Evaluation impact of point of use (POU) household water treatment devices (HWTDs) application on tap water quality and determine the removal efficiency of THMs and HAAs

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ABSTRACT

Application of household water treatment devices (HWTDs) is increasing due to the lack of confidence on supplying safe water by municipal drinking water distribution systems. The main objective of this study was to determine performance of HWTDs in the removal of trihalomethanes (THMs) and haloacetic acids (HAAs), color, turbidity, lead and copper from household tap water. The amount of THMs and HAAs in the inlet water samples was obtained more than the drinking water maximum recommended levels. No significant correlation was obtained between removal efficiency of disinfection by products (DBPs), and color and turbidity. Maximum concentrations of THMs and HAAs at the inlet water samples were 156.35 and 124.20 µg l⁻¹, respectively. Highest concentration of THMs and HAAs at the outlet water samples were 47.11 and 45.40 µg/l, respectively. HWTDs showed better performance in reducing HAAs than THMs. The devices showed maximum removal rate for dibromochloromethane (DBCM) and dichloroacetic acid (DCAA) with values of 85 and 74%, respectively. The results showed that HWTDs might not completely remove heavy metals and DBPs, however, these devices can help maintain the health of consumers with reducing the level of harmful compounds in municipal drinking water.

Keywords: Point of use (POU) water treatment; Disinfection by products (DBPs); Trihalomethanes (THMs); Haloaceticacids (HAAs); Drinking water

1. Introduction

In addition to the natural pollution, water resources are always at risk of contamination with municipal, industrial and agricultural effluents. In most drinking water treatment plants, conventional water treatment processes are used to reduce only water turbidity and disinfection. Consequently, they always concern the presence of specific contaminants in drinking water such as heavy metals, toxins and pesticides, chlorine resistant pathogens and toxic disinfection byproducts (DBPs). Then, people seek for special precautions and take further actions to avoid these contaminants such as purchasing bottled water or applying additional treatment on tap water by household water treatment devices (HWTDs). In general, HWTDs are widely used primarily to improve the test and odor of tap water or because of the health concerns of the toxic chemicals present in drinking water. United States Environmental Protection Agency (USEPA) reported that, Americans spend billions of dollars each year on purchasing HWTDs [1].

A unit of commercially available HWTDs generally, comprises one microfilter, one pre activated carbon cartridge, one nano or reverse osmosis filter and one post activated carbon filter, respectively. Reverse osmosis systems are able to reject up to 99% of various dissolved contaminants and

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particles, and toxic contaminants such as arsenic, asbestos, pesticides, herbicides, fluoride, lead, mercury, nitrate and radium. In comparison to the conventional water treatment processes, the main advantage of membrane technologies is that water can be treated in one stage without chemicals or utilities, while the treatment footprint is relatively small. Main function of the activated carbon filters is mostly reduction of colloids, chlorine, color, tastes and odor [3,4]. Also, disinfection by products can be removed with the membrane filters, granular activated carbon and advanced oxidation processes [5,6]. The high efficiency and simple operation make membrane filters promising candidates for the potential removal of DBPs and their precursors in highly organic surface waters [7]. Membrane systems episodically fail and must be regularly maintained to ensure that rejection efficiency remains at a maximum [4]. Then, it is necessary to replace filter cartridges and membranes at least once a year.

