Molecular-Mass Distribution of Dissolved Organic Matter of Water Sources and Drinking Water of Ufa

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Abstract—Using the size-exclusion chromatography method, the molecular-mass distribution of dissolved organic matter of drinking water and water sources of Ufa is studied. The influence of seasonal changes and various water treatment stages on the molecular-mass distribution of dissolved organic matter is shown.

When choosing a water treatment technology, information on the nature of contaminants, including the molecular mass (MM) of removed compounds, plays a significant role [1]. In contrast with simple organic substances, which are characterized by a single intrinsic MM value, humic substances (HSs) which are included in the dissolved organic matter (DOM) of natural waters are polydisperse; i.e., they have various MM values. For this reason, such a parameter as molecular-mass distribution (MMD) is used for their characterization, based on which the mean MM value is calculated.

Depending on the averaging method, three types of mean MM values are obtained, namely, mean-number (M_n), mean-weight (M_w), and z-average (M_z) [2, 3]:

(1) The mean-number MM value is calculated by averaging the molecular masses of DOM molecules with the molecular mass M_i by the number fraction:

$$\bar{M}_n = \sum n_i M_i \Big/ \sum n_i;$$

(2) The mean-weight MM value is calculated by averaging the molecules of the DOM assembly according to their mass (weight) fraction: $\bar{M}_w = \sum n_i M_i^2 \Big/ \sum n_i M_i;$

(3) The Z-average of MM is expressed by the following equation: $\bar{M}_z = \sum n_i M_i^3 \Big/ \sum n_i M_i^2$. This value characterizes the contribution of the heaviest molecules to the total MMD. This value is used only for DOM characterization.

In the given equations of the calculation of molecular mass, n_i is the number of molecules with the molecular mass M_i.

According to the published data, the mean-weight molecular mass (M_w) is the most widespread for HS characterization. Its value is influenced significantly by the nature of HS and by various environmental factors. In order to classify the fractional composition of HS, the polydispersity index of the specimen is often used, which characterizes the degree of heterogeneity of the substance according to molecular mass and is defined as the ratio of mean-weight molecular mass to mean-number molecular mass [2–4].

It should be noted that HSs are irregular polymers. Therefore, due to the variability of their composition, high polydispersity, and polyelectrolyte properties, existing experimental methods for the determination of the mean MM values have limited application to the analysis of the given compounds. For instance, the methods for the determination of MM based on the measurement of colligative properties of polymers (osmometry, cryoscopy, and ebullioscopy) are extremely sensitive to the presence of low-molecular impurities in the analyzed specimen. Therefore, their application for the analysis of HS preparations, which almost always contain low-molecular sol components, may significantly understate the mean-number MM value [5]. Conversely, the use of the sedimentation velocity method leads to inflated MM values [2]. The mean-weight MM values determined by ultrafiltration are affected greatly by the interaction of HSs with
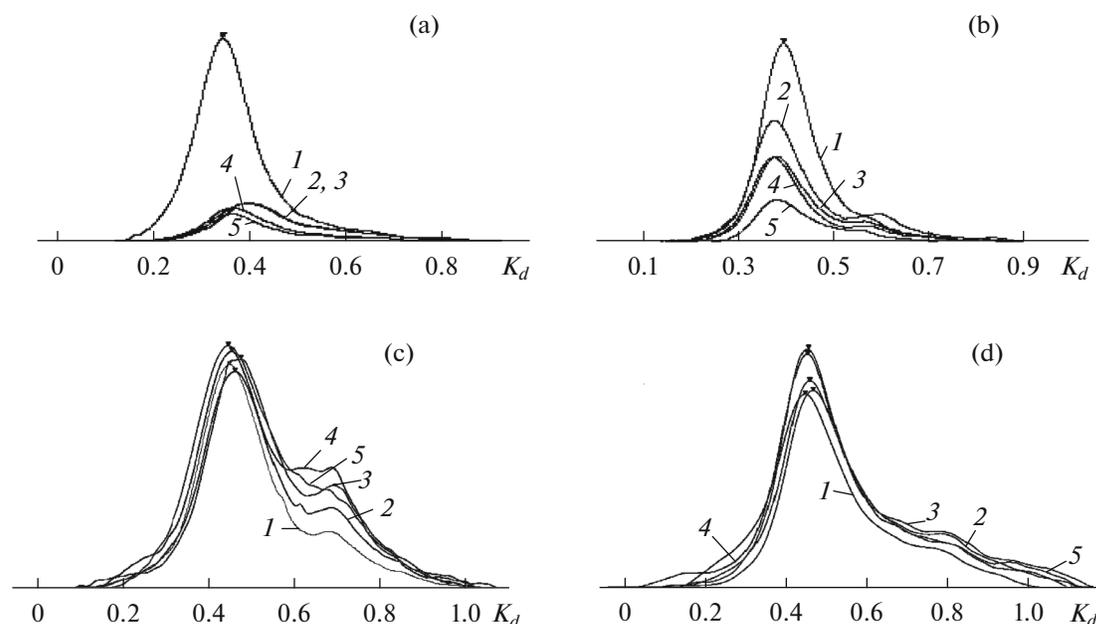
Fig. 1. Chromatograms of the specimens of surface and infiltration water prior to and after treatment: (a) May 2010, (b) July 2010, (c) November 2010, and (d) February 2011; (*1*) river water; (*2*) filtered and treated river water; (*3*) filtered, treated, and chlorinated river water; (*4*) infiltrated water; and (*5*) chlorinated infiltrated water (the absorbance recorded at the wavelength of 254 nm is indicated along the *y*-axis).

