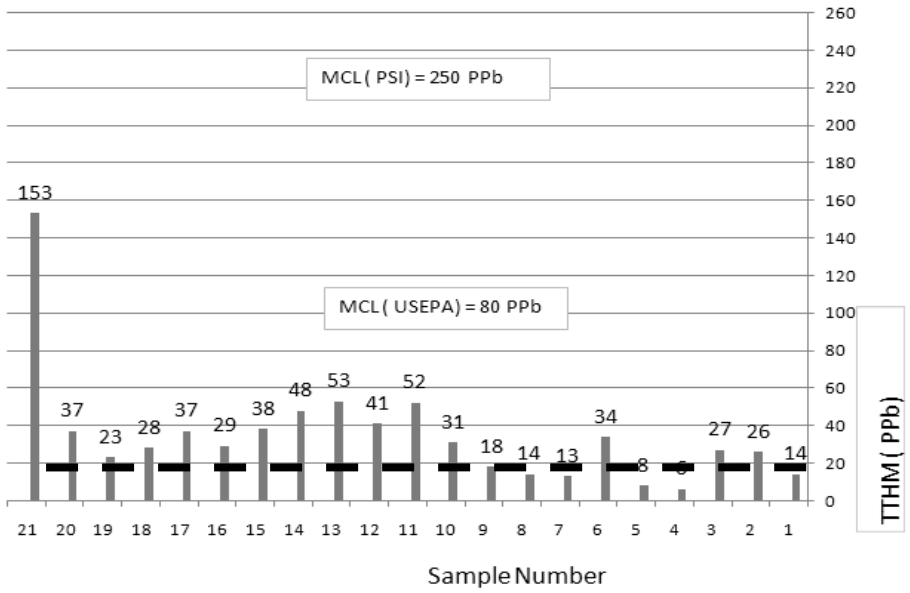

Figure (1): THM values for the city of Nablus showing the MCL values for the PSI and USEPA as a reference.

Discussion

The main objective from field survey is to check the occurrence of total trihalomethanes (TTHM) in Nablus City water system. Accordingly, 21 samples were taken from different components of this system including reservoirs, spring sources, pipe network and roof tanks.

The results show detectable levels of total trihalomethanes (TTHM) in all 21 samples. The total trihalomethanes (TTHM) concentrations in 20 samples were below the USEPA and PSI MCL (80 ppb and 250 ppb, respectively). Sample 21 (Al Qwareen Spring-trading centre) measured 153 ppb, which is above the USEPA MCL but still less than the MCL according to PSI. This high level of totaltrihalomethanes(TTHM) was expected by the Nablus water and wastewater department. In fact, they don't use this water directly, but instead they dilute it with water from other sources.

The occurrence of volatile organic halogen compounds, particularly THMs can be found in all kinds of waters, i.e. drinking water, surface water, deep water, rain water, seawater and even in polar ice and water (Abrahamsson and Klick, 1999). From water and soil the pollutants may transfer into living organisms, either directly or via the food chain. It is particularly hazardous for organisms at the end of the food chain, e.g. humans, who can take a big portion of concentrated pollutants through food. Volatile organic halogen compounds were determined in such materials as mother's milk, urine, and blood (Moore and Ramamoorthy, 1984).

THM concentration contents in drinking waters are considerably influenced by technological systems in water treatment station, i.e. which medium is applied: chlorine, chlorine dioxide, or ozone. In 1999, Sawiniak and Trybulec have found out that in the case of ozone or chlorine dioxide application THM contents are lower, although chlorine is used in final disinfection. Moreover, when ozone or chlorine dioxide is applied, bromoorganic compounds have better kinetics, even if too much chlorine in relation to bromin is added in the final chlorination.

Investigations have also proved that THM contents are getting lower in winter due to lower average temperature of water and air, and the contents of THM precursors and micro organisms are getting lower(Westerhoff. Et.al, 2004).

Conclusion

From the results obtained and discussions, the following conclusions were reached:

All TTHM values of field survey samples were less than PSI MCL (250 ppb) and the USEPA MCL (80 ppb), except one value of sample number 21 from Al Qwareen Spring-trading centre at 153 ppb, which is more than the MCL set by the USEPA. Also, different factors affecting the results like SPME parameters and in general the organics in soil may leach to the groundwater.

References

- Abrahamson, K. & Klick, S. (1990). "Determination of Biogenic and Anthropogenic Volatile Halocarbons in Sea Water by Liquid-liquid Extraction and Capillary Gas Chromatography". J. Chromatogr. 513. 39.
- 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.
- Bahri, S. & Driss, M. (2010). "Development of solid-phase microextraction for the determination of trihalomethanes in drinking water from Bizerte". Tunisia. Desalination. 250. 414.
- Bellart, A. Lichtenberg, J.J. & Kraner, R.C. (1974). "The occurrence of organohalides in chlorinated drinking water". J.AWWA. 66. (12). 703.
- Boormang, A. Dellarco, V. Dunninck, J.K. Chapin, R.F. Hunter, S. Fhauchman. Gardner, H. Cox, M. & Siels R.C. (1999). "Drinking water disinfection by-products: Review and approach to toxicity evaluation". Environmental Health Perspectives. 107. Supplement. 1207.
- Dunninck, J.K. Haseman, J.K. Lilija, H.S. & Wyand S. (1985). "Toxicity and carcinogenicity of chlorodibromomethane in Fischer 344/N rots and B6C3F1 nice". Fundam. Appl. Toxicol. 5. 1128.
- Krasner, S. W. (1999). Chemistry of disinfection by-product formation. In Formation and Control of Disinfection By-products in Drinking Water. Singer. P.C. (editor). American Water Works Association. Denver. CO.
- Luks-Betlej, K. & Bodzek, D. (2000). "Determination of Tri.-Tetrachloromethanes and Trichloroethane by Using Microextraction with GC-ECD Detection". Chem. Anal. (Warsaw) 45. 45.

- Moore, J.W. & Ramamoorthy, S. (1984). "Organic chemicals in natural waters". Applied Monitoring and Impact Assesment. New York. Springer Verlag.
- Palestinian Standards Institution: Drinking Water. 41/2005. 1-5.
- Palestinian Central Bureau of Statistics. Census final results in the west bank-summary (population and housing). 2007
- Sadiq, R. & Rodriguez, M.J. (2004). "Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review". Science of the Total Environment. 321. 21–46.
- Sawiniak, W. Trybulec, K. (1999). "Zmiany zawartosci THM-6w w uzdatnionej wodzie i podczas transportuw sieciach wodociagowych". Inzynieria i Ochrona Srodowiska. 3-4. 297. (in Polish).
- U.S. Environmental Protection Agency: Integrated Risk Information System. Cincinnati. OH: Office of Research and Development. Office of Health and Environmental Assessment. 1998b. <http://cfpub.epa.gov/ncea/iris/index.cfm>.
- Water and Environmental Studies Institute at An-Najah National University: Map of Nablus City boundary. Main water sources (wells and springs) and served villages. 2007.
- Westerhoff, P. Chao, P. & Mash, H. (2004). "Reactivity of natural organic matter with aqueous chlorine and bromine". Water Research. 38. 1502–1513.