SURVEY ON THE CONCENTRATION OF HALO ACETIC ACIDS IN TEHRAN DRINKING WATER

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EXTENDED ABSTRACT

The common method of water disinfection in the world is chlorination. Due to reaction between disinfectant and natural organic matter in water that can’t be removed during treatment process, disinfection by-products (DBPs) are formed. HAAs are considered as the second major DBPs in water. Associations between exposure to HAAs concentrations above the maximum contaminant level and injury to the liver, kidneys, eyes, nerves and reproductive systems have been noticed. Most studies in Iran investigating THMs in water; therefore, monitoring HAAs in Tehran water is felt. The result of this research is released for the first time in Iran. Drinking water in Tehran is provided mainly from Karaj, Jajrood and Lar rivers which enter respectively to the water treatment plant number 1, 2, 3, 4 and 5. Sampling was done in six consecutive months (first half of 2010) from surface and treated water. Temperature, pH, concentration of NOM (UV-254, TOC) in samples of surface water and pH, free residual chlorine and HAAs in treated water were analyzed. HAAs were measured using derivatization method with GC-ECD. Results of this study in Tehran show that NOM and HAAs concentrations in the spring are more than summer season. Average total organic carbon concentrations were observed in spring and summer, respectively 3.6-4.42 mg/L, 1.78-2.71 mg/L. Average HAAs in treated water by water treatment plant in Tehran showed that 41.7-55.6 µg/L in spring and 34.83-43.73 µg/L in summer season. The presence of HAAs is highly dependent to NOM compounds. The concentration of low bromide ion in surface water led to formation of DCAA and TCAA. Considering that maximum contaminant level (MCL) for HAAs by EPA standard is 60µg/L we can say that all the samples are less than standard level. The presence of HAAs in water is close to the standard level so authorities in water industry should pay more attention to this matter.

Keywords: NOM-HAAs-water resources-DBPs-Tehran.

1. INTRODUCTION

In the world the common method of water disinfection is chlorination [1]. The goal of Chlorination is to produce safe drinking water to decrease the incidence of water born infectious disease [2]. Disinfection by-products (DBPs) are formed due to reaction between disinfectant and natural organic matter (NOM), such as humic acid and fulvic acid, in water that can’t be removed during treatment process [3]. Over 500 DBPs have

1 Disinfection By-Products
2 Natural Organic Matters
been identified to date [4]. The most famous of these compounds include trihalomethanes, haloacetic acids, haloacetonitriles, haloaldehydes, chlorinated ketones, chlorophenols, chloropicrin [3, 5]. Among these products THMs is important in the first rank, and then HAAs, due to their potential reproductive, carcinogenic and mutagenic effects, are considered a public health threat [4, 6] and good indicators of overall DBPs in chlorinated water [7]. HAAs are non-volatile, ionic and highly hydrophilic that includes nine compounds; chloroacetic acid (MCAA), dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), bromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), dichlorobromoacetic acid (DBA), and dibromochloroacetic acid (DBCAA) [8]. Bromine acetic acids can be formed when disinfected water containing bromide ion [9]. There are numerous researches that showed connection these compounds with the occurrence of cancer, growth retardation, spontaneous abortion, and congenital cardiac defects [10]. Associations have been noticed between exposure to HAAs concentrations above the maximum contaminant level and injury to the liver, kidneys, eyes, nerves and reproductive systems [11]. Several research demonstrated that HAAs have more carcinogenic effect than THMs [7]. Animal studies have shown that prolonged exposure to DCAA and TCAA in drinking water resulted in liver cancer, also suggest a possible association between exposure these compounds and developmental effect (heart defect). Some animal studies proposed a possible link between exposure to DCAA or DBAA concentrations significantly higher than those found in drinking water [12]. DCAA is hepatoxic which promoted the cells accumulating the liver glycogen in rodents and produced neurotoxicity [7]. A recent study to the UK Drinking Water Inspectorate has proposed that HAAs should be classified as a “high priority” (the highest category in the list of regulatory chemical parameters to the routinely monitored) [4]. With considering the important subjects mentioned about with HAAs, some countries or international organization have regulated to control these compounds. The US Environmental Protection Agency according to the stage I DBPs has regulated maximum contaminate level (MCL) 60 μg/L for HAA5 (MCAA, DCAA, TCAA, MBAA, DBAA). This value was recommended according to the stage II reduced to 30 μg/L [6, 13, 14]. The World Health Organization (WHO) has a guideline value for MCAA, DCAA, and TCAA: 20, 50, and 200 μg/L, respectively [7]. Due to increasing concern about has on human health, particular attention has been recently paid to water treatment processes [10]. In Iran don’t have any standard for HAAs, only ISIRI (Institute of Standards and Industrial Research of Iran) has set MCLs for THMs (chloroform) [15]. No research has been done regarding the presence of HAAs in Iran water. Therefore, monitoring of these compounds in Tehran drinking water was conducted with using the method with lowest cost, time.

