Spectral properties of CDOM in a stratified reservoir with redox potential varying with depth

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Introduction

It is well known that natural water always contains a certain amount of **chromophoric dissolved organic matter (CDOM),** which plays an important role in natural biogeochemical processes. From the point of view of studying composition and distribution of CDOM, the meromictic water bodies are of particular interest. The ***meromictic water reservoirs*** are those *with stable vertical stratification*, which occurs due to the difference in the density of water layers. The examples of such reservoirs are coastal reservoirs isolated from the White Sea, which density stratification is the result of overlapping seawater with fresh runoff. Natural CDOM effectively absorbs the UV light and emit fluorescence, therefore absorption and fluorescence spectroscopy are widely utilized for its study. The aim of our work is to study the spectral characteristics of CDOM in coastal meromictic lake of natural origin in the Kandalaksha Bay of the White Sea, lake Bol'shie Khruslomeny (Oleniy Island, vicinity of Lesozavodsky village, Kandalaksha Bay, Murmansk Region, Russia).

Studied objects and Method

Samples of natural water were taken in the lake Bol'shie Khruslomeny. The hydrochemical parameters measured for each studied water layer are shown in Table 1. For CDOM analysis water samples were filtered through nylon filters with a pore diameter of 0.22 μm. Absorption spectra of natural water CDOM were recorded relative to distilled water on a Solar PB2201 spectrophotometer in the wavelength range 200 to 700 nm with a scanning step of 1 nm. Fluorescence spectra were measured with Solar CM2203 luminescence spectrometer at excitation wavelength λ_{ex} varying from 250 to 500 nm.

depth, m	t, °C	S, ‰	Eh
0	15.3	5.9	120
1	15.3	5.9	92
2	15.3	8	90
3	11.8	13.1	97
3.5	10.8	13.7	96
3.7	10.2	14.5	91
3.8	10	14.8	60
3.9	9.7	15.1	40
4	9.3	15.4	-123
4.1	9.1	15.6	-247
4.2	9.3	15.6	-269
4.3	8.9	16.2	-280
4.5	8.6	16.8	-296
5	8.7	18	-303
7	8.3	20.9	-326
10	9	23.2	-323
13.5	8.7	23.7	-331

Table 1. The hydrochemical parameters for different depth of water layers

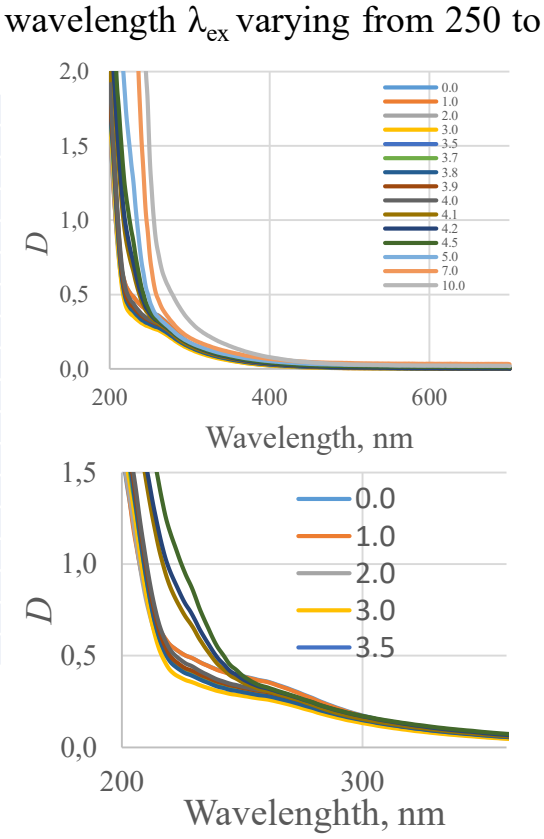

Fig 1. Absorption spectra for lake Bol'shie Khruslomeny and a section of this spectrum on an enlarged scale.