Despite wide application of household water treatment systems, there are limited studies on evaluation of performance of HWTDs for desalination and reduction of DBPs from potable water in the field. Disinfection process is an obligatory step in water treatment facilities, since providing safe drinking water, particularly from the view point of microbial quality [8]. Chlorine compounds and chloramine are widely used as a favorable drinking water disinfectant all around the world due to its cost effectiveness, simple handling and storage and having residual in the distribution system [9]. However, formation of DBPs as the consequence of chlorine reaction with natural organic materials is one of the major concerns of water chlorination [10,11]. Among the major DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs) are well-known and significantly produced during pre- and post-chlorination of surface waters [12]. HAAs are the second most prevalent chlorination byproduct [13]. USEPA has set maximum concentration level (MCL) of 80 and 60 µg/l for THM_s and HAAs, respectively [14]. International Agency for Research on Cancer (IARC) has listed them as carcinogenic material [15]. DBPs are concerned of their carcinogenic, reproductive and mutagenic effects [16]. Numerous studies have surveyed occurrence and concentration level of DBPs in drinking water distribution systems [17–19]. Then, based on the reports, in China and US about 11-30 percent of the consumers are using household water purifiers, and this figure rises to more than 90 percent in South Korea [20]. However there is insufficient information available about performance of HWTDs in the removal of DBPs and other toxic compounds in the literature [21]. This study was conducted to determine the extent to which HWTDs units could remove DBPs, particularly, THMs and HAAs from tap water and their impact on the water physicochemical properties.

2. Materials and methods

In this cross-sectional descriptive study, water samples were collected from inlet and outlet of 30 units of HWTDs in Tabriz, Iran. The data was collected from devices have previously been in operation at least for 6 month by the residents or their filters replaced during the last six month. The devices were from different companies, but all the selected HWTDs had similar treatment stages including one microfilter, one pre activated carbon cartridge, one nano or reverse osmosis filter and one post activated carbon filter. Samples were examined for selected physicochemical parameters, lead, copper, THMs and HAAs. The samples for analysis of physicochemical parameters were collected in cleaned and acid-washed 1.5 L polyethylene bottles, tightly capped and acidified to pH < 2 with 6 MHNO₃ until the analysis time. Electric conductivity (EC) and pH were measured using a portable EC meter at the sampling place. Alkalinity (as HCO_3^{-}) was determined at by titration using H_2SO_4 (0.25 N). The anions (SO₄⁻ and Cl⁻) were analyzed using an ion chromatography system (DionexICS-1500, SpectraLab Scientific Inc., Canada). Concentrations of the cations (Na⁺, Mg⁺⁺, Ca⁺⁺ and K⁺⁺) were measured by an inductively coupled plasma system (ICP-OESSPECTRO Analytical Instruments Inc., Germany). For quality control procedures, accuracy of the method was assured by triplicate analysis. A replicated analysis of the samples and standards established that level of obtained analytical precision and accuracy was at least 5% for all ions. Routine replicates from each device were collected in all sampling procedures to increase power of analysis. General procedures for sampling, preservation and all the chemical analyses were carried out in accordance to the standard methods. For sampling of THMs and HAAs, containers were 135 ml amber glass bottles, previously washed with detergent and rinsed with tap water, followed by distilled water and dried at ambient temperature and placed in a 105°C oven for 1 h. Then, 10 mg of sodium thiosulfate was added to the sampling bottles as dechlorination reagent. Before sampling, the water tap was allowed to run for 3 min. The bottles were carefully and completely filled above the bottle edge avoiding bubble formation. No air was left between the water and the cap. The samples sent to the laboratory in a tight cold box. The samples were stored up to a maximum of 10 d at 4°C in separate refrigerator without standard reagents. Residual chlorine levels were assessed using the DPD method and reported in mg/l free chlorine. Measurements of water turbidity followed by standard laboratory methods and were reported in nephelometric turbidity units (NTU).

Headspace techniques have been widely used in the determination of THMs, HAAs and other volatile compounds in water samples [22-24]. The method is applicable to a wide range of organic compounds that have sufficiently high volatility to be effectively removed from samples using an equilibrium headspace procedure. In the static headspace mode, an aliquot gas phase from the vial, in equilibrium with the sample is introduced into the carrier gas stream, which carries to the column. In dynamic headspace, gas extraction is carried out by continuously removing the gas phase. In the laboratory, the vials are rotated to allow for diffusion of the internal standards, surrogates, and matrix modifier throughout the matrix. The vials are placed in the autosampler carousel of the headspace analyzer and maintained at room temperature. Approximately 1 h prior to analysis, the individual vials are moved to a heated zone and allowed to equilibrate. The sample is mixed by mechanical vibration while the elevated temperature is maintained. Then, an autosampler pressurizes the vial with helium which forces a portion of the headspace gas mixture through a heated transfer line onto the GC column. THMs and HAAs were measured by a primary

