FLUORESCENT DIAGNOSTICS OF DISSOLVED ORGANIC MATTER: INFLUENCE OF UV RADIATION ON THE FLUORESCENCE SPECTRA

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This paper summarizes experimental results of a study of natural dissolved organic matter (DOM) fluorescence spectra excited with a UV radiation from a cw lamp source and a pulsed laser. The spectral changes caused by UV light depend on the dose of radiation and on its spectrum as well as on a water sample composition. The difference in UV lamp and laser source action on DOM is under consideration in this paper. A model of photochemical processes in DOM is proposed.

INTRODUCTION

The natural dissolved organic matter (DOM) is one of the most important component of water ecological systems. DOM contains the major part of organic carbon on the Earth and plays a key role in its circulation. DOM fluorescence is used as a natural indicator in the investigations into the hydrological processes.

The interest in effect of solar and laser UV radiation on DOM properties including its spectra is related to at least two circumstances: the ecological problem of the ozone layer degradation and the remote sensing with UV lasers exciting DOM fluorescence.

This paper summarizes experimental results on DOM fluorescence spectra under cw UV lamp and pulse UV laser irradiation.[1–3] New facts not considered in earlier publications are discussed as well. Besides, a model of the photochemical processes occurring in DOM under UV irradiation is proposed.

The fluorescence spectra of the samples after UV irradiation by a cw lamp were monitored with a "Jobin Yvon 3CS" device whereas the absorption spectra were recorded with a "Specord M 40" spectrofluorimeter.

The laser source provided simultaneously irradiation of a water sample and excitation of fluorescence. The laser fluorimeter was described earlier in Ref.1. The water circulated through a quartz cell of 1–cm diameter using a perystaltic pump. The number of laser pulses N that irradiate a certain volume of water was varied by varying the laser pulse repetition rate (from 1 to 1000 Hz) and circulation rate (up to 1 l/s).

The degree of fluorescence spectra transformation depended both on radiation dose and its spectrum and on the composition of a sample under both lamp and laser radiation.

INFLUENCE OF A CW LAMP IRRADIATION ON DOM FLUORESCENCE SPECTRA

Influence of UV radiation on DOM spectrum was early considered in Refs. 4 and 5. Authors of these papers studied the effect of UV radiation from the sun and Xe lamp on the fluorescence and absorption spectra of DOM in sea water. After continuous irradiation of sea water within the spectral range from 290 to 340 nm during a few hours, the intensity of DOM fluorescence decreased, its optical depth droped in the 290–340 nm spectral range and increased in the 340–390 nm spectral range. The opposite result was observed when irradiating within 340–390 nm spectral range. Both the fluorescence intensity and the optical depth in 290–340 nm spectral range became 20–30% higher. Fluorescence spectra were studied using excitation with radiation at $\lambda \sim 337$ nm from a nitrogen laser. It was assumed that change in the spectral properties was caused by two processes: DOM photodestruction and photochrome changes of a part of DOM.[4, 5]

A mercury lamp of PRK–7 type was used in our experiments. The water samples were irradiated by UV lamp for a long time (up to three hours) and after that the DOM spectra were recorded.

DOM samples of natural origin extracted from the Baltic Sea water were uniformly irradiated in a 1–cm diameter quartz cell. Different spectral ranges were separated by optical glass filters. The total spectral range of mercury lamp was divided into A, B, C, and V parts corresponding to transmission bands of filter combinations. The spectral range C relates to the wavelengths shorter than 300 nm; B relates to 300–325 nm wavelengths, A corresponds to 325–390 nm wavelengths, and V denotes the visible region. It is impossible to separate the ranges B and C by filters, hence the influence of illumination from $A + B + C$, $A + B$, and A ranges was examined. Differences in results obtained under irradiation with light of different spectral composition showed effects of B and C ranges on DOM spectral properties.

Analysis of the experimental findings allowed the following conclusions to be drawn.

1. Irradiation of samples by radiation whose spectrum covers the whole UV range always leads to the change in DOM fluorescence intensity and, in certain cases, to variations of the spectrum shape and shift of fluorescence maximum (Fig. 1). The DOM spectral parameters did not recover after UV irradiation in the course of three–days observation.

