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Study of Natural Organic Matter Fractions in Water Sources of Tehran

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Abstract: Natural Organic Matters (NOMs) are 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 (DBP_s) during the chlorination process. Formation of DBP_s 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. The objective of this study was to determine Natural organic matter and its fractions concentration in the surface water sources of Tehran. Water sampling was conducted monthly between May to July 2006 in three rivers Lar, Jajrood and Karaj as the main drinking water supplying sources in Tehran. Quantitative parameters of pH, EC, UV₂₅₄ and DOC were studied based on to standard methods. The XAD-7 resin method was used for fractionation of NOM. Results showed that NOM concentrations in Lar, Jajrood and Karaj rivers were 8.53, 12.9 and 11.3 mg L⁻¹, respectively. The HPO (hydrophobic) fraction was predominant compared to the HPI (hydrophilic) fraction in the all of water samples. The mean of total percent of HPO and HPI fractions were about 57 and 43%, respectively. Since the hydrophobic NOM fraction exhibits higher trihalomethane formation potential (THMFP) than hydrophilic NOM, Tehran water chlorination exhibits higher THMFP than haloacetic 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, THMFP, HAAFP, Tehran

INTRODUCTION

Many water sources throughout the world and especially surface waters contain natural organic matters (NOMs), 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 is a heterogeneous

mixture of organic compounds which interacts with many inorganic and organic pollutants, leading to the toxicity decrease of these pollutants. These categories of organics, 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.

NOM can be broadly divided into two fractions: hydrophobic (humic substances (HS)) and hydrophilic or non-humic substances (non-HS). 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).

Although harmless itself, NOM reacts with chlorine to form undesirable disinfection by-products (DBPs) during the disinfection process (Krasner *et al.*, 1989). 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 DPBs 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} (ISIRI, 1997).

Tehran citizens are provided with their drinking water from three rivers Lar, Latian and Amir Kabir dams. The upstream are very important water sources for about 12 millions people in the metropolitan area. However, information about the NOM characteristics of water sources of Tehran is not sufficient. Therefore, the objective of this study was to monitor and measure the NOM content and its fractions in the Tehran water sources.

MATERIALS AND METHODS

Water sampling: Experiments were carried out on samples taken from from three rivers that supply drinking water demand of Tehran City through the three Dams (Lar, Latian and Amir Kabir). Water samples were collected in the middle of the stream and at mid-depth. Water sampling was conducted monthly between May to July 2006.

NOM fractionation: The XAD resin method has been reported in many applications for fractionation of NOM. The division of NOM into hydrophilic (Non-humic substances) and hydrophobic (Humic substances) portions was based on the procedure proposed by Thurman and Malcolm (Thurman and Malcolm, 1981). The resin used was Amberlite XAD-7 which is a nonionic aliphatic acrylic polymer derives its adsorptive properties from its patented macroporous structure based on which; it is physically stable (<http://www.rohmas.com>).

It is very important to clean thoroughly the resin before each isolation process because the uncleaned resin will have a significant level of DOC bleeding. In this study, resin was cleaned by the sequential Soxhlet extraction method according to Method 5510C of Standard Methods (APHA, 2000). At first it was washed with 0.1 N 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 $<0.5 \text{ mg C L}^{-1}$ (APHP, 2000). Prefiltered water samples using a 0.45 membrane filtration were acidified to $\text{pH} = 2.0$ 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).

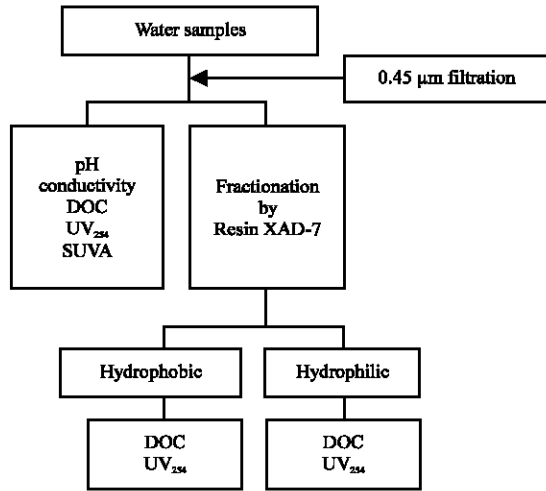


Fig. 1: Experimental procedure for the analysis of water natural organic matter. (Kim and Yu, 2005b)