membranes [6, 7]. In this case, it should be noted that all of the mentioned methods allow the determination of either the mean MM value of a polydisperse specimen or the mass distribution of the substance by fractions which correspond to the transmission ranges of filter membranes. A far more fundamental molecular-mass characteristic of a polydisperse substance is the MMD curve. The most available and widespread method for the investigation of MMD of polymers, in particular HSs, is exclusion chromatography [8].

In this work, the MMD of DOM was studied using exclusion chromatography in specimens of untreated and treated water of the Ufa River and the water of an infiltration water intake prior to and after chlorination. The seasonal dynamics of the MMD of DOM was also studied. In order to determine the molecular mass, polystyrenesulfonates were used as calibrating substances. The separation was carried out on a column filled with the Toyopearl HW55S gel. As an eluent, 0.028 M phosphate buffer was used. All solutions were equilibrated by the composition of the buffer prior to analysis by adding concentrated phosphate buffer to achieve a concentration of 0.028 M in the analyzed solution. In order to detect the components of DOM, a UV detector was used. Detection was performed at the wavelength of 254 nm.

Typical gel chromatograms of DOM are given in Fig. 1. The chromatograms are represented in unit scale of the accessibility coefficient (K_d), which is obtained during the normalization of the elution volumes of the specimens which pass through the gel-

chromatography column, according to the following equation:

$$K_d = (V_e - V_0)/(V_t - V_0),$$

where V_e is the elution volume of the water specimen, V_0 is the void volume of the column, and V_t is the total volume of the column.

Effect of Seasonal Changes on MMD of DOM for the Objects under Study

In the Table, the molecular-mass characteristics of the specimens of DOM of surface and infiltrated water within the studied period (2008−2011) are given.

It should be noted that the average annual mean-weight molecular mass of DOM of the Ufa River within the studied periods (July 2008−April 2009 and May 2010−February 2011) corresponded to 6000 and 5800 Da, whereas the molecular mass of infiltrated water was 5700 and 5500 Da, respectively. The observed trend (lower molecular masses in the DOM of ground water) coincides with the expected one, because the highest-molecular components of DOM are lost upon water filtration through the ground. The obtained mean molecular masses for DOM of the Ufa River are in good accordance with the published data for other water sources (3770−5400 Da), the analysis of which was carried out under conditions close to those used in this work (0.028 M phosphate buffer as eluent and polystyrenesulfonates as markers (Perminova et al., 2003)). The only difference was that Toyo-

pearl resins with large pore size (HW55S), which provide a more symmetric distribution of DOM components in the column as compared to HW50S, were used in our work.

