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Effect of Seasonal Dynamics and Chemical Treatment on the Quality of Dissolved Organic Matter in Water Sources and Potable Water of Ufa

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Abstract—The structural-group composition and seasonal variations of organic matter dissolved in potable water and water sources of Ufa is studied. The efficiency of removal and destruction rate of dissolved organic matter at different technological stages of water treatment is evaluated for a surface water intake.

Keywords: potable water quality, efficiency of water treatment technology, dissolved organic matter, seasonality
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Organic matter of water ecosystems is a complicated mixture of different organic compounds, which may be dissolved or suspended. They form a dynamic system, where the components permanently change their status under the effect of a combination of physical, chemical, and biological factors. The dissolved organic matter (DOM) in water bodies is composed of allochthonous organic substances transported from the water-catchment area and autochthonous substances formed in the water reservoir (Fig. 1). The latter are not dangerous from the sanitary-hygienic point of view contrary to the former, which may contaminate water and exert a toxic effect [1]. Since the substances of DOM participate in continuous processes of biotransformation in the water mass and bottom deposits, it is the most active component of water ecosystem, which responds to variations in the environment [2, 3]. The qualitative and quantitative composition of DOM depends on seasonal factors, including spring and autumn floods. In these periods, river water often receives soil humus, whose composition and structure differ from those of water humus. As a result, the compounds, which give water putrid, musty, and stagnation odors, may enter the river [4, 5]. The adverse effect on the quality of natural water may be also exerted by a sharp rise in DOM content at intensive turbidity of bottom deposits, illegal discharge of waste water into water source, working regime of hydro-electric power stations located upstream, and others [6].

It should be mentioned that DOM is the main precursor of side products formed at water disinfection. It has been proven that fulvic acids in the composition of DOM are difficult to remove by conventional approaches of water treatment and become the precursors of trihalomethanes (THM), halogenacetic acid (HAA), halogenacetonitrile, halogenated ketones, spirits, and bromated derivatives of these compounds [7–14]. These derivatives are the interaction products of nonorganic bromides (Br^-), which are present in natural water or enter it with disinfecting chlorine-containing chemicals (NaCl with admixture of NaBr) that may be transformed into active hypobromite acids (HOB_r) at contact with oxidation substances in water [15]. The amount of disinfection products with low maximum permissible content in potable water may be reduced by the improvement of the modern technology by introduction of ultra- and nano-purification, reverse osmosis, and others. Preliminary purification of water sources from humus substances in DOM (the precursors of the products of chlorine treatment) and the replacement of chlorine-bearing disinfectants may also be used [16–18].

In this connection, the study of the structural-group composition of DOM, determination of the indicators of its quality, and revealing of its seasonal dynamic are necessary for obtaining data on the quality of water supplied for treatment. Investigations of this kind should be used as a base to choose the optimum technology of water treatment for selective water purification from the contaminants, which are typical

