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Determination of Hydrophobic and Hydrophilic Fractions of Natural Organic Matter in Raw Water of Zahedan Water Treatment Plant

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ABSTRACT

Background: Over the past two decades, increasing natural organic matter (NOM) concentration levels in water resources have been reported in many countries. The properties of NOM can vary with source and time (season). The considerable seasonal variability and the trend towards elevated NOM concentration levels impose challenges to the water industry and the water treatment facilities in terms of operational optimization and process control.

Objectives: The aim of this study was to determine the concentrations and fractional distributions of NOM in raw water entering a water treatment plant in Zahedan city and to measure the parameters DOC, UV254, SUVA, TOC, hydrophobic and hydrophilic fractions, and pH, which may lead to a better understanding of the impact of source water on water treatment.

Patients and Methods: Representative water samples were collected monthly from October 2010 to May 2011 from the raw water entering the Zahedan water treatment plant (from Chahnimeh water source in Zabol city). Samples were transported to the water and wastewater laboratory of the School of Public Health at the Zahedan University of Medical Sciences for analysis.

Results: NOM in the examined sample exhibited highly humic nature, indicating a higher percentage of the hydrophobic fractions than the hydrophilic one in the total organic carbon. The annual average values of DOC, UV254, SUVA, and TOC were about 8 mg/L, 0.5 cm–1, 7 L/mg.m, and 9 mg/L, respectively.

Conclusion: The concentration of NOM in raw water entering the drinking water treatment plant in Zahedan is high and its seasonal variation does not follow a particular pattern. The bulk of the organic material fraction in this water source is hydrophobic.

▸ *Implication for health policy/practice/research/medical education:*

The content of this article is useful for water treatment plant managers and operators and drinking water providers to better operation and supervision of drinking water treatment plants and water resources.

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1. Background

Natural organic matter (NOM) is a complex mixture of a variety of polyfunctional organic compounds, ranging from simple to more complex compounds that are highly heterogeneous, having a mixture of two major types of functional groups: carboxylic and phenolic compounds (1). The relevance of NOM to water treatment operators is significant as some of its components can cause coloration of water, it can include compounds that cause unpleasant taste and odors, and it can act as a substrate for microbial growth (2). In addition, the presence of NOM can affect the quantities of coagulants and disinfectants required to treat the water: NOM can foul membranes, block activated carbon pores, and com-