Conclusions

We analyzed the CDOM spectral characteristics for lake Bol'shie Khruslomeny (Kandalaksha Bay of the White Sea). The difference in optical density and fluorescence quantum yield at various depths and their relationship with hydrochemical parameters was noticed. The study of CDOM in of coastal water bodies at different stages of isolation from the sea is important for understanding their evolution and for developing methods for environmental monitoring of aquatic ecosystems.

Results

CDOM absorption spectra is shown in Fig. 1. The absorbance decrease along with rising wavelength, with a small "shoulder" around 260-270 nm due to the presence of phenolic groups or aromatic amino acids. The example of fluorescence spectra is shown in Fig. 2 (for depth=4 m). When excited at 270 nm or shorter wavelengths, the CDOM fluorescence spectrum shows two overlapping bands: a "protein-like" band with a maximum at 300-350 nm and a humic type emission band with a maximum at 450-500 nm. An informative optical indicator for natural CDOM is the fluorescence quantum yield, Which is calculated using absorbance and fluorescence spectra by reference solutions method. Its dependences on the λ_{ex} in different water bodies have a similar character (maxima are observed at 340 and 370–390 nm), but the absolute values of the fluorescence quantum yield vary significantly in water layers taken at different horizons, which may indicate the variability in the CDOM structural characteristics. The lifetimes of the short and long-lived fluorescence components of the CDOM are calculated from the kinetics of fluorescence attenuation (under laser pulse excitation).

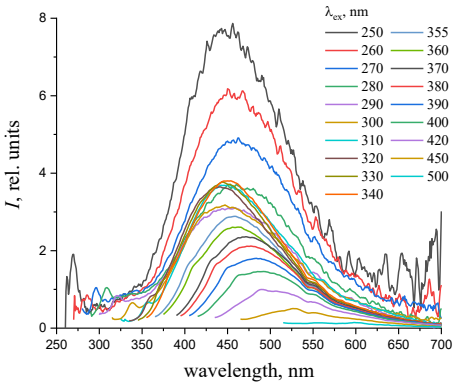

Fig. 3. Fluorescence spectra of CDOM excited with different wavelengths

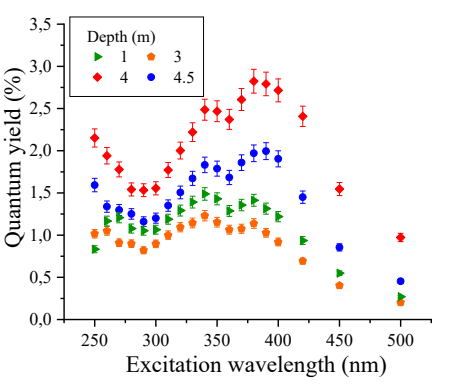

Fig. 4. Fluorescence quantum yield for CDOM

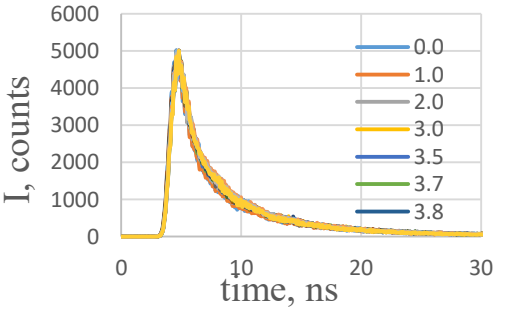

Fig. The kinetics of ROV fluorescence attenuation

depth, m	t1, ns	t2, ns	depth, m	t1, ns	t2, ns
0	1.991	9.385	4	2.181	9.259
1	2.054	9.617	4.1	2.176	9.138
2	2.172	9.334	4.2	2.22	9.256
3	2.181	9.259	4.5	2.259	9.276
3.5	2.171	9.256	5	2.307	9.347
3.7	2.154	9.098	7	2.327	9.237
3.8	2.193	9.156	10	2.303	9.052
3.9	2.177	9.137	13.5	2.25	8.94

Table 2. Lifetimes of two components of fluorescence kinetics.