column (DB-1701, 30 m × 0.25 mm i.d., 0.25 µm film thickness). To determine THMs, injector temperature was set at 250°C. GC temperature program was established 35°C for initial, held for 1.11 min, increasing intervals of 9°C/min up to 100°C, and then followed by 6°C/min increasing until 140°C. The detector was an electron conductivity detector, 150 µl volume (Agilent Technologies, Inc., USA); for THMs, detector temperature was arranged at 290°C; make up gas was mixture of 95% Ar+5% N₂ at flow rate of 25 ml/min. Head space operated for 5 min incubation at 70°C with 500 rpmstirring. For measurement of HAAs, injector temperature was fixed at 210°C; injection volume was 1 µl; splitless injection was hold for 45 s then purged at 30 ml/min. GC temperature program was arranged at 40°C for initial, held for 10 min, then increased by2.5°C/min up to 65°C, then set by 10°C/min increase until 85°C, then with 20°C/min up to 205°C and hold for 7 min. For measurement of HAAs, detector temperature was 290°C and make up gas was mixture of 95% Ar+5% N₂ at 20 ml/min flow rate. Carrier gas was Helium at constant pressure. Initial carrier gas velocity (at 40°C) was 33 cm/s. The detection limits for THMs were: 3.2, 2.5, 0.9 and 0.3 µg/l for TCM, BDCM, DBCM and TBM, respectively. The detection limits for HAAs were:0.76, 0.85, 0.79, 0.72 and 0.63 µg/l for TCAA, DCAA, MCAA, MBAA and DBAA, respectively. The linearity of the method was evaluated over standard solutions with concentrations at the range of $5-200 \,\mu\text{g}/l$ for each analyte. The average THMs and HAAs recoveries were between 65 and 115% with an average relative standard deviation of 12%.

A paired sample t-test was conducted by SPSS 16.0 to determine if there was a statistically significant difference in the measured concentrations of the parameters in the inlet and outlet of the devices. A Pearson's correlation and a lack-of-fit test using univariate analysis of variance were conducted to check for the existence of linearity between THMs and HAAs reduction by the devices and the removal efficiency of turbidity and color as surrogate parameters..

3. Results and discussion

In addition to the appearance of drinking water which should be transparent, clear and free from turbidity, its chemical and biological quality must be desirable. A group of chemicals in concentrations higher than permitted values in drinking water could threaten the health of humans. But presence certain amounts of calcium and magnesium ions in water are essential and nutritious for human health and at the low concentrations of the elements the drinking water would be unacceptable. However, there is insufficient scientific information on the benefits or hazards of regularly consuming drinking water low in minerals [25]. Therefore, the performance of HWTDs were determined in reduction of minerals and toxic chemicals such as lead, copper,THMs and HAAs and compared to the World Health Organization (WHO) guidelines (Table 1) [26].

The results show that there is a significant difference (p-value < 0.05) between the inputs and outputs of all parameters. Chlorine residuals, pH, turbidity and color are readily measured and provide opportunity for an appropriate response in monitoring of drinking water distribution system [25]. Residual disinfection is used to provide a partial safeguard against low-level contamination and regrowth of microorganisms within the distribution system. However, chlorination of a drinking-water supply will reduce the overall risk of disease but may not necessarily provide the supply safe, for example, has limitations against the protozoan pathogens and some viruses. The low level of residual chlorine at all samples from the inlets may indicate that the water or distribution system has a high oxidant demand. Also, the amount of turbidity and color was high in the water supply system. This could be due to poor water quality entering the distribution network as a result of problems in the water treatment plant or factors such as corrosion and the formation of biofilms in water distribution pipes and the presence of dead points in the network. Average turbidity should be below 0.1 NTU for effective disinfection [25]. The pH has decreased significantly at the outlet of all devices. The pH of water, in most natural waters, is controlled by the carbon dioxide-bicarbonate-carbonate equilibrium system. An increased carbon dioxide concentration will therefore lower pH of water. Decrease in pH also occurs as temperature is raised. Water pH can affect the degree of corrosion of metals any effect on health is likely to be indirect and due to increased ingestion of metals from plumbing and pipes and cause adverse effects on water taste, odor and appearance. The results showed that water turbidity has increased in produced water in some samples. The generated water is stored in a reservoir, which could results in an increase in the amount of heterotrophic bacteria due to the loss of the residual chlorine by the filters and a prolonged water residence time, thereby increasing the opacity of the water. Our previous study has showed that variety and density of microbial population has increased in the outlet of HWTDs due to disappearance of residual chlorine [27].

