

New Methodological Aspects of the Old Problem. Laser Diagnostics of Dissolved Organic Matter

S.V.Patsayeva

Physics Department, Moscow State University, Moscow 119899 Russia

ABSTRACT

Significant problems of environmental control require remote methods for dissolved organic matter (DOM) diagnostics in natural water to be elaborated. Currently, the fluorescent technique using water Raman scattering for fluorescence standardization is widely applied for DOM concentration measurement in water. This work summarizes the results of a few years of study of fluorescence of dissolved organic matter naturally occurring in water. Experimental studies of the influence of temperature and UV irradiation on DOM spectra have been carried out in this work. The features of fluorescence spectra of DOM under laser UV excitation (the effect of fluorescence saturation and photo-chemical destructions) have been observed. Recommendations on laser remote sensing of organic pollutions in water are given.

1. INTRODUCTION

Dissolved organic matter (DOM, Gelbstoff) is a significant part of natural water systems and determines their ecological state. That is why the elaboration of precise and sensitive methods to control the presence of DOM and its total quantity in water is now an actual problem. One such method is the fluorescent analysis based on the hypothesis of linear regression between fluorescent intensity and DOM concentration. However, a more careful investigation of DOM spectral characteristics has led us to conclude that the relation between fluorescence intensity and DOM content is very complex. There are many factors which break this correlation:

- 1) random variations of the excitation source intensity and other experimental conditions;
- 2) water column attenuation;
- 3) water temperature;
- 4) changes of the pH value in water;
- 5) presence of metal ions in water;
- 6) ultraviolet (UV) radiation from the sun and excitation radiation of laser or lamp sources.

The first two factors can be removed using the method of normalization of fluorescent signal by Raman scattering

signal of water with parallel detection of these signals. Normalized fluorescent intensity does not depend on fluctuations of the radiation source power or experimental conditions and is used as a parameter correlating with the concentration of organic pollutions, DOM in our case. It is important to emphasize that the use of the Raman scattering signal as an internal standard is the basic principle for remote sensing, when some experimental conditions cannot be controlled (Klyshko and Fadeev, 1978; Bristow, 1981).

The effect of pH on DOM fluorescence was studied by Smart (1976). The temperature effect up to 35 °C and the influence of metal ions and pH value on humic substance fluorescence have been investigated by Vodacek and Philpot (1987, 1989). The influence of UV solar radiation on the fluorescence spectra and absorption of DOM has been described by Ekimov (1989), Samokhina (1989).

The goal of this paper is to study the general appropriateness of the spectral characteristic of DOM under temperature variations and UV radiation from both continuous lamp and pulsed laser sources. An experimental study of the influence of temperature over the wide range of 0...80 °C and continuous UV irradiation on excitation and emission fluorescence spectra of natural dissolved organic matter is presented in this work. The features of fluorescence spectra of DOM under UV laser excitation (the effect of fluorescence saturation and photo-chemical destructions) have been observed. The optimal regime of fluorescent detection is under consideration.

2. INSTALLATION

Emission and excitation fluorescence spectra were detected under Xe-lamp excitation using the fluorimeter "Jobin Yvon 3CS" with computer data handling and correction for instrumental spectral sensitivity. Absorption spectra were detected using a spectrophotometer "Specord M40". For simultaneous sample irradiation and spectra excitation we used a Nitrogen laser emitting at 337 nm, with a power of one pulse $P=20$ kW, frequency of pulse repetition $f=1...1000$ Hz, $t=8$ ns, or fourth harmonics of a YAG-laser (266 nm). The water sample in a 1cmx1cm quartz cell was pumped with a peristaltic pump at a flowing speed of up to

1 liter/s. Laser fluorimeter included polychromator and optical multichannel analyzer Plasma Monitor (512 channels, model 1451, PARC). The wavelength dispersion was 0.37 nm per channel.

Water samples from the Baltic Sea and the Black Sea were investigated. Samples with different concentrations of DOM have been obtained using dilution of the sample by distilled water.

3. TEMPERATURE INFLUENCE ON FLUORESCENCE SPECTRA OF DOM IN WATER

1. As the temperature rises from 0 °C to 80 °C the intensity of both excitation and emission DOM fluorescence spectra decreases. A temperature decrease leads to an inverse effect.
2. Essential changes of fluorescence intensities do not lead to spectral shape changes. The wavelengths of fluorescence excitation and emission spectral maxima keep constant at all temperatures and equal 420 and 312 correspondingly with an accuracy of 2 nm. Here we mean the local maximum for the excitation spectrum. The emission spectrum width is also constant at 110 nm.

