

Spectral analysis of the natural organic matter adsorbed on particles of different size fractions

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Spectral characteristics of light absorption by the total organic matter (TOM), which comes to the water in a dissolved form and is adsorbed by the organic matter on particles of mineral suspension (AOM) are considered. The adsorption of TOM on particles of suspension leads to formation of the suspended particulate organic matter (POM). TOM and POM are organomineral complexes. The content of TOM and AOM was estimated by spectral absorption indices before and after filtration of water samples. Nuclear filters with a pore size from 0.25 to 4.5 μm were used in different combinations. The spectral dependence of the absorption index $a(\lambda)$ of TOM and AOM was approximated by the exponent $a(\lambda) = K \exp(-S\lambda)$, where K is a proportionality factor; S is the slope of the absorption spectrum at a semi-logarithmical scale, nm^{-1} . The total amount of AOM is shown to be dependent on the ratio of TOM to the content of the mineral suspended matter M . The S increases with the increase of the ratio TOM/M , while the number of POM particles and specific absorption index of light decrease. The decrease of filter pores leads to changes in spectral characteristics of light absorption for the filtered water (S of the filtrate increases). This is caused by the preferable absorption of TOM molecules with higher molecular weight, which are characterized by smaller values of S . For POM fractions of 2.87–4.5; 1.76–2.87; 1.09–1.76, and 0.5–1.09 μm , the slope of the spectrum is 0.0072; 0.0089; 0.0119 and 0.0143 nm^{-1} , respectively.

Introduction

The total organic matter (TOM) dissolved in natural water basins is a complex mixture of organic substances in the form of colloid and molecular compounds, which are products of activity of vital organisms and their decomposition after death.

The pool of the total organic matter consists of two different fractions: purely dissolved organic matter (DOM) and particulate organic matter (POM). Fractions that can penetrate through filter pores of 0.45–0.5 μm in diameter are usually attributed to DOM.^{1,2} The POM is subdivided into two fractions, whose particles were formed due to physical and chemical processes from an organic substance coming to water in the dissolved phase: colloidal fractions (COM) and fractions adsorbed on suspension particles (AOM). The last two fractions cannot be separated, but it should be noted that the POM content significantly correlates with the content of mineral suspended matter M . This indicates the fact that either colloidal particles catch small mineral particles or the latter serve as centers of formation of a big portion of colloidal particles. Mineral suspension with the adsorbed organic matter takes part not only in nutrition of zooplankton (filtration organisms) and bacteria, but also in processes of transformation of the matter and energy at boundary zones of such organomineral complexes (or organomineral detritus OMD). Besides, OMD also acts as a buffer component and has a significant effect on functional characteristics of bacterioplankton and phytoplankton.^{3–7}

The problem of the study was to estimate the portion of the dissolved organic matter, which is transformed into POM and to determine spectral characteristics of light absorption by different-size fractions of POM.

Material and methods

We used the data on waters of the Khanka Lake (Primorskii Krai) and its tributaries accomplished for 8 years throughout the lake area (4 seasons in 1992, March in 1993, July in 1995, August–September in 1996, September in 1997, August–September in 1998), as well as 1800 km of Yenisei river (in summer of 1994 and 1997) and 815 km of Angara river (in summer of 1992). The samples were taken with a bathometer (or with a pail for surface samples) from board of a vessel or a boat (at cross sections). The optical characteristics were measured with a DSFG-2 spectrometer,⁸ the control chamber was filled with bidistilled water.

For the Khanka Lake waters, with high content of the mineral suspended matter and high light scattering, the absorption index was measured in a 1 cm chamber placed in the center of the integrating sphere in order to reduce the error connected with light scattering. For Yenisei and Angara, the measurements were performed in a 5 or 10 cm chamber placed right up to the entrance window of the integrating sphere. The absorption, caused by phytoplankton chlorophyll, was subtracted from the absorption index in all cases. The chlorophyll content was estimated from its fluorescence.⁸

The mineral suspended matter was determined from the value of total light scattering at a wavelength of 550 nm, the TOM concentration was determined from spectra of light absorption and fluorescence,⁸ the adsorbed organic matter and its colloid fractions were determined from the difference between the values of light absorption for filtered and non-filtered samples through filters with pores of 0.25; 0.4; 0.5; 1.09; 1.76; 2.5; 2.87; 4.0; and 4.5 μm in diameter in different combinations.