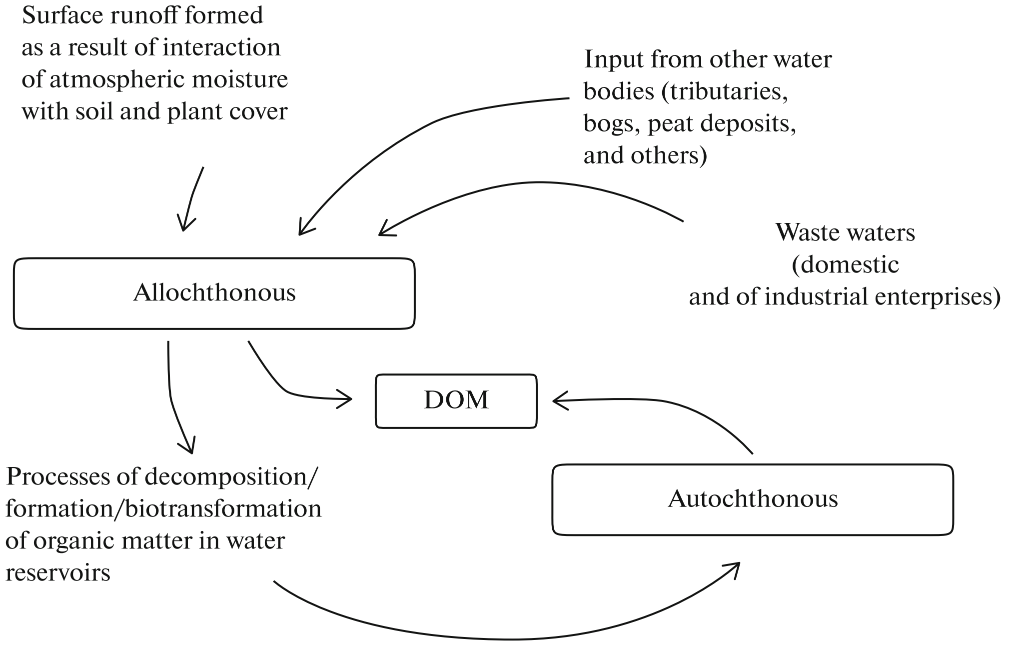

Fig. 1. Main sources of DOM in water bodies.

for the used source, and to predict the quality of the potable water.

The study of the structural-group composition of DOM and the revealing of quantitative indicators for the express-evaluation of its changes was started at the Ufavodokanal enterprise in 2008. Investigations were made for water from the Ufa River and infiltration holes of its banks, as well as for potable water from water intakes of the surface (SWI) and infiltration (IWI) types. The efficiency of the removal and destruction of DOM at the technological stages of water treatment was evaluated with respect to the season of the year: after the coagulation/flocculation, filtration, and chlorine application at SWI and for infiltration water prior and after chlorine application at IWI.

Investigation Method and Substantiation of Criteria of DOM Quality

The approach of NMR spectroscopy (^{13}C NMR) was used for the determination of structural-group DOM composition. The part of aromatic organic compounds in DOM was determined by the method of ultraviolet spectrophotometry. DOM of natural water contains a great variety of aliphatic and aromatic structures replaced by various functional groups: amine ($-NH_2$, $-NH-$, and $>N-$), amide ($-CO-NH_2$), imine ($>C=NH$), alcohol, and phenolic hydroxyls ($-OH$); aldehyde, ketonic, and quinon carbonyls ($>C=O$); carboxyls ($-COOH$); methoxyls ($-O-CH_3$); and the other groups, which can adsorb various kinds of radiation. The first ^{13}C NMR spectra of soil fulvic acids were obtained in 1976 [19]. The data showed that aromatic and aliphatic fragments are present in the carbon skeleton of these compounds and their amounts are comparable. These data were then confirmed by numerous investigations of humic substance (HS) of different origin [19, 20]. DOM represents a significant part of HS. Its quality may be evaluated by the total content of aromatic fragments, which depends on the seasonal dynamic and stage of water treatment. The use of this criterion is substantiated by the data of the quantitative and classification analysis of a large sampling of HS (more than 100 samples). It was shown that the structural parameters, including nitrogen content (data of the elemental analysis), the content of carbohydrate and aromatic fragments (data of ^{13}C NMR spectroscopy), and mean weighted molecular mass (data of gel-penetrating chromatography) were the most informative for the evaluation of the composition and genesis of HS [21].

The distribution pattern of functional groups obtained at the evaluation of the structural-group composition of DOM from water of the Ufa River by the ^{13}C NMR method (by the example of the sample taken in May 2010) is given in Table 1. Data on DOM from two typical samples of river water—low-color (the Istra River in the Moscow suburbs) and high-color (the Suwannee River, Georgia, USA)—are given for comparison.

DOM of the Ufa River is characterized by the highest content of aliphatic fragments (the total carbon in CH_n and CH_nO is 56%) and rather low content of aromatic fragments (the total aromatic carbon (ΣC_{ar}) in C_{ar} and $C_{ar}O$ is 23%). The amount of aromatic carbon of DOM in the Ufa River and the low-color Istra river are similar (ΣC_{ar}= 26%) and vary significantly from DOM of the high-color Suwannee River ΣC_{ar} = 30%). This regularity is reasonable because water of the Ufa River is low-color. It is also characterized by the lowest content of carboxyl groups in DOM among all the investigated samples. The effect of seasonal variations and water temperature on the distribution pattern of the functional groups was not revealed.