The observed trends on the seasonal dynamics of the molecular-mass distribution of DOM of Ufa River can be generalized as follows.

In the spring high-water period, the mean-weight molecular mass values grow from 6700 to 8300 Da (on average, nearly 7000 Da). This is presumably caused by the intense supply of high-molecular soil humus to the river during the spring flood period, which leads to the enrichment of DOM by high-molecular fractions.

In the summer specimens of river water, a decrease in the mean-weight molecular mass to 5700 Da is noted. However, the general MM range of DOM remains broad, which indicates the presence of a large number of organic compounds with various molecular masses in the surface water during this period.

In the autumn periods, further decrease in mean-weight molecular mass (on average, to 5000 Da) is observed for the DOM of river water. The water contains lower-molecular fractions of DOM as compared to the spring and summer specimens. This agrees with the literature data in that increased contents of the fraction of "older" HSs, which were exposed to a higher degree of humification and are characterized by lower mean-weight molecular mass values, are typical of aqueous ecosystems in the autumn period. In this case, the relevant processes are either the decomposition of high-molecular compounds during natural biodestruction or their sedimentation in the river ecosystem.

Winter specimens are characterized by a unimodal molecular mass distribution of DOM on the chromatograms, in contrast to the autumn specimens of river water. This indicates the presence of compounds with large dispersion of molecular mass in DOM in the water during this period. These changes of MMD of DOM in the winter specimens as compared to the autumn ones is probably related to the slow-down of the natural biodegradation of high-molecular DOM to lower-molecular compounds, which are prominent in the autumn water samples (Fig. 1).

The water of infiltration wells contains lower concentrations of DOM than the surface water and it is characterized by a seasonal dynamic of molecular-mass distribution. For example, the chromatograms of the specimens under study have maxima in the range of 5000 Da in the winter, spring, and summer periods. The spring flood, characterized by the supply of new organic compounds from outside, does not affect the MMD of the DOM of the underground water source, which confirms the proper operation of the filter beds of the wells of the infiltration water intake. The given water source is more likely characterized by endogenous changes, such as, for example, seasonal changes in the rate of biotransformation. This can be confirmed by the shift of the maximum of the mean-

weight molecular mass of DOM to the range of 2000–3000 Da in the autumn period.

Thus, underground water in this period mainly contains low-molecular fractions of DOM and biotransformation processes proceed quite extensively. The polydispersity of the well water specimens is low during this period, which also indicates the presence of compounds with nearly identical molecular mass. In the winter period, the biodestruction of DOM slows down; this determines the increase in the maximum mean-weight and mean-number molecular masses and the polydispersity of the sample.

Effect of Process Steps of Coagulation/Flocculation and Filtration on MMD of DOM for the Objects under Study

The stages of reagent treatment and filtration on the surface-type water intake have a variety of effects on the MMD of the DOM of treated water, depending on the season. This statement can be made on the basis of data analysis given in Fig. 2.

The results of the studies show that the coagulation/flocculation processes and filtration are most effective in the spring period from the viewpoint of the removal of high-molecular components of DOM, which enrich the river water during this period. The mean-weight molecular mass of DOM in the water after reagent treatment declines from 7000 to 4500–5000 Da (Fig. 2a). During this period, the fractional composition of DOM changes along with the decrease in its content upon water purification. On the one hand, the latter is presumably related to the presence of high-molecular soil compounds, which are more effectively removed by the chosen water treatment technology, in the river water taken during the spring flood. On the other hand, in the summer period, these stages of water treatment allow a decrease in the total content of DOM; however, its molecular-mass distribution practically does not change in this case. In the autumn and winter periods, the coagulation/flocculation and filtration processes also do not significantly affect the MMD of DOM.

Effect of Chlorination Stage on MMD of DOM of Water

The determination of the effect of the chlorination stage on the MMD of DOM is of particular interest. This is related to the fact that there are several works devoted to the significant transformation of DOM upon chlorination, where DOM acts as a source of trihalomethanes and other chlorinated compounds. The results of the effect of chlorination on the molecular-mass characteristics of DOM of surface and infiltration water are given in Fig. 3.

