UV-Vis Spectrometry and Size-Exclusion Chromatography Study of Seasonal Dynamics of Quality of Dissolved Organic Matter

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1. Introduction

The necessity of upgrading natural water treatment techniques which would improve performance of conventional techniques is urged by new achievements in understanding nature of dissolved organic matter (DOM) as well as by development of new analytical instrumentation [1, 2]. The important issue for research is elucidating the feature of DOM which impacts the most efficiency of water treatment technology used for drinking water production. This feature might be connected to the source of natural water, as well as to seasonal conditions. The objective of this research was to study seasonal dynamics of the quality of DOM in surface and infiltration waters using UV-Vis spectrometry and size-exclusion chromatography (SEC).

2. Materials and Methods

Nineteen raw and treated water samples were studied. The samples were taken from the surface water intake system (SWIS): four samples of surface water (SW) were taken from the River Ufa in July and November 2008, and in February and April 2009, four samples of filtered water (FW) were taken after the surface water passed several treatment steps (primary chlorination with low doses of chlorine, chemical treatment and high-rate filters with burnt rock filtering medium), and four samples of drinking water (FWCl) (filtered water undergone secondary chlorination). The water samples from infiltration water supply system (IW) were also included into the experimental data set represented by four samples of non-chlorinated water samples taken in July and November 2008. and in February and April 2009, and three samples of drinking water taken from the infiltration water supply system that passed chlorination in November 2008, and February and April 2009.

UV-Vis spectrometry analysis was conducted using spectrometer Cary-50 (Varian, USA) equipped with quartz cuvettes with optical path length of 1 cm.

SEC system consisted of a solvent pump, a packed column and a UV-detector with variable wavelength as described elsewhere [3]. The UV-absorbance was measured at 254 nm. The SEC column was 15x250 mm packed with Toyopearl HW-55S ("Toso-Haas", Japan). 0,03M phosphate buffer with pH 6,8 was used as a mobile phase at a flow rate of 1 ml/min. The column was calibrated using sodium polystyrenesulfonates (PSS) (Da): 4480, 14000, 20700, 45100, and 80840 (Polymer Standard Service, Mainz, Germany). Blue dextran (2000 kDa) served as a void volume probe, acetone – as a permeation volume probe.

Dissolved organic carbon (DOC) content was measured photometrically with Skalar SAN^{plus} Segmented Flow Analyzer («Skalar», Netherlands). The method is essentially based on decomposition of dissolved organic matter using ultraviolet irradiation and potassium persulphate oxidation to carbon dioxide. Carbon dioxide diffuses through special gas-permeable silicone membrane and is absorbed by phenolphthalein solution. Optical density of the phenolphthalein solution is measured at a wavelength of 550 nm.

3. Results and Discussion

UV-Vis absorbance spectra of the samples studied are given in Figure 1. They are typical for natural DOM. To characterize UV absorptivity of the water samples, specific UV absorbance (SUVA) was calculated at 254 and 280 nm which correspond to wavelengths characteristic of absorbance of aromatic groups. SUVA is defined as the UV absorbance of a water sample at a given wavelength normalized to DOC concentration. The results obtained are given in Table 1.

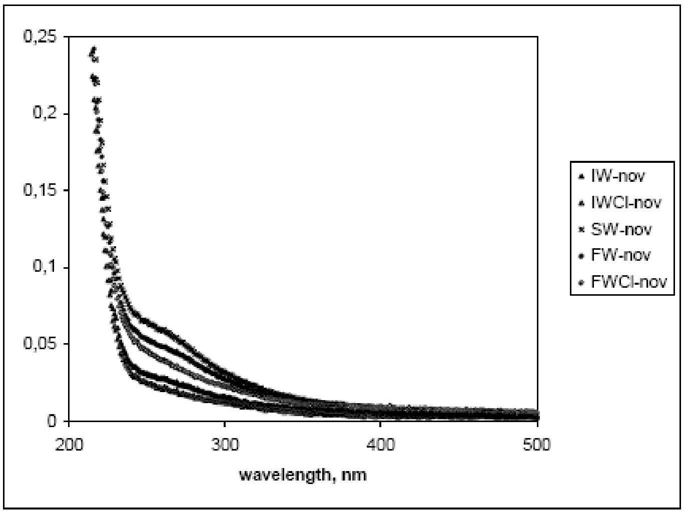

Figure 1: Typical UV-Vis absorbance spectra of the samples studied

As it can be seen from Table 1, the filtered river water sample (FW) has the highest SUVA value at both wavelengths, though, at the same time, its DOC concentration decreased 1,7 times compared to water from surface water supply (the River Ufa) (SW).