Therefore the approach of ^{13}C NMR spectroscopy has shown that about 25% of carbon in DOM of the Ufa River (the main water source of the city of Ufa) is represented by carbon incorporated into aromatic fragments. It should be taken into consideration that the high-substituted aromatic compounds first of all undergo the effect of various oxidants. Therefore their total content may be an indicator of variation in water quality at water treatment. It is necessary to find an express-indicator of the content of aromatic carbon, which may be used instead of it direct determination by the ^{13}C NMR spectroscopy, because this approach to DOM analysis has some disadvantages. The extraction of large amount of low-ash DOM samples from water sources is laborious, and the expenditures for their analysis are great because of long-term accumulation of ^{13}C NMR spectrum and the absence of sufficient amount of NMR spectrometers. The revealed indirect indicator of the content of aromatic carbon may be used for the monitoring of changes in DOM quality at seasonal dynamic and water treatment.

Effective Coefficient of Molar Absorptivity of DOM and its Variations at Seasonal Dynamic and Water Treatment

The approach of determination of specific absorption of UV radiation by DOM is less laborious and more rapid when compared to the ^{13}C NMR spectroscopy. The UV radiation is characterized by wave length 254 nm (specific UV absorption, SUVA) or effective coefficient of molar absorptivity at 254 nm (ε^*_{254}) [22–24]. The approach is based on the capability of aromatic fragments of DOM to absorb light of UV spectrum range. The higher the content of aromatic fragments in organic compound, the greater the absorption in this range. The wave length 254 nm was chosen by historical reasons: the source of UV radiation in the first commercial spectrophotometers was represented by low-pressure mercury lamps with banded spectrum and light emission in the UV range (wave length was 253.7 nm) [25]. In modern spectrophotometers, the source of UV radiation is usually represented by deuterium lamps with continuous spectrum to 360 nm, so it is possible to evaluate the optic density in all the range of UV radiation. As a result, the attempts to change the wave length for the characteristic of the aromatic rate of HS were made. Use of wavelength 280 nm was suggested, as it reflects better the maximal absorption of aromatic fragments [25]. After that, the parameter SUVA at 280 nm was used parallel to SUVA at 254 nm. In this connection, we evaluated the DOM quality of water sources in the city of Ufa by the effective coefficient of molar absorption at 254 and 280 nm. The coefficient was calculated by the equation [26]:

$$\varepsilon^* = A_{254}/C_{\text{org}}\, l;\ \ \varepsilon^* = A_{254}/C_{\text{org}}\, l,$$

where ε* is the effective coefficient of molar adsorption (SUVA); A_{254} and A_{280} are the optic density of the sample at 254 and 280 nm, respectively; C_{org} is mass concentration of dissolved organic carbon, mg/dm^3; and l is the thickness of the optic layer, cm.

Table 1. Structural-group composition of river DOM according to data of ^{13}C NMR spectroscopy

Sampling site	Content of functional groups, %					
	CH_n	CH_nO	C_{ar}	$C_{ar}O$	COO	C=O
Ufa River	39	17	17	6	9	12
Istra River	33	14	21	5	21	7
Suwannee River	18	26	24	6	20	7

Values of C_{org} were determined in the studied samples by the flow method of photochemical oxidation with the use of a San Plus (Scalar) automatic analyzer. The organic carbon in the sample was preliminary destructed by ultraviolet radiation in the presence of oxidizer to carbon dioxide. After the infusion through a gas-permeable membrane, it was absorbed by the buffering solution of phenolphthalein. The optic density of the color of the buffering solution of phenolphthalein was measured at wavelength 550 nm. The water sample was filtered through a membrane with pore diameter 0.45 μm prior to the analysis.

Data on ε* for DOM of the Ufa River (the SWI) for different seasons have shown that it varies from 0.02 (in autumn and winter) to 0.05 dm^3/(mgC cm) (at spring floods). The predominating values are revealed in summer and are assigned to the range 0.03–0.04 dm^3/(mgC cm). These parameters correspond to the data for DOM of river water [27].