According to the obtained data (Fig. 3a), during the spring flood, the DOM of river water subjected to the stages of reagent treatment becomes most susceptible to destruction by chlorine and is also removed by
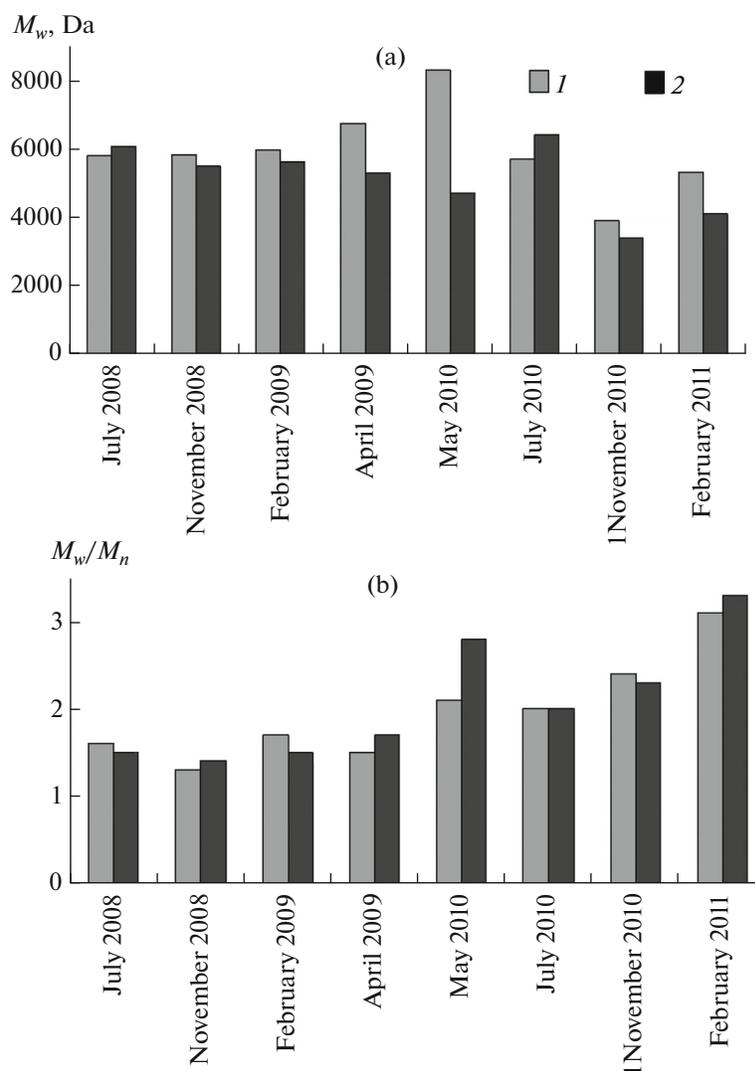
Fig. 2. Effect of the stage of reagent treatment and filtration on the (a) mean-weight molecular mass and (b) DOM of the Ufa River: (*1*) river water of the surface water intake and (*2*) river water of the surface water intake after reagent treatment.

the reagent treatment and filtration, as was mentioned earlier. In the case of spring water specimens, a decrease in the mean-weight MM of DOM is noted, along with an increase in the hydrophobicity of organic substances as a result of chlorination, which again indicates the difference in the nature of DOM in the surface water during the spring flood from the nature of DOM in other seasons. No substantial dependence of the mean-weight MM of DOM of the Ufa River in the summer and autumn periods on the water treatment technology was detected on the surface water intake. The maxima of the MMD curves of DOM in the low-molecular fraction of the chromatograms are clear, which testifies to the predominance of particular fractions of DOM in the water (Fig. 1). Thus, chlorination of the water of the surface water source in the summer period is "more predictable" and can result in side products of chlorination with

more or less stable composition. However, random factors, which can significantly influence this process (abundant rainfall, abnormal climatic changes), should be noted. In the winter period, the formation of low-molecular fragments of DOM proceeds less intensely; however, the action of the chlorinating agent is observable by the decrease in the mean-weight MM values of DOM.