The effect of UV light is to be taken into account when monitoring DOM in natural water.

2. The output energy of PRK–7 lamp is distributed approximately uniformly over the A, B, and C ranges: 18, 18, and 20%, respectively. However, the strongest effect on DOM spectra was observed for rigid UV irradiation at wavelength <325 nm (B and C regions). Under irradiation with light from C range the 15–25 nm red shift of the peak of fluorescence excitation spectrum was observed with the value of shift depending on the duration of irradiation. The wavelength of fluorescence maximum was found to be shorter after irradiation for a long time. The influence of radiation from B range is similar but weaker. Exposure to radiation from A range decreases the fluorescence intensity but no

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variations in shapes of excitation and fluorescence spectra are observed. Visible radiation did not effect the DOM spectral parameters. These data are in agreement with our findings and data from Refs. 4, 5.

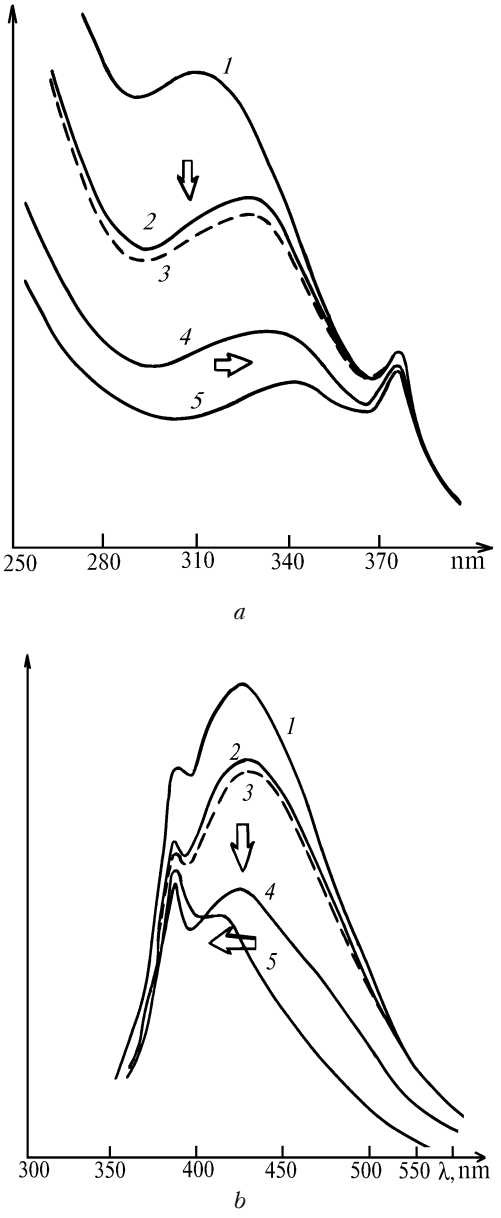

FIG. 1. Influence of mercury lamp irradiation on excitation (a) and fluorescence spectra (b) of DOM: initial sample before irradiation (1); after 20 *minutes of irradiation (2); in three days of "recovery" (3); total irradiation time of* 105 min (*4*); *total irradiation time of* 165 min (*5*).

3. We failed to reveal any regularities in absorption and fluorescence spectra behavior. This allowed us to assume that the fraction of DOM responsible for luminescence is negligible and it contributes to the whole absorption band of DOM only insignificantly.

VARIATIONS OF FLUORESCENCE BAND OF DOM IN WATER UNDER UV LASER IRRADIATION

The influence of pulsed radiation on DOM fluorescence spectra was studied with a nitrogen laser which is widely used for laser diagnostic of DOM in technological and natural waters.[1, 3]

Different water samples were examined: distilled water with small amount of DOM and water solutions of DOM from the Baltic Sea, the DOM concentration being varied by dilution with distillate.

The experimental results obtained are as follows:

1. The DOM fluorescence intensity decreases and the red shift of maximum in fluorescence spectrum is observed under UV laser irradiation. The higher is the total dose of radiation, the more significant are spectral variations. By the total dose W we mean the value $W = N \cdot E$, where N is the number of laser pulses irradiating a sample, $E = 0.16$ mJ is the pulse energy.