Results and discussion

The spectral behavior of the absorption index of the dissolved organic matter, which is also called yellow substance (YS), can be approximated by an exponential function

$$a(\lambda) = K \exp(-S\lambda),$$

where K is a factor of proportionality; S is the characteristic slope of the spectral absorption curve, nm^{-1} [Ref. 9]. At the semi-logarithmic scale, S determines the slope of the line of spectral distribution of the light absorption index $S = d\ln(a)/d\lambda$. The values of S are connected primarily with TOM composition.

According to different literature sources,^{10,11} S varies from 0.01 to 0.02 nm^{-1} . The experimental dependence $a(\lambda)$ deviates from the exponent in the long-wave range of the spectrum. The authors explain this by the scattering and absorption of light by suspension particles. In Ref. 12, the increase of the absorptive index in the long-wave range, as compared with the exponent, was observed also after filtration through membrane filters with pores of 0.6–0.7 μm in diameter.

In the inland waters under study S varied between 0.008 and 0.0183 nm^{-1} (Table 1).

To reduce the error connected with the light scattering, when calculating S by the formula $S = [\ln a_{\text{meas}}(400) - \ln a_{\text{meas}}(500)]/100$, the value $a_{\text{meas}}(800)$ was subtracted from the measured values $a_{\text{meas}}(\lambda)$. In other words, we assumed that the dissolved organic matter did not absorb the light at 800 nm and $a_{\text{meas}}(800)$ is equal to the scattering index $b(800)$.

The correlation coefficients for the values of $a(\lambda)$, calculated by the exponential function with following calculation of S for different stations and filtrates varied from 0.99 to 0.999. The smallest values of S were detected in the Khanka Lake, characterized by large values of M . At the same time, the connection between S and M has a low correlation coefficient ($r = 0.46$), that points to insignificant variations of light scattering in the $b(\lambda)$ spectrum. Subtracting $b(800)$ from the measured spectrum $a_{\text{meas}}(\lambda)$, we obtained the light absorption indices close to true ones.

In addition, it is seen from Table 1 that the Khanka Lake is characterized by small values of ratio of the total organic matter to the mineral suspended matter (TOM/ M) and that S variability is connected just with this parameter (Fig. 1).

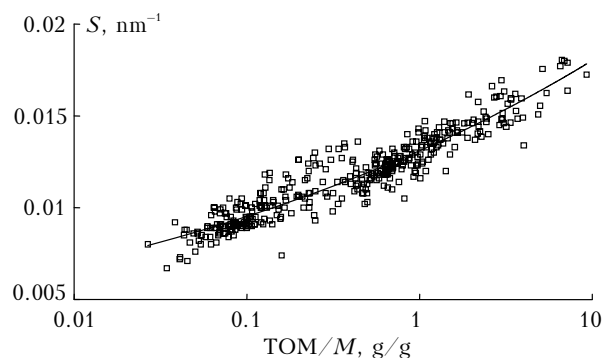


Fig. 1. The slope of the spectral curve of light absorption as a function of the ratio TOM/ M .

For the united array of data on all studied waters the connection between S and TOM/ M is well approximated by the power function $S = 0.013(\text{TOM}/M)^{0.14}$ with the correlation coefficient $r = 0.93$. The specific light absorption index (a_{sp}) is also connected with TOM/ M : $a_{\text{sp}} = 0.45(\text{TOM}/M)^{-0.52}$ ($r = 0.92$). As TOM/ M increases, the share of the adsorbed organic matter AOM decreases and POM also decreases.

Filtration of water samples removes POM particles and changes both absolute values of the light absorption index and spectral characteristics of absorption (Figure 2, Table 2).