The mentioned tendencies are also confirmed by the behavior of the polydispersity of the studied specimens which were exposed to chlorination (Fig. 4). On the whole, an increase in the polydispersity of DOM in the water of surface intake should be noted, which indicates the disintegration of the DOM components upon water chlorination.

The determined tendencies of the change of the characteristics of DOM (decrease in MMD and increase in polydispersity under the action of chlori-
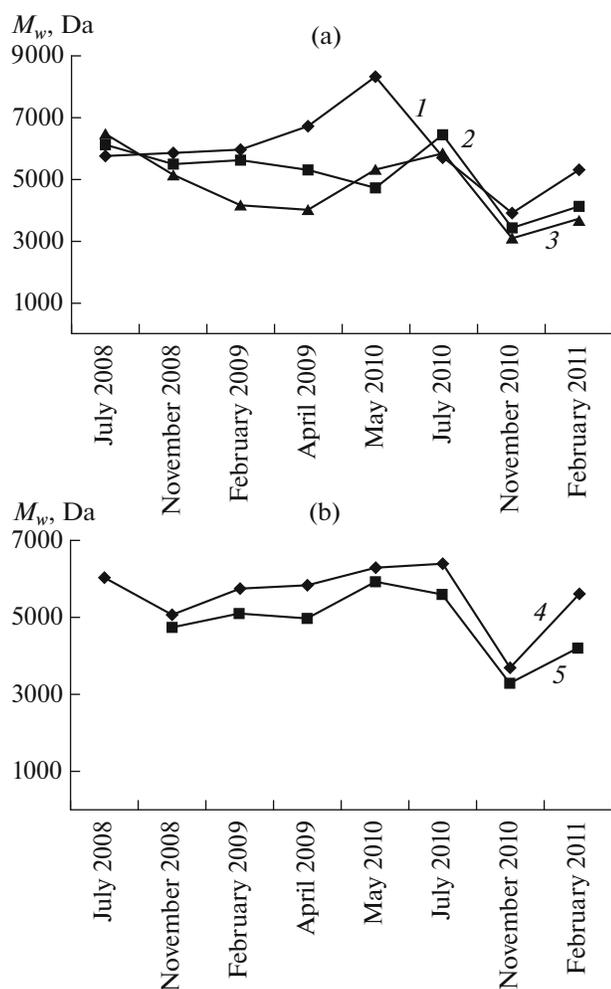
Fig. 3. Effect of the stage of chlorination on the (a) mean-weight molecular mass of DOM of the Ufa River and (b) infiltration water: (*1*) river water of the surface water intake, (*2*) river water of the surface water intake after reagent treatment, (*3*) river water of the surface water intake after reagent treatment and chlorination, (*4*) water of infiltration water intake prior to chlorination, and (*5*) water of infiltration water intake after chlorination.

Fig. 4. Effect of the stage of chlorination on the (a) polydispersity of DOM of the Ufa River and (b) infiltration water: (*1*) river water of the surface water intake, (*2*) river water of the surface water intake after reagent treatment, (*3*) river water of the surface water intake after reagent treatment and chlorination, (*4*) water of infiltration water intake prior to chlorination, and (*5*) water of infiltration water intake after chlorination.

nating agent) were also observed for the water of the infiltration intake during the first period of observations (from July 2008 to April 2009). However, during the period from July 2010 to February 2011, the polydispersity of the chlorinated specimens was lower as compared to the initial ones. In addition, the high polydispersity of the DOM of the initial water should be noted. In this case, intense disintegration of the DOM components as a result of chlorination presumably leads to a decrease in the MMD of DOM, as shown in Fig. 4b.