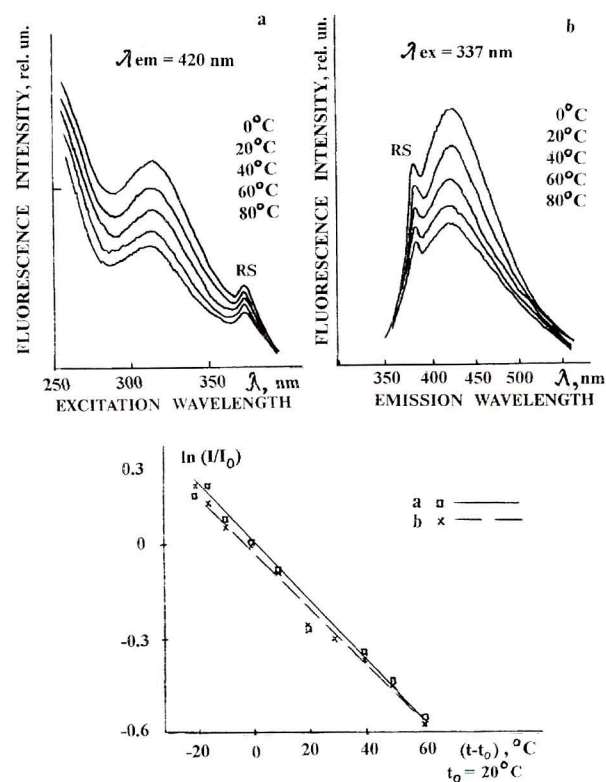


Fig. 1 - Temperature dependence of excitation (a) and emission (b) DOM fluorescence spectra. Detection wavelength is 420 nm (a) and excitation wavelength is 337 nm. RS - water Raman scattering.

3. The temperature effect on spectral intensity is a reversible process.

4. The temperature dependence of maximum intensity both for emission and excitation spectra is well described by the exponential function $I=I_0 \exp(-a(t-t_0))$, where the sign "o" corresponds to temperature $t_0=20$ °C. The coefficient $a=0.0082$ has been obtained for emission spectra and $a=0.0078$ for excitation spectra.

Thus the temperature influence on DOM fluorescence spectra in natural water does not exceed 5% if the temperature is varied by 5 °C, and may be easily taken into account during *in situ* measurement of the DOM concentration using a correction factor.

4. INFLUENCE OF CONTINUOUS ULTRAVIOLET IRRADIATION ON DOM FLUORESCENCE SPECTRA

Water samples of DOM were irradiated evenly in volume in 1 cm x 1 cm quartz cells by a Hg-lamp or a Xe-lamp with different colour glass filters and interference filters.

1. The strongest influence on spectra appears as a result of shortwave UV radiation (200...300 nm): spectra are distorted by shape, the maximum of excitation spectrum shifts to higher wavelengths up to 15-25 nm, depend on the time of irradiation. UV light in the 300...325 nm range affects the DOM fluorescence spectra like shortest UV light, but with less efficiency. Radiation with longer wavelengths (325...400 nm) leads to a decrease in intensity and width, but does not affect any spectral maxima shift. Visible light does not affect any DOM spectral characteristics.

2. The shortest UV irradiation (200...300 nm) influences the excitation fluorescence spectra in the region of 200...300 nm more than in the spectral range 300...400 nm. So the changes in the emission fluorescence intensity are more essential, if spectra are excited at 266 nm than at 337 nm. On the contrary, the nearest UV radiation affects mostly a spectral range higher than 300 nm. It is seen from Fig. 2 that DOM fluorescence decreasing after irradiation in the range 300...390 nm prevails when spectra are detected using 337 nm excitation over 266 nm. Since the minimum wavelength of solar light irradiating the surface water is higher than 300 nm, the effect of decreasing fluorescence will be less, if we use shortwave excitation. Consequently, inaccuracy in DOM content measurement can be decreased using fourth harmonics of a YAG-laser (266 nm) for spectra excitation.

3. UV radiation affects all spectral characteristics irreversibly. The investigation time was up to 3 days.

4. Absorption spectra failed to reveal any correlation with UV irradiation. It was also shown that there is no correlation between absorption and fluorescence spectra behaviour. This leads us to assume that the part of DOM responsible

for luminescence does not contribute much to the absorption spectrum.