The effluent of the device is mixed with a portion of the water from outlet of the pre-activated carbon cartridge to adjust the produced water salts, so the amount of TDS at all samples were at desirable amount. The results showed that almost all anions and cations, lead, copper and disinfection byproducts have declined considerably.

Given the fact that water quality in the distribution network is constantly changing and these variations can be very wide in different parts of the network. Therefore fluctuations in the quality of water entering the filters can affect their performance. Also, the duration of operation of the devices and the volume of water passed through could create a great effect on their effectiveness.

Lead concentration in more than 50% of the inlet water samples was higher than WHO guideline of 10 μ g/l. The solubility of lead increases markedly as the pH is reduced below 8. Lead is rarely present in tap water as a result of its dissolution from natural sources; rather, its presence is primarily from household plumbing systems containing lead in pipes, solder, fittings or the service connections to homes. The amount of lead dissolved from the plumbing system depends on several factors, including pH, temperature, and water hardness and standing time of the water. Lead is a general toxicant and accumulates in the skeleton. Children and pregnant women are most vulnerable to adverse health effects of lead [28]. International Agency for Research on Cancer (IARC) has classified lead and inorganic lead compounds in Group 2B (possible human carcinogen). Copper in a drinking-water supply usually arises from the corrosive action of water leaching copper Table 1

Summary data and paired sample T-test analysis for inlet and outlet of household point of use water treatment systems

Parameter*		Statisti	cs							WHO
Paired-sample T-Test, Sig. (2-t	s ailed)	Mean	Minimum	Maximum	25 th percentile	50 th percentile	75 th percentile	90 th percentile		guideline
Residual	In	0.000	0.1	0.0	0.4	0.0	0.1	0.1	0.2	0.5
chlorine	Out		0.0	0.0	0.0	0.0	0.0	0.0	0.0	
	Eff.**		100.0	100.0	100.0	100.0	100.0	100.0	100.0	
pН	In.	0.006	7.00	6.80	7.80	6.80	6.80	7.20	7.60	6.5-8.5
1	Out.		6.75	6.60	6.80	6.70	6.75	6.80	6.80	
	Eff.		_	_	_	_	_	_	_	
Turbidity	In	0.006	0.8	0.2	3.3	0.4	0.7	1.0	1.0	0.1
5	Out.		0.4	0.2	1.1	0.3	0.4	0.5	0.9	
	Eff.		27.0	-134.5	85.0	11.9	35.1	57.1	72.7	
Color	In	0.000	4.8	1.0	8.5	3.9	5.5	6.0	6.5	NA
	Out		3.5	1.0	6.0	2.5	3.5	4.5	5.5	
	Eff.		17.1	-71.4	61.5	0.0	22.5	45.8	54.1	
TDS	In	0.000	465	210	690	310	485	600	647	1500
	Out		69	12	230	25	34	106	179	
	Eff.		85	45	97	82	91	94	96	
Total	In	0.000	186	100	270	116	214	233	248	100
hardness	Out		23	0	88	8	14	37	60	
	Eff.		87	26	100	80	91	96	100	
Cl-	In	0.000	43	4	110	13	48	55	91	200
	Out		10	2	72	4	6	10	21	
	Eff.		79	0	100	69	90	95	100	
$SO_4^{}$	In	0.000	58	14	117	27	48	87	100	200
	Out		8	1	21	3	8	10	18	
	Eff.		92	19	100	92	97	100	100	
Ca ⁺⁺	In	0.000	48	24	77	32	52	59	65	75
	Out		7	0	25	4	5	8	17	
	Eff.		90	18	100	85	98	100	100	
Mg ⁺⁺	In	0.000	18	6	78	10	18	22	28	30
	Out		3	0	8	1	2	4	6	
	Eff.		79	11	100	71	87	95	100	
k+	In	0.000	3	1	5	3	4	4	4	100
	Out		1	0	3	0	2	2	2	
	Eff.		83	15	100	73	94	100	100	
Na+	In	0.000	32	12	54	25	34	39	49	200
	Out		10	0	42	2	5	19	23	
	Eff.		71	11	100	45	83	95	97	
NO_3^-	In	0.000	12	3	27	5	8	19	26	50
	Out		4	0	17	0	2	6	12	
	Eff.		72	-3	100	55	87	99	100	
HCO ₃ -	In	0.000	160	122	210	136	161	179	195	200
	Out		29	6	107	12	19	38	73	
	Eff.		80	20	94	71	86	92	93	
Alkalinity	In	0.000	126	32	172	110	132	147	160	NA
	Out		24	8	88	10	15	31	60	
	Etf.		80	20	94	71	86	92	93	