We have also determined the content of dissolved organic carbon (DOC) and the effective coefficient of molar adsorption (ε*) for DOM of water of the Ufa River in different seasons and at various technological stages of water treatment. The obtained data have shown that the efficiency of water treatment (the removal of DOM and most adsorptive (aromatic) fractions of DOM) is the highest in the period of spring flood (Fig. 2). The stage of treatment by chemicals and filtration is more effective as compared to the disinfection stage. A drop in DOM content at disinfection is in general smaller than the decrease in the amount of aromatic compounds in DOC at their oxidation destruction by chlorine-containing disinfec-

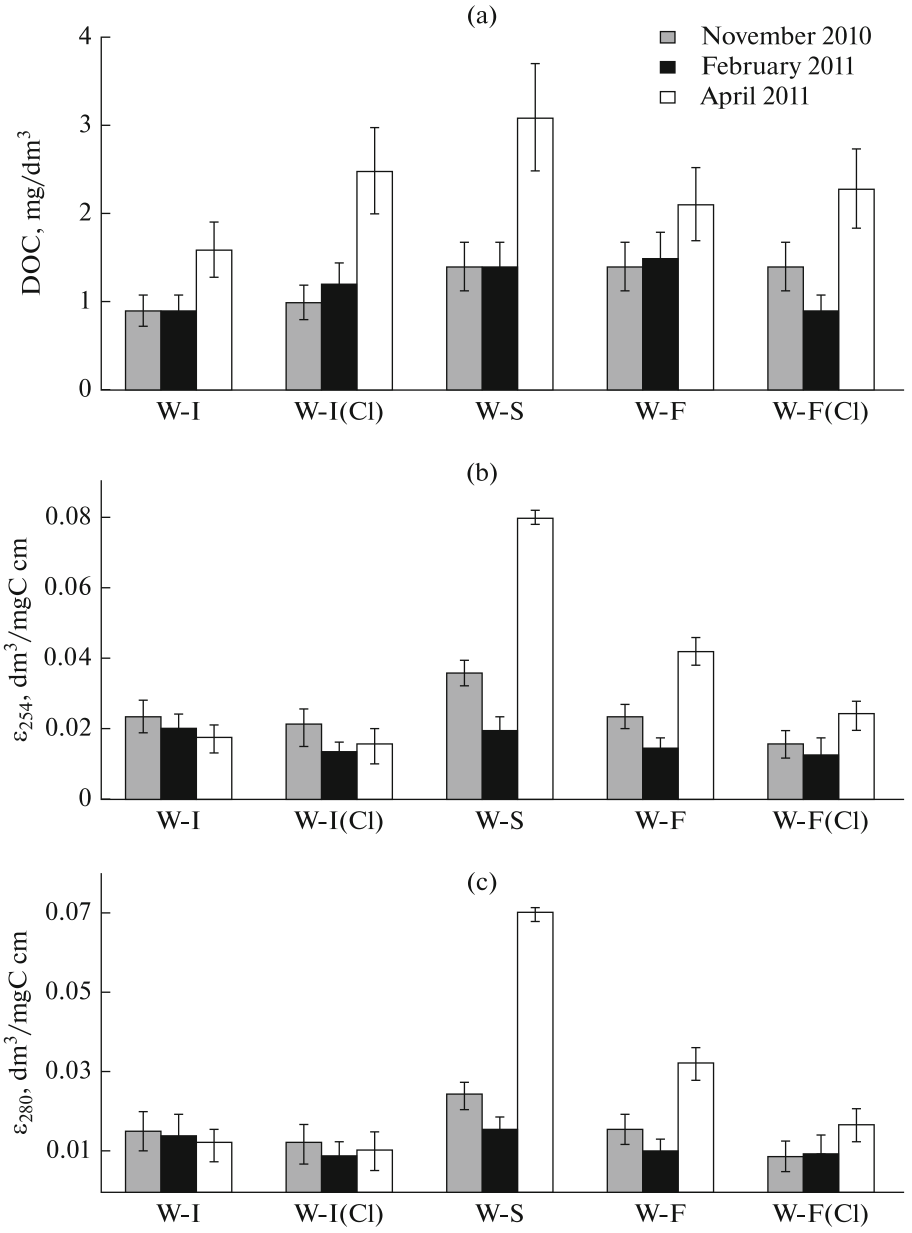

Fig. 2. DOC content (a) and effective coefficient of molar adsorption of the studied water at 254 nm (b) and 280 nm (c). W-I and W-S are infiltration and surface water, respectively, W-F is water after treatment by chemicals, W-Cl is water after chlorine application, W-F(Cl) is water after treatment by chemicals and chlorine application.

tion agent. This conclusion is confirmed by the published data. Since the aromatic compounds in natural DOM are high-substituted, this process is more probable.