During *in situ* monitoring UV solar irradiation of surface water leads to errors of DOM content measurement up to 50% using a nitrogen laser operating at 337 nm for spectra excitation. Errors could be decreased using a shorter excitation wavelength, for example fourth harmonics of a YAG-laser with excitation at 266 nm.

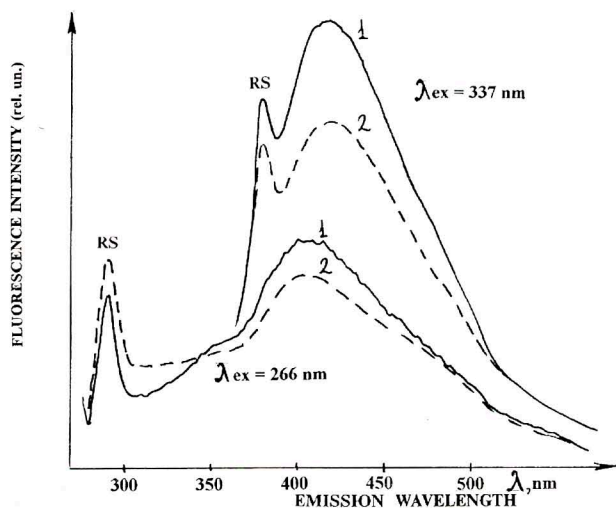


Fig. 2 - Continuous UV radiation influence on excitation emission fluorescence spectra of DOM: 1 - initial spectrum, 2 - after one hour of UV irradiation by Hg lamp in the range 300...390 nm.

5. INFLUENCE OF UV LASER IRRADIATION ON DOM FLUORESCENCE SPECTRA

Currently laser fluorescent methods are widely applied for environmental control including organic pollution measurements in water. But the influence of laser UV irradiation on DOM fluorescence spectra including the effect of fluorescence saturation has not been studied yet in detail. In these two sections some photo-chemical processes under laser excitation and effect of DOM fluorescence saturation are observed.

5.1 The Effect of Laser Pulse Repetition Rate on Dom Fluorescence

1. Irradiation by UV laser source without water sample flowing always affects the fluorescence intensity.
2. Spectral changes of DOM fluorescence depend on the number of laser pulses N , which irradiate the same volume of water sample.

- With the maximal speed of water flowing and $f=2.5$ Hz each laser pulse irradiates a new volume of sample $N=1$.

- $N=1...30$. The spectral shape and maximum wavelength are practically constant. The intensity of the maximum decreases by 10% at most compared to the "uninfluenced" sample with $N=1$.

- $N > 30$. The spectral maximum shifts to longer wavelengths and the spectral intensity decreases by 10...50%.

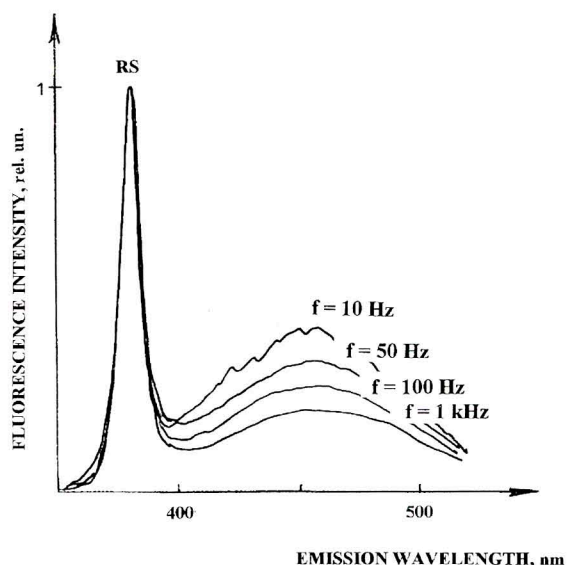


Fig. 3 - The DOM fluorescence spectra with various frequencies of a nitrogen laser (337 nm) pulse repetition (f) from 10 to 1000 Hz. All spectra are normalized by water Raman scattering (RS).