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pete with taste and odor compounds for available adsorption sites, reducing adsorption efficiency. NOM also plays a crucial role in the transport and fate of metals in aquatic environments (2, 3). Any NOM that is not removed by the applied treatment process can, upon subsequent disinfection, react to form by-products such as trihalomethanes (THMs) (3). The link between organic matter in drinking water and the formation of disinfection by-products (DBPs) after chlorination was first revealed by Rook (4). Since then there has been a steady accumulation of literature on the health risks of DBPs, their formation, and methods to minimize their presence in drinking water. Two classes of DBPs, trihalomethanes (THMs) and haloacetic acids (HAAs), are considered to be the dominant DBPs on a weight basis in potable water (5). It is established that many DBPs are mutagens, carcinogens, or toxicants (6). Some species are regulated to limit their exposure to humans; for example, the limits set by the United States Environmental Protection Agency are 80 $\mu g\ L^{-1}$ for THMs and 60 $\mu g\ L^{-1}$ for HAAs, while the United Kingdom and world health organization limit for THMs is 100 $\mu g\ L^{-1}$ (5, 7, 8). Aquatic NOM can be classified roughly into two groups: (a) non-humic solutes, consisting of compounds belonging to the well-known classes of organic substances such as amino acids, hydrocarbons, carbohydrates, fats, waxes, resins, and low-molecular acids, and (b) very complicated heterogeneous humic solutes. Also, these two groups are not entirely distinguishable from each other (5). NOM may have distinctive characteristics associated with its origin (e.g., vegetation, soil, and wastewater). For example, dissolved organic carbon (DOC) from aquatic algae has a relatively large nitrogen content and low aromatic carbon and phenolic contents. On the other hand, terrestrially derived DOC has relatively low nitrogen content yet large amounts of aromatic carbon and phenolic compounds. Thus, the aromatic content, which is believed to be a major reactive component, varies with different sources. The contribution of each carbon source also depends on the season, and the hydrological and biogeochemical processes involved can alter the chemical composition and physical structures of the NOM. The specific UV absorbance (SUVA, defined as UV absorbance divided by DOC) seems to be well correlated to the aromatic content of NOM. Thus, SUVA is a valuable parameter when evaluating NOM reactivity and treatability (9). Traditionally, the treatment of water for potable use has been achieved by the use of conventional coagulation/flocculation using inorganic coagulants. Due to the considerable impact of NOM on water quality and supply, optimization of water treatment processes for NOM removal (i.e., enhanced coagulation using elevated coagulant doses and strict pH control) has been more common. Another shift away from chemical based treatments on both environmental and health grounds has been evident recently in water-treatment research and practices. The increasing usage of adsorbents such as ion-exchange resins and activated carbon as well as membrane filtration technologies is evident around the world as examples of this trend (5). Physical and chemical fractionation of aquatic NOM at a specific pH can be used to classify organic solutes into broadly defined hydrophobic and hydrophilic fractions (10, 11). The different NOM fractions exhibit different properties in terms of treatability by coagulation, coagulant demand, chlorine and ozone reactivity, and by-product formation potential (5). In addition, NOM composition and properties, and thereby the treatability of NOM, vary with place (location) and time (season) resulting in various negative aspects; this study was therefore conducted to determine the NOM properties in raw water entering the Zahedan drinking water treatment plant.

2. Materials and Methods

Representative water samples were collected monthly from October 2010 to May 2011 from the raw water entering the Zahedan water treatment plant (from Chahnimeh water source in Zabol city). Samples were transported to the water and wastewater laboratory of the School of Public Health at the Zahedan University of Medical Sciences for analysis. Glass bottles with TFE-lined caps were used to collect samples. Before use, all sampling glass bottles were washed with acid (3% nitric acid) and covered with an aluminum foil seal and kept at a temperature of 400 °C for at least one hour. The caps were washed with detergent and then with distilled water, and sealed with no carbon-aluminum plates (heated for one hour at 100 °C).

Since water samples can get contaminated rapidly, analysis was carried out immediately after collection. Where analysis could not commence immediately, the samples were either stored at 4 °C or relevant preservatives were added depending on the parameter to be determined and the duration of the preservation as described by APHA. For conservation, the pH of the water samples was decreased to lower than 2 using phosphoric acid. Some parameters such as DOC, ultraviolet absorption at 254 nm (UV_{254}), and pH were analyzed based on standard methods. The DOC of the samples was measured using a TOC analyzer (ANATOC series II) and UV_{254} was determined by a UV visible spectrophotometer (T80) (12). The calibration curve used in this study follows the equation $[NOM] = (30.48 \times ABS) - 2.0549$, $r = 0.9918$.

This equation has been obtained with the use of potassium hydrogen phthalate standard solution. For determination of the SUVA (L/mg.m) indicator, UV_{254} (cm^{-1}) was divided by DOC (mg/L). In order to fractionate NOM into hydrophilic and hydrophobic fractions, the samples were first passed through a fiber glass filter (0.45 μm) (Whatman) and then purified using the Amberlite XAD-8 resin as per the standard method and the study by Huizhong *et al.* (13). The pH of water samples was measured by a pH meter (Denver Ultra basic-UB10). To adjust the pH, 1 N solutions of perchloric acid and sodium hydroxide were used. High-purity water (Ultra Clear, Germany) was used in all experiments. All chemicals were of analytical grade (Sigma-Aldrich, Germany).