2. MATERIAL AND METHODS

Tehran is the capital of Iran and Tehran Province. With a population of 8,429,807 inhabitants. It is also Iran's largest urban area and city, one of the largest cities in Western Asia, and is the world. [16]. Tehran drinking water is provided from surface and groundwater resources. Karaj, Jajrood, Lar are three major rivers in Tehran water supply. In Tehran, there are five treatment plants that numbers 1 and 2, 3 and 4, 5 are feed respectively from Karaj, Jajrood and Lar rivers. All of treatment plants are used chlorine gas for disinfection.

2.1. Surface water Sampling

Experiments were carried out on samples that taken from three rivers such as (Karaj, Jajrood and Lar Rivers). Water samples were collected in the middle of the stream and a mid depth. Water sampling was conducted monthly from April to December 2009. Parameters that measured on water samples include pH, Temperature, Total Organic
Carbon (TOC) and UV-254 (UV absorbance at a wavelength of 254nm) and SUVA. NOM content was characterized by using two indicators such as TOC and UV-254. Samples for measurement of these parameters were collected in 40ml amber glass bottles. The pH and Temperature were measured at the sampling sites. Samples were carefully stored in the dark at 4°C and carried to the laboratory for analysis. Total Organic Carbon (TOC) was determined by colorimetry (Method No.10129, low range (0.3-20 mg L⁻¹), DR/5000 device). The UV absorbance UV-254 was analyzed in accordance with the standard method No.5910B (Ultraviolet Absorption Method) by using a Lambda25 UV/Vis spectrophotometer. Specific UV absorbance (SUVA) (L mg⁻¹ m⁻¹) was calculated as a ratio of UV absorbance at 254 nm (1 m⁻¹) with DOC (mg L⁻¹). This parameter was used as an indicator of carbon aromacity in water. Potassium hydrogen Biphthalate (KHP) was used to check the precision of the spectrophotometer [17].

2.2. Water sampling of treatment plant
Experiments were carried out on samples that taken from Tehran water treatment plants No.1, 3-4 and 5, these treatment plants provided part of drinking water for Tehran city. Water samples collected from the outlet water of treatment plant. Samples were collected every 2 weeks at each sampling point during 9 months (April to December 2009). Samples were analyzed from the point of pH, free residual chlorine and HAAs. pH and free residual chlorine (mg L⁻¹) were measured in site sampling with phenol red and DPD tablets, respectively. For HAAs analysis samples were stored in 40 ml amber glass container with screw capped and with PTFE-faced septa. The ammonium chloride was added to the samples bottles onsite as a dechlorinating agent to convert free chlorine to monochloramine, monochloramine has less reactivity than free chlorine [18]; also for avoiding of DBPs formation during the samples collection and shipping [7]. After water sampling, samples were kept in 4°C and shipped to the laboratory immediately and samples were refrigerated (4°C) until extraction.

2.3. Glassware and reagents
Monochloroacetic acid (MCAA, >99%), Dichloroacetic acid (DCAA, ≥98%), Trichloroacetic acid (TCAA, 99.5%) were obtained from Merck company. Monobromoacetic acid (MBAA, 99%) and 2-3 Dibrompropionic acid (98%) used as the internal standard were purchased from Sigma-Aldrich. Dibromoacetic acid (DBAA, ≥97%) was supplied by Fluca. The derivatization reagent dimethyl sulfate (DMS), as well as the ion-pairing agent tetrabutylammonium hydrogen sulfate (TBA-Hso4), dechlorinating agent, ammonium chloride and anhydrous sodium sulfate were obtained from Merck at high purity. TOC
reagent (low range) provided of Hach Lange. Water Hplc grade was purchased for analysis of Merck Company. Samples for measurement of HAAs were collected in 40ml amber glass vials and for analysis were poured in 10ml vials (specific vial GC). These vials were cleaned before sampling and analysis according to the following methods: 1) Rinse with detergent and consecutively with deionized water 2) 1/10 HCL/Water for 8hours 3) again with deionized water 4) finally with water Hplc grade and bake at 110°C overnight.