Table 1: UV absorbance (A) and SUVA of the autumn samples studied (at 254 and 280 nm)

Sample	Dissolved organic carbon (DOC), mg/L	A_{254}	$SUVA_{254}$, L/(mgC·cm)	A_{280}	$SUVA_{280}$, L/(mgC·cm)
IW-nov	1,7	0,0293	0,0173	0,0215	0,0126
IWCl-nov	1,5	0,0232	0,0154	0,0165	0,0110
SW-nov	4,2	0,0622	0,0148	0,045	0,0107
FW-nov	2,5	0,0511	0,0204	0,038	0,0153
FWCl-nov	2,7	0,0429	0,0159	0,030	0,0111

The results obtained indicate that water treatment steps (filtration of water samples) mostly cause a decrease in aliphatic matter and increase in aromatic one. Secondary chlorination causes partial decomposition of aromatics-rich organics, which is reflected as a decrease in SUVA values for chlorinated water samples (FWCl and IWCl) as compared to less chlorinated (FW) and non-chlorinated (IW) samples. The similarity of DOC values for the SW samples might indicate an increase in low-molecular chloroorganic compounds – chlorination by-products.

Typical SEC chromatograms in K_d scale are given in Figure 2. Molecular weight characteristics calculated from the chromatograms obtained are given in Table 2.

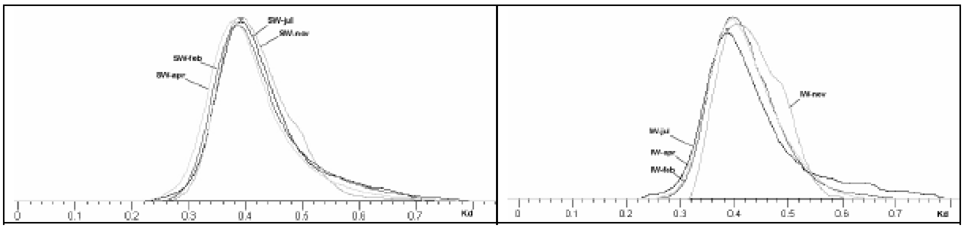

Figure 2: Typical chromatograms of the samples studied: surface (left) and infiltrated water

IW-samples taken in autumn are characterized with the lowest M_w and M_p values, summer samples have the highest ones, and winter and spring values – medium values. Maximum molecular weight (MW) of spring samples is caused by the high rate of humus formation in the spring. Increased microbiologic activity in summer is accompanied by degradation of organic matter and a decrease in average MW of DOM of IW. In autumn and winter, when the rate of humus formation is the lowest. M_w and M_p are the lowest.

Spring samples have maximum M_w and M_p for SW which is caused by floods. Provided that DOM being highly concentrated in river waters is more susceptible to decomposition during water treatment, it is reflected in maximum decrease in M_w and M_p of spring samples after filtration and chlorination. Decreasing M_w and M_n after chlorination in autumn, winter and spring water samples might indicate their enrichment with low-molecular weight chlorination byproducts. This is in sync with the results of UV-Vis study of autumn water samples. For a summer sample (FW-jul) after chlorination (FWCl-jul) an increase in M_w and M_n was observed that might be indicative of more complete decomposition of low-molecular weight components of DOM in summer samples as compared to those of other seasons.

Table 2: Molecular-weight characteristics of the samples studied

Sample	Molecular weights, Da			Polydispersity
	Weight-average (M_w)	Number-average (M_n)	Peak (M_p)	(M_w/M_n)
IW-jul	6050	4050	6700	1,5
IW-nov	5070	4130	5820	1,2
IW-feb	5750	4290	6260	1,3
IW-apr	5860	4460	6230	1,3
IWCl-nov	4740	3500	5260	1,4
IWCl-feb	5110	3430	5950	1,5
IWCl-apr	4990	2590	6110	1,9
SW-jul	5780	3590	6440	1,6
SW-nov	5830	4340	6560	1,3
SW-feb	5960	3510	6870	1,7
SW-apr	6730	4350	7310	1,5
FW-jul	6070	4150	6770	1,5
FW-nov	5480	3970	6280	1,4
FW-feb	5620	3690	6420	1,5
FW-apr	5270	3140	6190	1,7
FWCl-jul	6510	5150	6890	1,3
FWCl-nov	5160	3560	5820	1,5
FWCl-feb	4160	2120	5210	2,0
FWCl-apr	4010	2410	4730	1,7

4. Conclusions

The seasonal dynamics of structural and molecular weight characteristic of dissolved organic matter is determined by seasonal changes in microbiological activity and in the rate of humus formation including seasonal floods for surface water. In accordance with the results of UV-Vis and SEC studies, efficiency of surface water treatment during spring season drops substantially.

References

1. E.M. Perdue, in G.E. Likens (Ed.), *Encyclopedia of Inland Waters,* Academic Press, NY, 2009, p. 806-819.
2. J. Peuravuori and K. Pihlaja, in L.M.L. Nollet (Ed.), *Handbook of Water Analysis,* CRC Press, NY, 2nd edn., 2007, p. 435-447.
3. I.V. Perminova, F.H. Frimmel, A.V. Kudryavtsev, N.A. Kulikova, G. Abbt-Braun, S. Hesse, V.S. Petrosyan, *Environ. Sci. Technol.,* 37 (2003) 2477-2485.