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Determination of Hydrophobic and Hydrophilic Fractions of Natural Organic Matter in Raw Water of Jalalieh and Tehranspars Water Treatment Plants (Tehran)

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Abstract: The aim of this research was to determine hydrophobic and hydrophilic fractions of Natural Organic Matter (NOMs) in drinking water Sources of Tehran. Water sampling was conducted monthly from Aug 2006 to Jan 2007 in two drinking water treatment plants (Jalalieh and Tehranspars) in Tehran. Quantitative parameters of pH, EC, UV₂₅₄ and DOC were studied based on standard methods. The XAD-7 resin method was used for fractionation of NOM. Results showed that NOM concentrations in Jalalieh and Tehranspars water treatment plants were 2.47 and 1.63 mg L⁻¹, respectively. The mean of total percent of HPO (hydrophobic) and HPI (hydrophilic) fractions were about 41 and 59%, respectively. Since the hydrophobic NOM fraction exhibits higher trihalomethane formation potential (THMFP) than hydrophilic NOM, Tehran water chlorination exhibits higher THMFP than halo acetic acid formation potential (HAAFP). The information obtained from this study may be further employed in the design of the control technique and management strategies for the water treatment plant, especially for DBP_s reduction.

Key words: Natural Organic Matter (NOM), fractionation, hydrophobic, hydrophilic, drinking water, Tehran

INTRODUCTION

Natural Organic Matter (NOMs) is abundant in natural water resources and in many ways may affect the unit operations in water treatment. Although, NOMs are considered harmless but they have been recognized disinfection by-products precursors (DBPs) during the chlorination process. Formation of DBPs highly depends on the composition and concentration of NOM, which can be broadly divided into two fractions of hydrophobic (humic) and hydrophilic (non-humic) substances (Zazouli *et al.*, 2007). The Humic Substances (HS) are comprised of humic and fulvic acids and non-humic substances (non-HS) include carbohydrates, lipids and amino acids (Croue *et al.*, 1993; Owen *et al.*, 1995). NOM is typically dominated by humic materials, but proteins, polysaccharides and other classes of biopolymers also contribute to NOM. In addition to them, monomeric species such as simple sugars and amino acids are present in water sources. The non-humic fraction of the NOM may generally more biodegradable and, as such, supports bacterial regrowth in water distribution systems (Karnik *et al.*, 2005).

NOM was derived both from natural degradation of some organic substances within the ecological systems and from human activities (Panyapinyopol *et al.*, 2005). The chemical nature, or structural, of NOM in a drinking water supply is determined by its source materials and by biogeochemical processes that take place in the watershed (Huang *et al.*, 2004). The structures and concentration of NOM are different from one location to another location due to natural ecosystem differences and the human activities. NOM cannot easily be removed using conventional water treatment processes. Therefore, they may enter the municipal water distribution network and reach to the points of use.

It is generally known that formation of DBPs highly depends on the concentration of NOM as a main contributor and other factors such as NOM composition and water treatment methods (Kim and Yu, 2005a). Moreover, NOM acts upon potable water quality by contributing to biological regrowth in the distribution system and producing color, taste and odor (Owen *et al.*, 1995).

NOM properties, including structure (aromatic versus aliphatic, or hydrophobic versus hydrophilic), size

[(average relative molecular mass (RMM)], RMM distribution and charge density, are the important factors in the formation of disinfection by-products (DBPs) (Korshin *et al.*, 1997). Few reports on correlations between NOM fraction and THMs and HAAs (Haloacetic Acid) formation have been made (Kim and Yu, 2005a). DBPs of significant consequence in the water treatment industry include trihalomethanes (THMs) and haloacetic acids (HAAs), both of which are suspected human carcinogens and are currently regulated by EPA Stage I statute for DBPs with maximum contaminant levels (MCLs) of 80 and 60 $\mu\text{g L}^{-1}$, respectively. Stage II limitations will lower the MCL for THMs and HAAs to 40 and 30 $\mu\text{g L}^{-1}$, respectively. This restriction will provide new challenges for conventional potable water treatment plants, which are often struggling to meet current EPA MCLs for both contaminants. And also ISIRI (Institute of Standards and Industrial Research of Iran) has set MCLs for chloroform 0.2 mg L^{-1} (Anonymous, 1997). Tehran is a capital of Iran. Tehran citizens are provided with their drinking water from four water treatment plants such as Jalalieh and Tehranpars plant. However, information about the NOM characteristics of Tehran drinking water is not sufficient. Therefore, the aim of this research was to determine hydrophobic and hydrophilic fractions of Natural Organic Matter in Tehran drinking water.