(Continued)

Table 1 (Continued)

Summary data and paired sample T-test analysis for inlet and outlet of household point of use water treatment systems

Parameter*		Statistics								
Paired-samples T-Test, Sig. (2-tailed)		Mean	Minimum	Maximum	25 th	50 th percentile	75 th	90 th		guideline
		mean			percentile		percentile	percentile		
Cu	In	0.003	12	8	17	10	11	16	17	2000
	Out		6	1	11	4	5	7	11	
	Eff.		49	-3	93	21	56	73	93	
Pb	In	0.001	12	8	19	8	12	17	19	10
	Out		7	2	12	3	7	9	11	
	Eff.		47	7	75	24	52	70	75	
TCM	In	0.002	34	19	65	22	30	44	65	300
	Out		13	8	23	11	12	14	22	
	Eff.		57	31	81	46	54	71	81	
BDCM	In	0.002	29	21	56	22	23	32	54	60
	Out		13	8	21	11	12	14	20	
	Eff.		51	33	81	39	48	64	79	
DBCM	In	0.000	17	12	28	13	16	20	27	100
	Out		3	1	7	1	2	3	7	
	Eff.		84	63	95	77	89	91	94	
TBM	In	0.049	10	1	32	2	3	25	31	100
	Out		2	0	6	1	1	5	6	
	Eff.		61	11	83	51	66	78	82	
TCAA	In	0.000	18	12	28	13	18	24	28	200
	Out		5	1	12	1	5	9	12	
	Eff.		73	46	95	55	75	92	95	
DCAA	In	0.000	15	11	22	14	15	17	21	50
	Out		4	0	8	3	4	6	8	
	Eff.		74	44	100	66	76	81	98	
MCAA	In	0.000	22	11	35	13	22	27	35	20
	Out		6	2	10	4	6	9	10	
	Eff.		71	56	85	61	72	80	84	
MBAA	In	0.000	4	1	12	2	3	4	11	NA
	Out		1	0	2	1	1	1	2	
	Eff.		65	25	89	55	67	77	89	
DBAA	In	0.011	20	5	49	8	14	35	48	NA
	Out		8	1	22	3	5	13	22	
	Eff.		56	25	92	35	53	78	91	
TTHMs***	In	0.000	90	57	156	62	78	119	155	NA
	Out		31	19	47	26	32	34	46	
	Eff.		62	45	79	54	57	76	79	
THAAs***	In	0.000	79	52	124	57	78	96	122	NA
	Out		25	9	45	17	21	33	45	
	Eff.		70	54	83	63	71	76	82	

* All parameters measuring unit was mg/l: except pH (no unite); turbidity (NTU); color (Pt-cobalt unite); Cu; Pb; THMs and HAAs (µg/l). ** Eff.: Removal efficiency

*** TTHMs: Total trihalomethanes; THAAs: Total haloacetic acids

from copper pipes. Copper concentrations in treated water often increase during distribution, especially in systems with an acid pH or high-carbonate waters with an alkaline pH. The guideline value for copper was considered to be protective against acute gastrointestinal effects of copper. Copper can give rise to taste problems at concentrations above 5 mg/l [25]. At the all HWTDs, apart from the storage tank water which is usually an epoxy coating, all connections are used in the PVC. So the main cause of lead and copper occurrence in the input and output of the devices are the water supply system.