In summer, the parts of the stages of the treatment by chemicals, filtration, and chlorine application remain similar, but are less pronounced. In autumn and winter, the efficiency of removal of DOC and aromatic compounds is irregular. It may testify to their heterogenic nature in water at spring floods and the rest periods of year (for example, soil and water humus), as a result of which the efficiency of their removal at the treatment by chemicals and filtration differs, as well as the oxidation destruction by the applied chlorine-containing agent. So, the part of organic aromatic compounds in the potable water from the SWI (evaluated by the effective coefficient of molar adsorption) is variable. These conclusions are confirmed by the long-term monitoring of water quality of the main water intakes of Ufa (Table 2).

It should be mentioned that water treatment at the SWI rather effectively decreases the amount of organic substances even at small initial DOC content in the surface water source (the Ufa River). From 20 to 50%

Table 2. Purification rate of water (%) evaluated by parameters of dissolved organic carbon (DOC) and effective coefficient of molar adsorption (ε*) at the surface and infiltration water intakes (SWI and IWI, respectively) in the periods of 2002–2014 (for DOC) and 2012–2014 (for A_{254}, ε^*_{254})

Parameter	Water purification rate, %		
	SWI	IWI	
	Ufa River → SWI	Ufa River → water from boreholes	Water from boreholes → IWI
DOC, mg/dm^3			
Winter	22	52	6
Spring	45	50	−3
Summer	26	55	−21
Autumn	21	55	14
Mean purification rate, %	29	53	−1
A_{254}			
Winter	35	62	12
Spring	53	67	15
Summer	52	65	13
Autumn	37	62	16
Mean purification rate, %	44	64	14
ε^*_{254}, dm^3/(mgC cm)			
Winter	−5	13	0.3
Spring	41	35	17
Summer	32	23	26
Autumn	28	14	2
Mean purification rate, %	24	21	11

SWI—potable water from surface water intake after technological stages of water treatment (coagulation/flocculation, filtration and chlorine application); IWI—potable water from infiltration water intake after chlorine application.

of DOM are usually removed by the widely spread methods of potable water preparation with the use of coagulation, flocculation, precipitation, and filtration [28]. In our experiment, water treatment at SWI resulted in removal of 21–45% of DOC within the experimental period.

Changes in the content of DOC, optical density, and coefficient of molar adsorption in water of the IWI after chlorine application are similar to those at the SWI (Table 2). The content of DOC drops after natural filtration of river water through the filtering layers of boreholes by 50% on the average, i.e. the removal of high-molecular natural organic compounds from water is satisfactory. The content of aromatic compounds in DOC drops at filtration and disinfection stages similar to the SWI.

We have studied structural-group composition of water of the main water source of the city of Ufa and determined the content of aromatic carbon in DOM in the initial and potable water of different types of water intake, using direct and indirect approaches. We have revealed regular tendencies of seasonal changes in the parameters used for the evaluation of DOM quality (the content of DOC, the optic density in the ultraviolet range of spectrum, and the effective coefficient of molar adsorption). We have evaluated the efficiency of water purification at different stages of water treatment in various seasons of year. Investigations of this kind should be used as a base for the choice of an optimum technology of water preparation for selective purification of contaminants typical for the particular water source.

The applied methods of NMR spectroscopy showed that the content of some aliphatic and aromatic fragments is significant (the latter are high-substituted). It has been revealed that the drop in the content of DOC and aromatic fragments in DOC at water treatment at surface and infiltration water intakes undergoes seasonal variations: the greatest decrease in DOC is seen in the periods of spring floods, and the content of aromatic carbon strongly drops in spring and summer. The former is determined by the stages of the treatment by chemicals and filtration, and the latter is related to these stages and the disinfection stage. Monitoring of the content of DOM and organic aromatic compounds in it (which are the precursors of side products at chlorine application) should be performed at different stages of water treatment. It is necessary for the optimization of the production of high-quality potable water.

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