MATERIALS AND METHODS

Determination of NOM fractions: For dividing of NOM fractions was used the XAD resin method. The division of NOM into hydrophilic and hydrophobic portions was based on the procedure proposed by Thurman and Malcolm (Thurman and Malcolm, 1981). The resin used was Amberlite XAD-7 is a nonionic aliphatic acrylic polymer derives its adsorptive properties from its patented macroporous structure based on which; it is physically stable (<http://www.rohmass.com/>). The resin was cleaned by the sequential Soxhlet extraction method according to Method 5510C of standard methods (Anonymous, 2000). At first it was washed with 0.1N NaOH for 5 days. Then, the resin was flushed sequentially for 24 h each with hexane, methanol, acetonitrile and methanol. After the resin was filled in the glass column (ID: 11 mm and 20 cm long column), the resin was rinsed with 0.5 N NaOH. Then, the resin was flushed sequentially for 24 h each with methanol, acetonitrile and methanol. Finally, the resin column was rinsed sequentially (three cycles) with 0.1 N NaOH, 0.1 N HCl and distilled water to remove remaining impurities. The rinse of resin column was repeated until the DOC concentration of the effluent of final distilled water rinsing step showed $<0.5 \text{ mg C/L}$

(Anonymous, 1995). Prefiltered water samples using a 0.45 membrane filtration were acidified to pH = 2.0 with 0.1 N HCl and passed into a resin column to separate NOM into hydrophilic and hydrophobic fractions (Karnik *et al.*, 2005). Hydrophilic NOM is the effluent through the resin, but hydrophobic is adsorbed. Adsorbed hydrophobic NOM can be eluted from the resin using 0.1 N NaOH. These fractions were analyzed with following analytical techniques: DOC, UV-abs, specific ultraviolet absorbance (SUVA).

Water sampling and analytical techniques: Experiments were carried out on samples taken from two water treatment plants that supply part of drinking water demand of Tehran City. Water samples were collected from influent water to plants. Water sampling was conducted monthly Aug 2006 to Jan 2007. Samples were analyzed from the point of pH, conductivity and Dissolved Organic Carbon (DOC) according to Standard Methods (Anonymous, 2000). Conductivity and pH were measured at the sampling sites by using a portable analyzer. Samples were carried to the Laboratory, prefiltered with a 0.45 μm membrane filter to remove particles and stored in a refrigerator at 4°C for the analysis of DOC, UV₂₅₄ (UV absorbance at a wavelength of 254 nm) and SUVA, as shown in Fig. 1. Dissolved Organic Carbon (DOC) of unfractionated and fractionated samples was determined with a Total Organic Carbon (TOC) analyzer (Shimadzu, Japan, Model: TOC-VCSH, Serial No: 3993668) in accordance with the Standard Method 5310B. The UV absorbance UV-254 was analyzed in accordance with the Standard Method 5910 B (Ultraviolet Absorption Method) by using a Lambda 25 UV/Vis spectrophotometer. Specific UV absorbance (SUVA) ($\text{L mg}^{-1} \text{ m}$) was calculated as

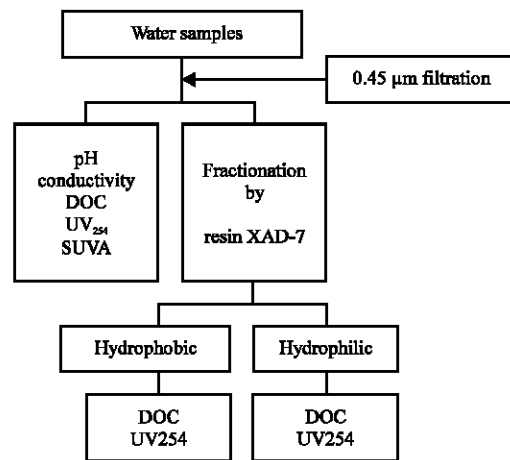


Fig. 1: Experimental procedure for the analysis of water natural organic matter (Kim and Yu, 2005b)

a ratio of the UV absorbance at 254 nm (1 m^{-1}) with DOC (mg L^{-1}) (Anonymous, 2000). Potassium hydrogen Biphthalate (KHP) was used to check the precision of the spectrophotometer.