2. At the highest rate of water circulation and a pulse repetition rate of 2.5 Hz every laser pulse irradiated a new portion of the sample ($N = 1$). Let us call the sample with $N = 1$ as "unexcited" sample.

3. For $N = 1 \ldots 30$, the shape of DOM fluorescence spectrum as well as the position of spectral maximum changes but slightly. Fluorescence intensity drops not more than 10% in comparison with the "unexcited" sample (Fig. 2).

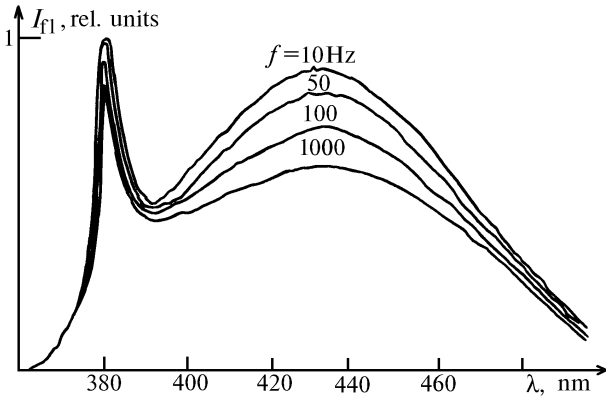

FIG. 2. Fluorescence spectra of DOM in water recorded at different laser pulse repetition rates f.

4. Further increase in N leads to the red shift of fluorescence band and from 10% to 50% drop in fluorescence intensity, the "unexcited" sample being a reference one (Fig. 3).

5. The variations of DOM fluorescence spectra depend on both UV dose and composition of a sample. Distillate demonstrated significantly weaker changes in DOM fluorescence spectrum shape than the natural water did. The difference in the fluorescence spectra is well pronounced when the spectrum of the "unexcited" sample is subtracted from the spectrum of a sample irradiated by N pulses. The peak of difference spectrum is shifted to shorter wavelengths with respect to the initial fluorescence spectrum (the peaks of spectra for distillate and natural DOM solution coincide).

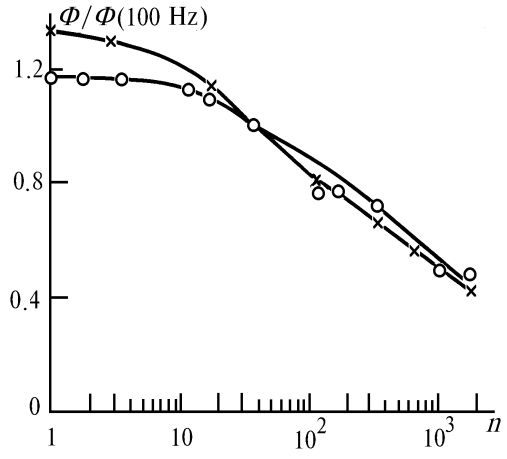

FIG. 3. The fluorescence parameter Φ normalized to its value at f = 100 Hz as a function of the number of laser pulses N irradiating one and the same sample portion: distilled water (crosses) and natural DOM (open circles).

6. Relaxation mechanism of DOM luminescent properties was examined in a separate run without water circulation. To keep the total irradiation dose constant in all experiments, the sample was exposed to laser pulses during 5 minutes at a pulse repetition rate of 1 kHz (the total number of laser pulses was $3 \cdot 10^5$). After this procedure the fluorescence intensity was halved. Then the fluorescence spectra at different pulse repetition rates from 10 Hz to 1 kHz were monitored. The spectra were recorded in the course of 5000–pulse series. The fluorescence intensity was found to be different at different pulse repetition rates. It was 69% of its "unexcited" value at 10 Hz and 57, 52, and 50%, respectively, at 100, 500, and 1000 Hz. Hence, it is reasonable to assume that there are some relaxation mechanisms with characteristic time from 1 ms to 0.1 s (corresponding to pulse repetition rates of 1 kHz and 10 Hz).