3. Results

Many previous studies mention the existence of a significant relationship between TOC concentrations and the potential of formation of HAAs and THMs in aqueous solutions. The results of the present study showed that the potential of DBP formation in the Zahedan city drinking water resource is very high. This material is important because it discolors water, stimulates the formation of toxic by-products as well as the corrosion of metals and synthetic organic materials, has an adverse effect on absorption, detrimental effect on the membranes, stimulates regrowth of microorganisms, and causes cancer in humans.

Table 1 shows some typical properties of raw water entering the Zahedan drinking water treatment plant, and *Figure 1* shows the changes of organic carbon and dissolved hydrophobic and hydrophilic components in the raw water entering the plant. This figure shows that as the weather becomes warmer, the levels of organic carbon in the water also increase. The minimum DOC concentration was observed in December (5 mg/L) and the maximum was observed in March (11 mg/L). The maximum amount of hydrophobic fraction was observed in February (6 mg/L) and the minimum was observed in December (3 mg/L). The maximum amount of hydrophilic fraction was observed in March (5 mg/L) and the minimum was observed in October (1.5 mg/L). The risk of the formation of DBPs is therefore maximum during March and February. *Figure 2* shows the variation of UV_{254} for the raw water entering the plant. This figure revealed that UV_{254} follows the same trend as DOC. A good correlation was obtained between UV_{254} and DOC ($R_2 = 0.93$), as illustrated in *Figure 3*. In general, a higher DOC corresponds to a higher UV_{254} value. The absorption of ultraviolet or visible light by organic molecules corresponds to the excitation of electrons and is observed for certain functional groups (14). Humic substances (HS) contain a variety of chromophores that absorb a wide range of wavelengths found in the solar spectrum. The most prominent chromophores are aromatic structures and conjugated bonds. In the visible range (400–800 nm), HS absorb mostly the short wavelength part of light, resulting in the typical yellow-brown color of natural water. There is

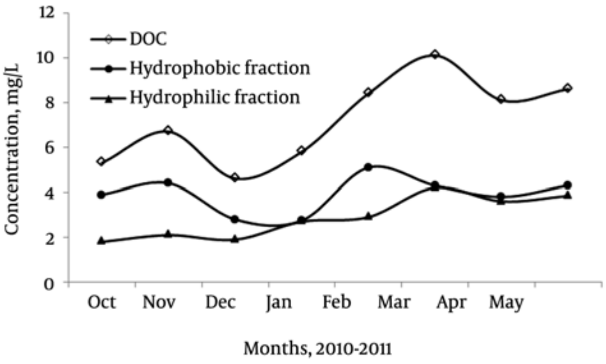

Figure 1. Variation of Organic Carbon and Dissolved Hydrophobic and Hydrophilic Components in the Raw Water Entering Zahedan Drinking Water Treatment Plant, 2010–2011

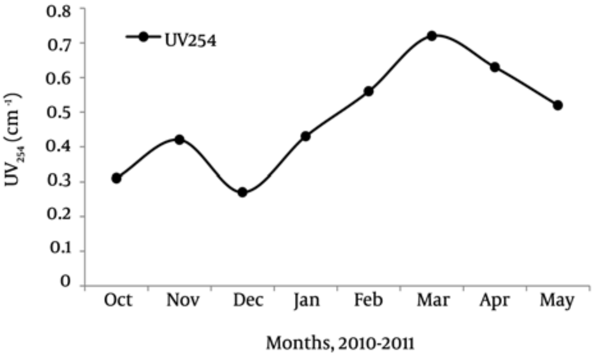

Figure 2. Variation of Ultraviolet Absorption at 254 nm (UV254) in the Raw Water Entering Zahedan Drinking Water Treatment Plant, 2010–2011

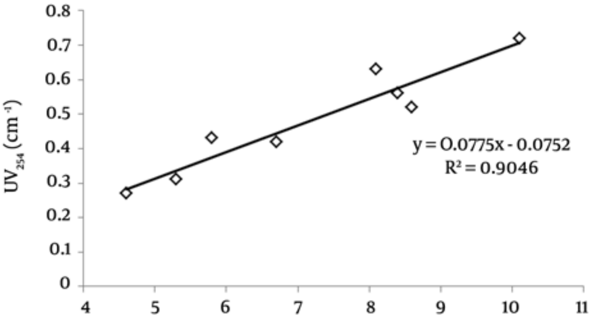

Figure 3. Correlation Between Dissolved Organic Carbon and UV254 in the Raw Water Entering Zahedan Drinking Water Treatment Plant, 2010–2011