Specific ultraviolet absorbance (SUVA) at 254 nm was used as an index of aromaticity contained in humic substances because humic substances have greater aromatic carbon contents than nonhumic materials (Singer, 1999).

RESULTS AND DISCUSSION

As shown in Table 1, Dissolved Organic Carbon (DOC) concentration of unfractionated water samples was 2.47 mg L^{-1} and in the range of 0.79 to 4.598 mg L^{-1} . And also mean DOC of HPI and HPO fractions were 0.98 and 1.49 mg L^{-1} respectively. The results of SUVA measurements showed that water was composed of HPO and HPI fractions but the fraction of hydrophobic NOM was higher than that of hydrophilic NOM. The hydrophobic NOM was between about 55 and 70% but the hydrophilic NOM was between about 30 and 45%.

The results of Table 2 indicated that the mean DOC concentration of unfractionated water from the Tehranpars water treatment plant was 1.63 mg L^{-1} and in the range of 1.1 to 2.8 mg L^{-1} . As Table 2 showed that raw water from Tehranpars water treatment plant was composed of HPO and HPI fractions but the fraction of hydrophobic NOM was higher than that of hydrophilic NOM. The average DOC of HPI and HPO fractions were 0.69 and 0.94 mg L^{-1} , respectively. The hydrophobic NOM was between about 46 and 65% but the hydrophilic NOM was between about 35 and 53%.

Therefore, the results indicated that NOM content was found to be occupied to a major portion by the hydrophobic fractions (HPO). The other characteristics of the water sources studied during this research are given in Table 1 and 2.

The data presented in Table 3 show that the percent distribution of NOM in the water, which the fraction of hydrophobic NOM was higher than hydrophilic NOM. The hydrophobic NOM was between 46 and 70% for all waters. The remaining was hydrophilic fraction. It was disclosed that the hydrophobic fraction was predominant compared to the hydrophilic in the water sources of Tehran. The studies of Panyapinyopol *et al.* (2005) showed that hydrophilic fraction in drinking water treatment plant in Bangkok, Thailand, was the major component in the water sample (66%) whilst the percent of hydrophobic fraction was 44% (Panyapinyopol *et al.*, 2005). Fearing *et al.* (2004) reported that DOC concentration in water at Albert water treatment works in the north of England was 7.8 to 11.2 mg L^{-1} . They were sampled water at three different times during the period of a year during (Apr. 2002 to Mar. 2003) and as can be seen the nature of the water can vary throughout the year (Fearing *et al.*, 2004).

The results on the water quality at the Rusko water treatment plant in Tampere, Finland revealed that TOC was lowest in December and then rising towards the summer, varying between 5.1 and 6.3 mg L^{-1} . UV_{254} absorbance varied between 0.136 and 0.103 . Highest values were obtained in winter and spring (Matilainen *et al.*, 2005). The results were obtained from the Lake Lansing, Michigan State (USA), showed that TOC content varied between 8.6 to 11.6 mg L^{-1} and UV_{254} absorbance was 0.160 - 0.180 . The hydrophobic fraction

Table 1: NOM characteristics of raw water in Jalalieh water treatment plant

Month	pH	EC ($\mu\text{s cm}^{-1}$)	UV_{254} (cm^{-1})	DOC (mg L^{-1})	SUVA ^a	DOC-HPI (mg L^{-1}) ^b	DOC-HPO (mg L^{-1}) ^c
Aug. 2006	7.40	306.00	0.0928	3.700	2.51	1.60	2.100
Sep. 2006	7.94	314.00	0.0808	2.328	3.47	0.70	1.628
Oct. 2006	7.60	310.00	0.0651	1.890	3.44	0.60	1.290
Nov. 2006	7.45	325.00	0.0518	1.500	3.45	0.60	0.900
Dec. 2006	7.75	374.00	0.1439	4.598	3.13	2.07	2.528
Jan. 2007	7.70	433.00	0.0292	0.790	3.70	0.29	0.500
Average	7.64	343.67	0.0773	2.470	3.28	0.98	1.490