7. Decrease of the UV irradiation dose by glass filters (with known transmittance being changed from 100% to 0.1%) results in an increase in the fluorescence parameter Φ. This fact is caused by the fluorescence saturation as was considered in detail in Ref. 3. No transformation of the shape of fluorescence band was observed in this case.

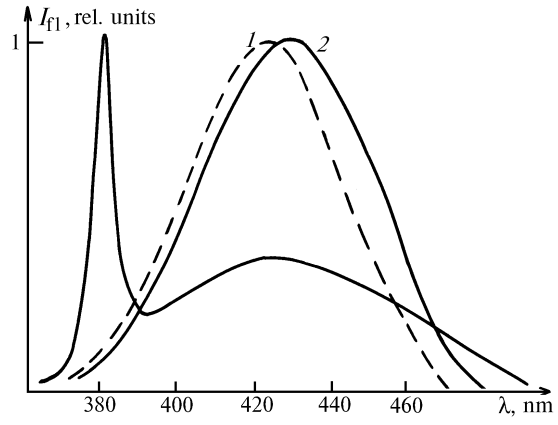

FIG. 4. Difference spectra of DOM fluorescence for different types of water: distilled water (1), and natural DOM sample (2). DOM fluorescence spectrum in distillate is presented for a comparison. All spectral curves are normalized to their maxima.

The effect of UV laser irradiation is to be taken into account in DOM concentration measurements using luminescence excited by a laser radiation. To reduce the influence of photochemical effects, the water sample should be circulated through the fluorimeter cell. The circulation rate depends on the laser pulse repetition rate.

DISCUSSION

The main differences between the influence of irradiation from a lamp and laser on DOM fluorescence band with 420–nm peak are as follows:

Processes reversibility. The lamp influence is irreversible. Laser pulses lead to both irreversible changes and reversible ones with the relaxation time from 1 ms to 0.1 s.

Spectral shape variations. The strongest variations are caused by exposure to light from a lamp with the wavelengths shorter than 325 nm. Decrease in the fluorescence intensity, changes in the shape of excitation spectra, and the blue shift of fluorescence maximum are observed in this case. Laser irradiation results in red shift of the fluorescence peak accompanied by a decrease in its height. This influence depends on radiation dose (pulse energy and exposure time) as well as on laser pulse repetition rate.

Summarizing the above mentioned experimental data we suggest the following model of DOM transformation under UV irradiation. Our model is based also on the data of additional spectral study reported in Ref.3.

1. DOM is composed of a great number of organic molecules. Their molecular weights are different. Only a small portion of these molecules are luminescent. This fluorophor (or luminescent centers) type causes the peak at 310 nm in the fluorescence excitation spectrum. The broad structureless band with a steady increase in intensity results from organic sensitizers that transfer the photoexcitation energy to fluorophors. The major part of DOM does not apparently contribute to the process of photoexcitation transport.

2. Under continuous irradiation from a lamp, destruction of a portion of DOM occurs. The molecules, which have the absorption band falling into the spectrum of exciting radiation, are destructed to the highest degree. This results in transformation of excitation spectrum and reduces the fluorescence intensity. Under long exposure (about 3 hours in our experiments) a part of fluorophors is destructed also, and changes in the shape of fluorescence spectrum as well as blue shift of its peak are observed. All these changes are irreversible.

3. A few processes take place simultaneously in DOM under laser irradiation. A part of sensitizers and a part of fluorophors are apparently destructed irreversibly similar to the action of a cw lamp. Other part of fluorescent centers undergoes photochemical transformation with the relaxation time of the order of 0.01 s. This time is comparable with the time period between laser pulses.

At low pulse repetition rate (< 50 Hz) the properties of the latter part of molecules recover and changes in DOM fluorescence as compared to the "unexcited" sample are insignificant, being caused only by the total irradiation dose.

If the pulse repetition rate exceeds 50 Hz, substantial part of flourophors absorbing photons has no time to relax. Hence, the fluorescence intensity drops. The higher is the pulse repetition rate, the lower is the fluorescence intensity (see Figs. 2 and 3).

In our opinion, most likely the reason of the shift of DOM fluorescence peak is photochemical reaction producing new fluorescent centers. Proton phototransportation could be a possible mechanism of this reaction.

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