The amount of TTHMs and THAAs, respectively in more than 50 and 75% of the inlet water samples was more than the MCL values recommended by USEPA.

66

Fig. 1 shows distribution pattern of sampled HWTDs in the city and performance of the devices on water hydrochemical faces in the seven regions. Stiff diagrams represent graphical picture of water chemical analyses, first developed by H.A. Stiff in 1951. The Stiff pattern is a relatively distinctive approach of showing differences or similarities in water and alterations in water composition with spatial changes. Cations calcium magnesium and sodium and anions bicarbonate, sulfate and chloride (meq/l) were used for analysis comparison. Each different pattern represents a different type of drinking water in the water distribution system and at the inlet of HWTDs. The width of the pattern indicates an approximate of total ionic content. Results indicate irregular patterns that calcium and bicarbonate are predominant ions. The diagrams illustrate significantly different water ion composition within the city.

Fig. 2 presents the hydrochemical faces of the water samples obtained from inlet and outlet of the HWTDs using piper diagram. As clearly revealed by the piper plots, most of the various water sources of the area have distinct hydrochemical faces. The central diamond diagram helps to determine the hydro-chemical faces (mixing property). Combined concentrations of alkali metals (Ca + Mg), HCO₃, SO₄ and Cl are the main ions. The piper diagram also indicates the dominance of alkaline water (Ca + Mg + HCO₃) and mixed water (Ca + Na + Cl) in the inlet water samples. At the all inlet samples weak acidic roots are greater than the strong acidic roots (HCO₃ > Cl + SO₄). This may be mainly attributed to the dominance of acidic volcanics and or reverse weathering in the source water [29]. As indicated on the central diamond, all the inlet samples of the study area are categorized into 2 hydro chemical faces of Ca + Mg + HCO₃ and Ca + Na + HCO₃ from the seven regions. Na and K bicarbonate water type may include ground waters that have been modified by further water interaction of volcanic and sedimentary rocks [29]. The main source of drinking water is from river, but in the eastern part of the city well water is also injected into the network. The Piper diagram shows that most of the outlet water samples fall in the field of mixed alkaline and alkaline earth metals (Na + Ca), while the anions HCO₃ and Cl dominate over SO₄ ions. To modify the amount of produced water salts, a portion of the raw water after passage through the active activated carbon filters is added to the outlet water from the membrane RO filter, which generates water with the mixed faces.

Pearson's correlation analysis was adopted to reveal correlations between turbidity, color, TTHMs and THAAs in the inlet, outlet and the removal efficiencies for sampled HWTDs; results are presented in Table 2. This was performed to determine the relationship between DBPs elimination with reduction of water physical parameters by HWTDs. Based on the results, no significant correla-



Fig. 1. Distribution pattern of sampled HWTDs in the city and the performance of devices on the water hydrochemical faces in the seven regions.



Fig. 2. Major chemical constituents in trilinear (Piper) diagram from inlet (In) and outlet (Out) of the HWTDs samples in the city of Tabiz.

tions were obtained between removal efficiency of DBPs and physical water parameters. However, at the inlet water samples positive relationships were obtained between turbidity and TTHMs and THAAs concentrations.