^a: Specific UV absorbance ($\text{L m}^{-1} \text{ mg}^{-1}$), ^b: Hydrophilic fraction, ^c: Hydrophobic fraction

Table 2: NOM characteristics of raw water in Tehranpars water treatment plant

Month	pH	EC ($\mu\text{s cm}^{-1}$)	UV_{254} (cm^{-1})	DOC (mg L^{-1})	SUVA ^a	DOC-HPI (mg L^{-1}) ^b	DOC-HPO (mg L^{-1}) ^c
Aug. 2006	7.50	336.00	0.1100	2.800	3.93	1.04	1.760
Sep. 2006	7.75	314.00	0.0741	1.676	4.42	0.59	1.086
Oct. 2006	7.50	326.00	0.0513	1.500	3.42	0.60	0.900
Nov. 2006	7.85	399.00	0.0471	1.300	3.62	0.58	0.720
Dec. 2006	7.60	374.00	0.0393	1.429	2.75	0.74	0.689
Jan. 2007	7.90	404.00	0.0264	1.100	2.40	0.59	0.510
Average	7.70	358.83	0.0580	1.630	3.42	0.69	0.940

^a: Specific UV absorbance (L m mg^{-1}), ^b: Hydrophilic fraction, ^c: Hydrophobic fraction

Table 3: Distribution of NOM fractions in drinking water sources of Tehran

Water treatment plant	Fraction (%)	
	Hydrophilic	Hydrophobic
Jalalieh	40	60
Tehranpars	42	58
Average	41	59

was making up approximately 50% of the TOC. The percent of hydrophobic and hydrophilic fraction was approximately equal (Karnik *et al.*, 2005).

The study of NOM in the Han River, Korea, revealed that NOM concentration was 3.12 mg L⁻¹ as DOC and 0.037 cm⁻¹ as UV₂₅₄. The raw water contained higher hydrophilic fraction than the hydrophobic fraction. In addition, SUVA was 1.185 (L mg⁻¹ m) that represent hydrophilic fraction more than the hydrophobic fraction. The hydrophilic NOM was between about 55 and 70% for all waters. They concluded that since the hydrophilic NOM exhibited higher HAAFP than hydrophobic NOM, chlorination of the Han River water produced higher Haloacetic Acid Formation (HAAs) than trihalomethane formation (THMs).

SUVA gives a relative indication of the hydrophobic content in water and give reasonable predictions of THMFP (Krasner *et al.*, 1996). SUVA can also be used to describe the composition of the water in terms of hydrophobicity and hydrophilicity. It has been considered that SUVA is greater than 4 (SUVA >4), NOM has more hydrophobic (humic) fraction in nature and it plays a major role in the formation of DBPs. And also SUVA is less than 2 (SUVA <2), hydrophilic (non-humic) substances play a major role in the formation of DBPs. If SUVA is 2-4, water is a mixture of hydrophobics and hydrophilics (Owen *et al.*, 1993). In this study, SUVA was between 2 and 4, therefore, water is mixture of HPO and HPI fractions.

Distribution of hydrophobic and hydrophilic fractions in water depends on month, season and weather. Seasons also play a major part in the DOC distribution of raw water and it has been reported that for Albert raw water, the hydrophobic material distribution can range from 65 to 80% (Goslan *et al.*, 2002). The data presented in Table 1 and 2 show that the HPO fraction was higher than HPI, evidently showing the monthly variation during the collection period from Aug. 2006 to Jan. 2007. Weather might have an effect on NOM fraction, Excluding in Dec. 2006, the NOM concentration gradually was decreasing in the raw water. it should be mentioned, that this study was only based on the quality of the water source during six months. Therefore, future research should be conducted to monitor and seasonal variation on the quality of NOM fractions.

CONCLUSIONS

The information obtained from this survey show that NOM fractions differ at water sources. It depends on several factors, especially watershed properties. Moreover, it can conclude that chlorination of Tehran water caused to formation of higher THMFP than halo acetic acid (HAAFP). Finally, these results can be further employed in the design of the control technique and management strategies for DBPs.

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