2.4. Method for analyzing HAAs

Different methods are used for analysing of HAAs. Method No.6251 Standard method book don't used in new research because using of diazomethane. More researches are used Method No.552.2, 552.3 EPA. In this paper was used direct derivatization of HAAs by dimethyl sulfate to avoid boring preconcentration step, to reduce the analysis time and considering the importance of green chemistry in new research. All analysis for HAAs was carried out by a Varian cp-3800 gas chromatography with electron capture detector (GC-ECD). Head space sampler technique model combi pal was used. Separations were conducted on a wcot fused silica cp-sil8b capillary column, 50m, 0.32mm, 0.25µm, with helium as carrier gas, at a linear velocity of 35ml/min and pressure 5 psi. Nitrogen was used as makeup gas. The column was held at 40°C for 3min, Ramp 5°C/min to 50°C, 50°C held for 2min, Ramp 5°C/min to 80°C/min, 80°C held for 1min, Ramp 5°C/min to 110°C, 110°C held for 1min, Ramp 30°C/min to 250°C, final temperature 250°C held for 1min. Injection temperature 275°C, split 20 and detector temperature was set at 300°C. Star version 6 software was used for data analysis.

2.5. Head space procedure

5ml water sample was pour into a 10ml headspace vial. After adding 5gr anhydrous sodium sulfate (Anhydrous sodium sulfate was heated to 400°C overnight to remove interfering organic substances and then stored at 110°C until use [18]), 25 µl 2-3 dibromopropionic acid as internal standard, 200mg tetrabutyl ammonium hydrogen sulfate (TBA-Hso4) as ion-pairing agent [19], the vial was closed, 250µl of derivatization reagent was then injected through the septum in space above the aqueous solution, then the vial automatically put in incubator GC device. Temperature and time incubation was 60°C and 30min respectively. Incubation rotation was 750rpm and speed injection 250µl/second was set. Before sample injection, calibration curve was plotted with 6 concentration of mix HAAs (10, 20, 40, 60, 100 and 200µg/L). All stages were repeated three times for each concentration.

3. RESULTS

3.1. Indicators for chlorinated DBP precursors

The main operational and measured water quality characteristics for raw and treated water from the utility during the period under investigation are presented in following Tables. Table 1 and 2 show results to the parameters of temperature, pH, TOC, UV-254 and SUVA in the water surface in Tehran in the spring and summer. The amount of natural organic matter is determined by two parameters, TOC and UV-254. The average TOC in the rivers Karaj, Lar and Jajrood in spring respectively about 3.98 and 4.42 and 3.6 mg/L and in summer were observed respectively 2.71, 2.76 and 1.78. The mean UV - 254 nm in the River Karaj, Lar and Jajrood in spring respectively 0.1724, 0.1829 and 0.1616 cm^-1 and in summer were 0.1296, 0.132 and 0.093 cm^-1. This table also shows the specific absorbance. This parameter represents the ratio UV-254/DOC_100 (SUVA) and constitutes an indicator of carbon aromacity in water (in this case TOC was used in calculating SUVA because the investigated water has very low turbidity, DOC representing 95% and more of TOC. The higher the SUVA, the higher the content of...
humic substances SUVA in water surface Tehran is more than four and expression components of hydrophobic water.

**Table 1:** The average concentration of NOM in Tehran surface water resources in spring

<table>
<thead>
<tr>
<th>Rivers</th>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>UV-254 (cm⁻)</th>
<th>SUVA (L/mg.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karaj</td>
<td>7.5</td>
<td>3.98</td>
<td>0.1724</td>
<td>4.328</td>
</tr>
<tr>
<td>Jajrood</td>
<td>7.43</td>
<td>4.42</td>
<td>0.1829</td>
<td>4.18</td>
</tr>
<tr>
<td>Lar</td>
<td>7.8</td>
<td>3.6</td>
<td>0.1616</td>
<td>4.5</td>
</tr>
</tbody>
</table>

**Table 2:** The average concentration of NOM in Tehran surface water resources in summer

<table>
<thead>
<tr>
<th>Rivers</th>
<th>pH</th>
<th>TOC (mg/L)</th>
<th>UV-254 (cm⁻)</th>
<th>SUVA (L/mg.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Karaj</td>
<td>7.46</td>
<td>2.71</td>
<td>0.1296</td>
<td>4.78</td>
</tr>
<tr>
<td>Jajrood</td>
<td>7.4</td>
<td>2.76</td>
<td>0.132</td>
<td>4.783</td>
</tr>
<tr>
<td>Lar</td>
<td>7.9</td>
<td>1.78</td>
<td>0.093</td>
<td>5.22</td>
</tr>
</tbody>
</table>

Table 3 and 4 show the mean concentration Halo acetic acids(µg/L) in water treated by treatment plant 1, 3 and 4, 5 that were observed in spring, respectively 49.01, 55.56 and 43.73 and in summer 41.7, 48.82 and 34.83 µg/L. Also due to the low bromide ion in water resources only were observed di and trichloroacetic acids compounds, which in water treatment plant No. 1 was about 76% and 24% of the total samples, the water treatment plant No 3 and 4, respectively 78% and 21% of total water treated and in treatment plant No. 5 respectively 70% and 30% of the samples.