The results also showed linear association between concentrations of THAAs and turbidity at the outlet water samples. Testing of DBPs is very difficult and time consuming. To counter this, using simple physicochemical water quality parameters such as color, turbidity and UV absorbance as surrogates has recently been extended in full and pilot scale experiments [30]. Then, Pearson's correlation and lackof-fit test was conducted by univariate analysis of variance between the removal of TTHMs and THAAs and color and turbidity (Table 3). Significant correlation was not obtained between TTHMs and THHAs removal and reduction efficiency of the surrogates. Univariate analysis of variance showed no linear correlation between the removal efficiency of the DBPs and the two physiochemical parameters. Low slope of the line and Y-intercept suggest turbidity as a better surrogate to predict DBPs reduction by HWTDs, but, more experiments are need to apply the surrogates with higher confidence in the monitoring of DBPs removal by HWTDs.

Trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (TBM) are totally called THMs. HAAs are the second most prevalent water chlorination byproduct [13,31] and the most predominant five species are named trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), monochloroacetic acid (MCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA). Individual removal of THMs and HAAs species by HWTDs was more evaluated. As shown in Fig. 3, generally, HWTDs showed better performance in reducing THAAs than TTHMs. In terms of TTHMs, the devices showed approximately 85% (the highest value) reduction in DBCM concentration (p-value = 0.002). The highest removal of HAAs was belonging to DCAA at about 74%. The results show that brominated THMs were removed effectively, but, chlorinated species of haloacetic acids were decreased more than the brominated types.

Fig. 4 shows descriptive statistics of THMs and HAAs in the inlet and outlet of HWTDs. The maximum mean concentrations of TTHMs and THAAs at inlet water samples were obtained 156.35 and 124.20 µg/l, respectively. Also, the highest maximum concentrations of 65.29 and 48.50 µg/l were for TCM and DBAA, respectively. The lowest concentration from inlet water samples were for TBM (0.91 µg/l) and MBAA (0.80 µg/l). The median levels of TTHMs and THAAs from the inlet samples were 77.59 and 77.70 µg/l, respectively. The levels of TTHMs and HAA5 were higher than those measured in other cities such as Athens, Greece [32], Quebec, Canada [33], Seoul, Korea [18], and Massachusetts, USA [34]. The highest concentration of TTHMs and THAAs at the

Pearson corre	lation cı	oefficients m	natrix amonį	g the chemical cc	onstituents	concentrati	ion between inle	t and outlet o	of HWTDs (Sig	. 2 tailed)		
Parameter		Turbidity			Color			TTHMs				THAAs
		In	Out	Removal efficiency	In	Out	Removal efficiency	In	Out	Removal efficiency	In	Out
Turbidity	Out	0.24 (0.198)										
	Eff.	0.49** (0.006)	-0.44° (0.016)									
Color	IJ	0.17 (0.364)	-0.17 (0.376)	0.02 (0.919)								
	Out	0.19 (0.324)	-0.24 (0.210)	0.15 (0.432)	0.60** (0.000)							
	Eff.	0.01 (0.979)	0.08 (0.691)	-0.14 (0.462)	0.74** (0.000)	-0.01 (0.976)						
TTHMs	In	0.58 (0.080)	0.51 (0.132)	0.41 (0.240)	0.14 (0.696)	-0.07 (0.850)	0.17 (0.636)					
	Out	0.14 (0.698)	0.29 (0.410)	0.06 (0.881)	0.18 (0.628)	-0.24 (0.502)	0.25 (0.485)	0.22 (0.535)				
	Eff.	0.40 (0.257)	0.24 (0.502)	0.28 (0.434)	0.07 (0.846)	0.15 (0.690)	0.00 (0.999)	0.74^{*} (0.015)	-0.47 (0.176)			
THAAs	In	0.64^{*} (0.045)	0.39 (0.272)	0.38 (0.275)	0.05 (0.901)	0.13 (0.722)	0.06 (0.863)	0.83^{**} (0.003)	0.28 (0.435)	0.61 (0.059)		
	Out	0.59 (0.071)	0.54 (0.105)	0.14 (0.705)	-0.17 (0.636)	0.26 (0.461)	-0.15 (0.681)	0.63 (0.050)	-0.08 (0.825)	0.69* (0.029)	0.83** (0.003)	
	Eff.	-0.21 (0.555)	-0.46 (0.177)	0.32 (0.362)	0.40 (0.255)	-0.48 (0.156)	0.46 (0.178)	-0.17 (0.645)	0.40 (0.258)	-0.45 (0.195)	-0.32 (0.371)	-0.77**(0.009)
* Correlation is * Correlation is	s signific significe	ant at the 0.0 int at the 0.05	11 level 5 level									