Table 1. Water Quality Parameters of the Raw Water Entering Zahedan Drinking Water Treatment Plant

Parameters	Minimum	Average	Maximum	Standard Deviation
$UV_{254,}$ 1/cm	0.29	0.49	0.73	0.154
DOC, mg/L	4.72	7.21	10.37	1.91
SUVA, L/mg.m	5.87	6.82	8.21	0.8
Hydrophilic fraction, mg/L	1.52	2.70	5.04	1.11
Hydrophobic fraction, mg/L	2.97	4.51	5.68	1.06
pH	7.50	7.80	8.0	0.15
Total solid content, mg/L	425.60	426.93	490.88	25.28
EC, µS/cm	665	728.75	798	47.02
Turbidyty, NTU	6.44	10.36	16.30	3.71

a raw correlation between color and humic content or MW (15, 16). Unlike many other organic compounds, HS do not exhibit distinguishable peaks in the UV range (200–400 nm). Instead, a smooth increase of absorbance with decreasing wavelength is observed. This observation is explained by the existence of numerous high energy bonds and aromatic rings that are abundant in these water samples (14). The maximum of UV$_{254}$ was observed in March (0.737 cm^{-1}) and the minimum was observed in December (0.291 cm^{-1}), with an average of 0.509 ± 0.141 cm^{-1}. The ratio of UV$_{254}$ and DOC, SUVA, is often used as an indicator of the aromatic carbon content of HS (17). Higher SUVA values (> 4) indicate higher aromatic carbon content in HS. Edzwald and Tobiason (18) have found a relationship between the SUVA value and the hydrophobicity and hydrophilicity of HS. Generally, higher SUVA values indicate higher hydrophobicity. The changes in SUVA for the raw water entering the Zahedan drinking water treatment plant are shown in *Figure 4*. Since the value of SUVA is greater than 4 for all months, it can be concluded that most of the organic carbon material content of this water source consists of high molecular weight and hydrophobic components with humic properties. The maximum values of total TOC, DOC, and UV$_{254}$ for the raw water entering the Zahedan water treatment plant are 12.962 mg/L, 10.37 mg/L, and 0.84 cm^{-1}, respectively. According to the study by Krasner *et al.* (1996), in water resources with high TOC concentration, the formation potential of THMs is equal to at least 50 µg THFP/mg C (16). For such a water source, the risk of formation of DFBs is also very high (> 50 µg THFP/mg C).

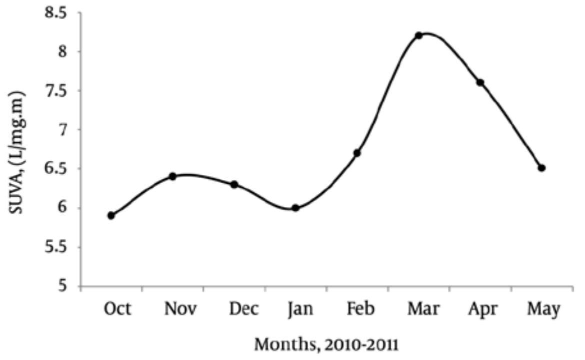

Figure 4. Variation of Specific UV Absorption (SUVA) in the Raw Water Entering Zahedan Drinking Water Treatment Plant, 2010–2011

4. Conclusion

The results of this study showed that the concentration of DOC in the water source of the Zahedan drinking water treatment plant is high (about 8 mg/L). Also, if chlorine is used for water disinfection in this plant, the potential for the formation of DBPs is very high due to the high organic material content. Therefore, this water source needs special attention.

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Authors' Contribution

Authors' worked equally.

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