**Table 3:** The average concentration of HAAs in Tehran treated water in spring

<table>
<thead>
<tr>
<th>Water treatment plant</th>
<th>pH</th>
<th>Free residual chlorine (mg/L)</th>
<th>HAAs (µg/L)</th>
<th>DCAA(µg/L)</th>
<th>TCAA(µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>7.66</td>
<td>0.88</td>
<td>49.01</td>
<td>37.92</td>
<td>11.08</td>
</tr>
<tr>
<td>No.3,4</td>
<td>7.73</td>
<td>0.93</td>
<td>55.56</td>
<td>46</td>
<td>11.23</td>
</tr>
<tr>
<td>No.5</td>
<td>7.9</td>
<td>0.88</td>
<td>41.7</td>
<td>26.96</td>
<td>10.18</td>
</tr>
</tbody>
</table>

3.2. Presence of precursors that forming Halo acetic acids

Presence of NOMs as precursors forming DBPs is very important. The amount and type of these products are depending on the characteristics natural organic matter. Research conducted by Nikolaou [13] [20] and Golfinopolous [21] states that natural organic materials including various organic compounds and its concentration depending on the plant near the water source. As will be observed concentrations of organic carbon and UV -254 of three rivers and Halo acetic acids in all treatment plant in spring is higher than the summer. Studies by Uyak [22] in Turkey, Rodriguez [23] in Quebec Canada and Serodes Canada [24] are showing the highest precursors of DBPs in spring. In general the presence of total organic carbon and UV absorption at 254 nm in water, depending on water source, climate and seasons are different and can be one of the important reasons for increasing organic carbon and UV absorption in the presence of spring water flowing caused by rainfall, melting due Runoff upper layers of ice and snow that are usually considered humic containing materials.
3.3. Seasonal variations Halo acetic acids
Seasonal variations of DBPs are associated by changing the amount of natural organic matter and water source characteristics. As can be seen changing parameters such as pH, temperature and residual chlorine is not affecting on concentration Halo acetic acids, in fact can say that changes these compounds during different seasons depending on TOC and UV-254. Regression results in the Karaj River shows that UV-254 and TOC are having great relationship with \( R^2 = 0.96 \), sig < 0.001, which is showing great relation between these two parameters exists, the regression model for Halo acetic acids and TOC, \( R^2 = 0.615 \), sig = 0.06 and, in the regression analysis for Halo acetic acids and UV-254 \( R^2 = 0.72 \), sig = 0.031 and is therefore UV-254 as a variable affecting the activity indicators and precursors Halo acetic acids are considered and due to high correlation between UV-254 and TOC, TOC is not included in the models. Jajrood and Lar rivers regression results and also high correlation between TOC and UV-254 are. The relationship between UV-254 and Halo acetic acids indicate that increasing UV-254 in the spring of Halo acetic acids also increased. Despite the prediction is more Halo acetic acids formed at temperatures higher (summer), but occur presence of desirable precursors Haloacetic acids formed during the spring and the melting snow and spring rains are seen.

3.4. DCAA and TCAA in the presence of water
Various studies conducted in Taiwan [7, 10], Canada [24, 25], Greece[21], South Korea[26], Turkey[22], England [27] observed that di and tri Chloro acetic acids are major acid species. In the study conducted by Rodriguez (2004) only two species were observed. In this study, in all samples only di, tri Chloro acetic was observed and boromo acetic composition was not showed. Chlorine and bromine in the reaction process and the competitive chlorination than bromine ions react with natural organic matter with ratio1 / 10 is[28], can say that concentration bromide ion in all the waters studied in is very low. Rodriguez et al in 2004 and 2007 reduce dichloroacetic acid levels in treated water in the summer due to being provided favorable conditions within microbial filters in treatment plants. In fact, Williams and Fauntleroy in 2005 reported that a special species of bacteria (Burkholderia and Sphinogomonas) may decompose dihalogenate disinfection products in hot water in summer (20-15 degrees) [29].

4. CONCLUSIONS
Most studies in Iran have been investigated trihalometans monitoring compounds; therefore feel Halo acetic acids and results for the first time in Iran are presented. The results show that the average concentration of total organic carbon and UV absorption in the Karaj River, Jajrood and Lar spring respectively about 1.5 and 1.3 times, 1.6 and 1.3 times, 2 and 1.7 times higher than the average of these parameters is in summer. Also due to high correlation and the presence of natural organic matter and Halo acetic acids, concentration of these concentrations in spring waters treated was observed higher than summer. Considering Halo acetic acids in treated water in Tehran, and consider the standard that the U.S. Environmental Protection Agency limit 60µg / L for these compounds can be said is expressed in all samples Halo acetic acids concentration is less than the limit be. Also, di and tri chloroacetic acid levels were below the WHO guideline for these compounds (respectively 50 and 200 µg/L). The presence of these compounds in water levels being closely monitored due to the standard can be a warning for authorities is in the water industry.

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