Table 1. Variability ranges (average) of the mineral suspended matter content, slopes of the light absorption spectrum, content of the total organic matter, specific light absorption index $a_{\text{sp}}(400)$, ratio TOM/ M , percentage of POM fractions in the studied waters

Waters	M , mg/l	S , nm^{-1}	TOM, mg/l	$a_{\text{sp}}(400)$, m^2/g	TOM/ M , g/g	POM, %	Number of samples
Khanka	2.3–130 (42.0)	0.0080–0.0168 (0.0105)	1.2–21.6 (6.2)	0.14–4.59 (1.35)	0.03–1.04 (0.21)	27–84 (78)	220
Yenisei	1.4–55.0 (3.7)	0.0105–0.0149 (0.0130)	1.4–21.8 (3.6)	0.20–1.08 (0.44)	0.40–4.02 (1.05)	8–31 (23)	100
Angara	0.5–28.5 (6.2)	0.0117–0.0183 (0.0153)	4.6–65.2 (17.4)	0.11–1.10 (0.36)	0.44–9.20 (3.2)	7–51 (20)	54

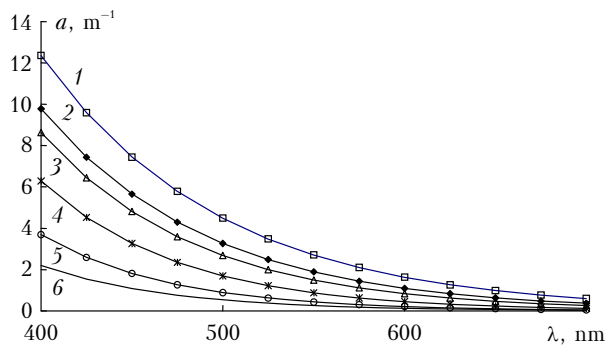


Fig. 2. Spectral dependences of the index of light absorption by water of the Khanka Lake and filtrates of the water: a non-filtered sample (1); filtrates through filters with pore diameters of 4.5, 2.87, 1.76, 1.09, and 0.5 μm (2–6).

Table 2. Some parameters of the Khanka Lake water and its filtrates

Sample, filtrate	S , nm^{-1}	$a(400)$, m^{-1}	$\frac{a_s(400)}{a_s(400)}$	K , m^{-1}
Non-filtered sample	0.0101	12.36	1	709
Filtrate, μm :				
4.5	0.0110	9.78	0.79	786
2.87	0.0117	8.62	0.70	922
1.76	0.0131	6.20	0.51	1184
1.09	0.0142	3.69	0.30	1093
0.5	0.0143	2.20	0.18	700

For station at the Khanka Lake, M was 52 mg/l , TOM was 5.1 mg/l , $a_{\text{sp}}(400)$ was 2.4 m^2/g , TOM/ M was 0.10 g/g .

Since TOM/ M establishes the portion of the dissolved organic matter, which passes into POM due to absorption, it can be supposed that the change of spectral characteristics of light absorption of S and a_{sp} is connected with preferential adsorption of TOM having smaller S and larger specific indices of light absorption. It is well-known that preferential absorption is observed for compounds of the dissolved organic matter with higher molecular weight.^{13,14} Therefore, larger POM molecules have smaller S and higher specific indices of light absorption.

Small values of S are characteristic of humic substances (0.0104–0.0107 nm^{-1}), and large molecules in humic substances seem to have even smaller slopes (to 0.007 nm^{-1}).

Besides, an increase of S can be connected with intermolecular interactions in boundary zones (layers, which are neighboring to the boundary surface of mineral particles, in which the main mass of AOM is concentrated). These interactions lead to broadening of absorption bands. This process can also lead to some increase of the slope for AOM (see Table 2). The appearance of intermolecular interactions is quite possible because the spatial density of adsorbed AOM molecules varies from 150 to 500 kg/m^3 , i.e., it can reach a half of the density of water microorganisms. The thicknesses of the adsorbed layers in the studied waters varied from 0.2 to 0.5 μm depending on the AOM mass. In fact, the mineral suspension increases the concentration of the organic matter, which comes into the water in a dissolved form, by tens and hundreds of thousands times.

A change in the slope of the spectral absorption curve with a decrease of filter pores is also characteristic for the differences between light absorption by a non-filtered sample and different filtrates (Table 3).

In addition, it should be noted that AOM slopes for fractions of larger particles are smaller as compared to small particles. The coefficient of proportionality K in the exponential function, which is used in the approximation, also increases with the decrease of filter pores (Table 3). The part of POB, which is adsorbed by a certain size fraction of mineral particles, can be estimated from the ratio of light absorption indices for filtrates $a_f(400)$ and non-filtered samples $a_s(400)$ (Tables 2–5).