Analytical techniques: Samples were analyzed from the point of pH, conductivity and Dissolved Organic Carbon (DOC) according to Standard Methods (APHP, 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) (L/mg.m) was calculated as a ratio of the UV

absorbance at 254 nm (1/m) with DOC (mg L⁻¹) (APHP, 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

Table 1 present the results of water quality measurement and NOM fractions of raw waters from three rivers. As shown in Table 1, Dissolved Organic Carbon (DOC) concentration of unfractionated water samples from the Lar River was 8.53 mg L⁻¹ and in the range of 7.6 to 9.8 mg L⁻¹. The results of SUVA measurements showed that water was composed of both HPO and HPI fractions but the fraction of hydrophobic NOM was higher than that of hydrophilic NOM. The hydrophobic NOM was between about 54 and 68%.

And also the mean dissolved organic carbon (DOC) concentration of unfractionated water from the Jajrood River was 12.9 mg L⁻¹ and in the range of 10.4 to 12.1 mg L⁻¹. And also mean DOC of HPI and HPO fractions were 6.1 and 6.83 mg L⁻¹, respectively. Jajrood river water was composed of HPO and HPI fractions but the fraction of hydrophobic NOM was higher than that of hydrophilic NOM. The hydrophilic NOM was between about 54 and 68%.

The results of Table 1 indicated that the mean Dissolved Organic Carbon (DOC) concentration of the Karaj river water was 11.33 mg L⁻¹ and in the range of 9.7 to 13.8 mg L⁻¹ and was particularly high. 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 summarized in Table 1.

Table 1: Characteristics of three Rivers water

River	Month	pH	EC (μs cm ⁻¹)	UV254 (m ⁻¹)	DOC (mg L ⁻¹)	SUVA ^a	DOC-HPI (mg L ⁻¹) ^b	DOC-HPO (mg L ⁻¹) ^c
Lar	May	7.6	224.00	18.95	7.60	2.49	2.4	5.20
	June	7.8	248.00	21.38	9.80	2.18	4.1	5.70
	July	7.1	268.00	20.24	8.20	2.47	3.7	4.50
	Mean	7.5	246.67	20.19	8.53	2.38	3.4	5.13
Jajrood	May	7.2	203.00	40.84	10.40	3.93	5.7	4.70
	June	7.3	266.00	53.5	12.10	4.42	6.3	5.80
	July	7.6	287.00	55.42	16.20	3.42	6.2	10.00
	Mean	7.4	252.00	49.92	12.90	3.92	6.1	6.83
Karaj	May	7.8	264.00	21.24	9.70	2.18	3.4	6.30
	June	7.5	224.00	40.25	10.50	3.83	2.9	7.60
	July	7.6	245.00	46.25	13.80	3.35	7.5	6.30
	Mean	7.6	244.00	35.91	11.33	3.13	4.6	6.70

^aSpecific UV absorbance (L/m.mg). ^bHydrophilic fraction. ^cHydrophobic fraction

DISCUSSION

The data presented in Table 2 show that the percent distribution of NOM in the water, which the fraction of hydrophobic NOM was higher than that of hydrophilic NOM. The hydrophobic NOM was between 52 and 61% for all waters. So, 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 from 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 then rising towards the summer, varying between 5.1 and 6.3 mg L⁻¹. UV254 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 UV254 absorbance was 0.160-0.180. The hydrophobic fraction 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.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

Table 2: Distribution of NOM fractions in drinking water sources of Tehran
NOM fractions (%)

River	Hydrophilic	Hydrophobic
Lar	39.84	60.16
Jajrood	48.38	51.62
Karaj	40.59	59.41
Mean	42.94	57.06

Table 3: Changes of NOM concentration during May to July

Month	NOM concentration (mg L ⁻¹)		
	Lar	Jajrood	Karaj
May	7.6	10.4	9.7
June	9.8	12.1	12.1
July	8.2	16.2	13.8

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 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 65-80% (Goslan *et al.*, 2002). The data presented in Table 2 and 3 show that the HPO fraction was higher than HPI, evidently showing the monthly variation during the collection period from May to July. Weather might have an effect on NOM fraction. As shown Table 3, Excluding Lar River. The NOM concentration gradually was increasing in the Jajrood and Karaj rivers. The information obtained from this survey can be further employed in the design of the control technique and management strategies for DBPs. For example, the choice of coagulant aids might be chosen to ensure the selective removal of the target organic precursors. Finally, it should be mentioned, that this study was only based on the quality of the water source during three months. Therefore, Future work should be conducted to monitor the seasonal variation on the quality of NOM fractions.

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