Table 3

Results of Pearson's correlation (2-tailed, $\alpha = 0.01$) and lack-of-fit test using univariate analysis of variance between removal of TTHMs and THAAs and color and turbidity as surrogates

Physical	TTHMs								
parameters	Pearson's correlation	Univariate analysis	Univariate analysis of variance						
	coefficient (p-value)	Slope (p-value)	Slope (p-value) Y-intercept			p-value*			
			В	Standard error	p-value				
Turbidity	0.28 (0.434)	0.13 (0.434)	56.9	7.7	0.000	0.000			
Color	0.00 (0.999)	-0.88 (0.203)	82.3	14.1	0.004	0.000			
	THAAs								
	Pearson's correlation	Univariate analysis	s of varian	ce					
	coefficient (p-value)	Slope (p-value)	Y-inte	rcept		p-value			
			В	Standard error	p-value				
Turbidity	0.32 (0.362)	0.10 (0.362)	65.5	5.1	0.000	0.000			
Color	0.46 (0.178)	0.91 (0.049)	50.5	7.9	0.003	0.000			

*p-values > 0.05 show significant linear correlation between reduction of THMs and HAAs and color and turbidity as surrogates.



Fig. 3. Performance of point of use household water treatment devices (HWTDs)in reduction of individual species of THMs (A) and HAAs (B).

outlet water samples were 47.11 and 45.40 μ g/l, respectively which are significantly lower than the MCL estabilished by USEPA. Pieri et al. reported average concentration of 76 μ g/l in urban drinking-water distribution systems at two areas of



Fig. 4. Statistical summary of THMs and HAAs in the inlet and outlet of HWTDs.

Nicosia, Cyprus [35]. Charisiadis et al. reported high variance of water total THM between households with minimum and maximum concentrations of 3.1 and 129 μ g/l, respectively [19]. The mean removal efficiency for TTHMs and THAAs were 62 and 70%, respectively.

70

4. Conclusions

Due to the conscious of people about unsuccessfulness of conventional water treatment plants in the removal of toxics and complains about taste, odor and opacity of municipal drinking water, point of use treatment (PUT) is becoming popular around the world. Then, this cross-sectional descriptive study was conducted to determine the extent to which HWTDs were able to remove DBPs of THMs and HAAs and selected physicochemical parameters, lead and copper from tap water. The results showed that water turbidity has increased in produced water in some samples. The results illustrated significantly different water ion composition within the city. However, almost all anions and cations, lead, copper and disinfection byproducts were declined considerably by HWTDs. The amount of TTHMs and THAAs, respectively in more than 50 and 75% of the inlet water samples was more than MCL recommended by USEPA. The piper diagram also indicated the dominance of alkaline water in the inlet water samples. The Piper diagram showed that most of the outlet water samples fall in the field of mixed alkaline and alkaline earth metals (Na + Ca), while the anions HCO₂ and Cl dominated over SO₄ ions. Based on the results, no significant correlations were obtained between removal efficiency of DBPs and physical water parameters. According to the Pearson's correlation test, no significant correlation was obtained between TTHMs and physiochemical surrogate parameters. The maximum mean concentrations of TTHMs and THAAs at inlet water samples were obtained 156.35 and 124.20 µg l⁻¹ respectively. The highest concentration of TTHMs and THAAs at the outlet water samples were 47.11 and 45.40 µg l⁻¹, respectively. The mean removal efficiency for TTHMs and THAAs were 62 and 70%, respectively. Finally, HWTDs were not able to complete removal of heavy metals and DBP. However, using these devices could help reduce the harmful compounds entering the body through drinking water and maintain the health of consumers.

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72