For waters of Yenisei ($M = 3 \text{ mg}/\text{l}$, TOM = 2.6 mg/l , $a_{\text{sp}}(400) = 0.74 \text{ m}^2/\text{g}$, TOM/ $M = 0.91 \text{ g}/\text{g}$) magnitudes of S are significantly larger than for the Khanka Lake, and the slope variations with filtration are less pronounced (Table 4). The portion of POM for this station is 18%. The absolute values of the absorptive index decrease insignificantly with the decrease of filter pores.

Table 3. Differences of characteristics between non-filtered water of the Khanka Lake and its filtrates and differences of characteristics between the sample and filtrates

Sample minus filtrate, difference between neighboring filtrates	S , nm^{-1}	$a(400)$, m^{-1}	$\frac{a_f(400)}{a_s(400)}$	K , m^{-1}
Sample minus filtrate, μm :				
4.5	0.0079	2.58	0.21	60
2.87	0.0077	3.74	0.30	80
1.76	0.0081	6.07	0.49	157
1.09	0.0091	8.67	0.70	334
0.5	0.0097	10.15	0.82	500
Difference, μm :				
4.5–2.87	0.0072	1.16	0.09	21
2.87–1.76	0.0089	2.34	0.19	83
1.76–1.09	0.0119	2.60	0.21	298
1.09–0.5	0.0143	1.49	0.12	445

Table 4. Some parameters of water of Yenisei, its filtrates, and differences of characteristics between the sample and filtrates

Sample, filtrate	S , nm^{-1}	$a(400)$, m^{-1}	$\frac{a_i(400)}{a_s(400)}$	K , m^{-1}
Non-filtered sample	0.0143	1.90	1	579
Filtrate, μm :				
4	0.0144	1.74	0.92	540
0,4	0.0146	1.63	0.86	561
0,25	0.0150	1.56	0.82	627
Sample minus filtrate, μm :				
4.0	0.0138	0.16	0.08	39
0.4	0.0126	0.26	0.14	41
0.25	0.0116	0.34	0.18	35

Table 5. Some parameters of water of the river Manzi (a tributary of the river Angara), its filtrates, and differences of characteristics between the sample and filtrates

Sample, filtrate	S , nm^{-1}	$a(400)$, m^{-1}	$\frac{a_i(400)}{a_s(400)}$	K , m^{-1}
Non-filtered sample	0.0165	8.64	1	6399
Filtrate, μm :				
4	0.0168	8,32	0.96	7018
2.5	0.0167	8.22	0.95	6470
0.4	0.0171	7.63	0.88	7056
Sample minus filtrate, μm :				
4.0	0.0105	0.32	0.04	22
2.5	0.0140	0.42	0.05	114
0.4	0.0132	1.01	0.12	197

For waters of Manzi (a tributary of the river Angara) ($M = 6.9 \text{ mg/l}$, $\text{TOM} = 64.0 \text{ mg/l}$, $a_{\text{sp}}(400) = 0.14 \text{ m}^2/\text{g}$, $\text{TOM}/M = 9.2 \text{ g/g}$) magnitudes of S are larger than for the Khanka Lake and Yenisei, and variations of water parameters after filtration are even less pronounced than for waters of Yenisei (Table 5). The portion of POM for this station is 12%, although the content of the mineral suspension is higher almost by 3 times. Absolute values of the absorption index decrease insignificantly, when filter's pores decrease.

Conclusion

Spectral characteristics of light absorption through filters with different pore diameters and high

correlation coefficients can be approximated by exponential functions, which are typical for non-filtered samples. This points to the fact that POM, removed with filtration, are formed from the dissolved organic matter both due to adsorption on mineral particles and, apparently, due to formation of large colloidal complexes. The decrease of filter pores causes an increase of S of spectral curves of light absorption, a decrease of specific absorption indices, and a growth of the ratio TOM/M . These variations are connected with preferential absorption of TOM molecules with larger molecular weight and having smaller values of S and higher values of the specific light absorption index. At the same time, since the spatial density of AOM in boundary layers is high, such variations of TOM parameters can be connected with intermolecular interactions in layers of the adsorbed organic matter.

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