Thus, during the study of the molecular-mass distribution of the DOM of the water specimens prior to and after water treatment on the water intake of the surface and infiltration types, we observe enrichment
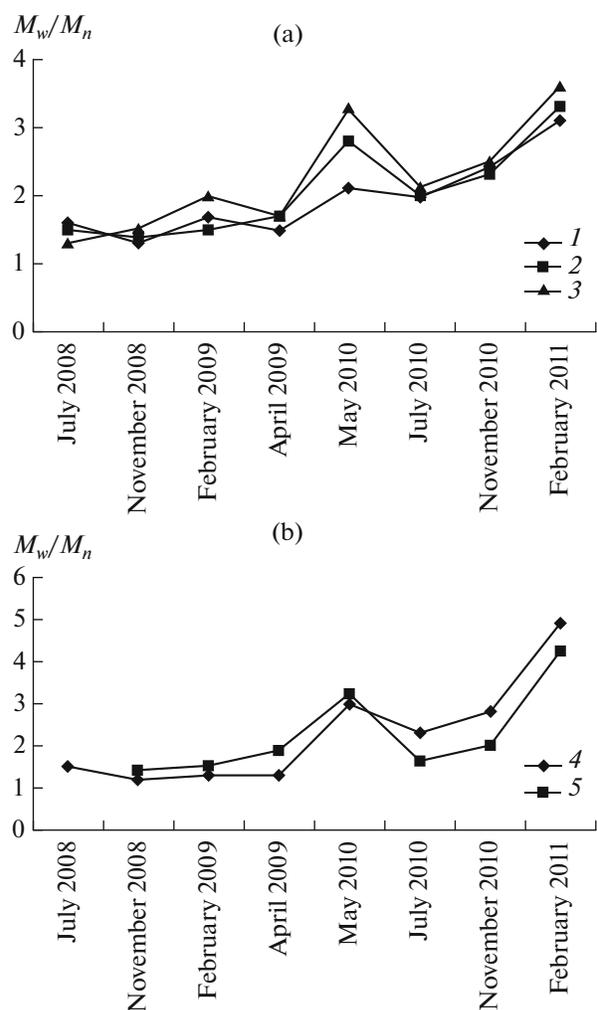
of the DOM of surface water in the spring flood period by high-molecular components of soil humic substances, which differ from the components that are intrinsic to river water in other seasons. The stages of reagent treatment and filtration of the considered water treatment technology at the water intake of the surface type are highly effective in removing high-molecular components of DOM during these periods. The chlorination of water which has been subjected to the stages of reagent treatment and filtration on the surface water intake in the spring period leads to the formation of compounds with lower MM and heterogeneity of the component composition of DOM and the hydrophobicity of the samples increases. The MMD of DOM of the water of the surface intake in

Mean-weight (M_w), mean-number (M_n), and peak (M_p)* molecular masses and polydispersity of the studied DOM samples

Sampling date	Molecular mass, Da			Polydispersity M_w/M_n
	M_w	M_n	M_p	
Infiltrated water				
July 2008	6050	4050	6700	1.5
November 2008	5070	4130	5820	1.2
February 2009	5750	4290	6260	1.3
April 2009	5860	4460	6230	1.3
May 2010	6300	2100	7000	3.0
July 2010	6400	2700	7200	2.3
November 2010	3700	900	3500	2.8
February 2011	5600	1100	5000	4.9
Surface river water				
July 2008	5780	3590	6440	1.6
November 2008	5830	4340	6560	1.3
February 2009	5960	3510	6870	1.7
April 2009	6730	4350	7310	1.5
May 2010	8300	4000	8200	2.1
July 2010	5700	2900	6100	2.0
November 2010	3900	1100	3600	2.4
February 2011	5300	1700	5100	3.1

* MM of DOM at the elution volume corresponding to the maximum of gel chromatograms.

the summer, autumn, and winter periods is characterized by lower molecular mass values, their narrower distribution, and more uniform hydrophilic composition of DOM. During the spring flood, the MMD of DOM of the underground water source does not change, which proves the proper operation of the filter beds of the wells of the infiltration water intake. The highest changes of the MMD of DOM of the water of the underground water source are observed in the autumn period: the polydispersity of the samples and their mean-weight molecular mass decrease, presumably due to the occurrence of natural biotransformation and humification. As a result of the chlorination of the underground water, the mean-weight molecular mass values in the treated water decrease compared to these values in the water before chlorination to an identical extent during the entire calendar year.

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