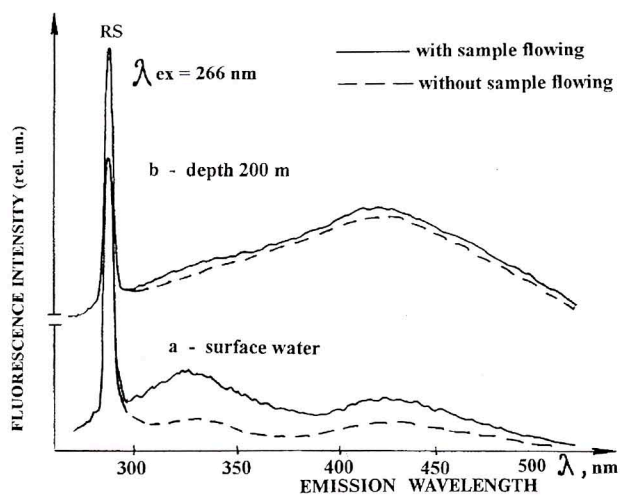


Fig. 4 - Fluorescence spectra excited by fourth harmonics of a YAG-laser (266 nm) for two water samples from the Black Sea (expedition in August 1991) - surface water sample and water from a depth of 200 m. Concentration of organic carbon is equal correspondingly to 4.0 and 5.6 mg/l. Spectra are detected under different experimental conditions: with sample flowing (solid line) and without sample flowing (dashed line) through the volume excited by the laser source.

The band at 290 nm is Raman scattering of water.

3. Some experiments on photochemical destruction of DOM were carried out without water pumping using various frequencies of laser pulse repetition $f = 10 \dots 1000$ Hz. First, the sample was irradiated by laser light with $f = 1$ kHz during 5 min, the total number of laser pulses was about 300 000. The spectral intensity decreased by 50%. Then fluorescence spectra from a previously irradiated sample were detected. One can suppose that there are some relaxation processes for DOM, characterized by different relaxation times from 1 ms to 0.1s (according to $f = 10 \dots 1000$ Hz).

4. Spectral changes of DOM fluorescence and photo-chemical destructions depend on the type of irradiated sample. For distilled water with a small concentration of DOM these changes are much less than for natural DOM samples. It is a very interesting fact, that for seawater (Black Sea expedition in August 1991) from a depth of 200 m such spectral changes practically have been absent. But for surface seawater there are essential photo-chemical destructions. The DOM concentration in the last two samples was practically the same. In this experiment we have used fourth harmonics of a YAG-laser for sample irradiation and for spectra excitation.

Thus $N = 1 \dots 3$ is the optimal regime of spectra investigation under laboratory conditions. The intensity of the maximum does not decrease more than by 3% compared to the "uninfluenced" sample.

5.2 The Effect of Saturation of Dom Fluorescence

The effect of fluorescence saturation is caused by the limited lifetime of an organic molecule in an excited state and appears as a nonlinear dependence of fluorescence response versus exciting laser pulse power. In this work the fluorescence spectra with various values of laser pulse energy have been obtained under experimental conditions with maximal speed of water flowing to minimize photo-chemical effects. We decrease the intensity of the laser source using different colour glass filters with known attenuation coefficient at the excitation wavelength.

Fig. 5 illustrates the effect of saturation of DOM fluorescence. To compare different spectral responses resulting from saturation of fluorescence all spectra in Fig. 5 are normalized by water Raman intensity. The spectral shape is independent of laser pulse attenuation, but normalized fluorescence intensity decreases with increasing pulse power. The effect of fluorescence saturation of DOM is negligible during *in situ* monitoring, but it has to be taken into account in laboratory studies. In calibration experiments, the same content of DOM can produce difference in normalized fluorescence intensity, if data obtained under laboratory conditions are compared with data of remote sensing of ocean water.

CONCLUSIONS

This experimental study permits us to estimate the influence of temperature variation and UV radiation on fluorescence spectra of dissolved organic matter and to correct results obtained in field experiments.

- 1.) The temperature influence on DOM fluorescence spectra in natural water is relatively small and may be easily taken into account during *in situ* measurement of the DOM concentration using a correction factor.
- 2.) UV solar irradiation of surface water leads to errors of DOM concentration measurement up to 50% using a nitrogen laser operating at 337 nm. We cannot take this natural factor into account, because the process of photo-chemical destructions of humic substance is very complex. Errors could be decreased using a shorter excitation wavelength, for example fourth harmonics of a YAG-laser (266 nm).
- 3.) To minimize the photo-chemical processes caused by UV laser irradiation in laboratory studies one needs to pump the water sample; the speed of water flowing depends on the frequency of laser pulse repetition.
- 4.) The effect of fluorescence saturation of DOM is negligible during *in situ* monitoring, but it must be taken into account in laboratory studies.
- 5.) The obtained results give evidence that there is no relation between absorption and fluorescence spectra behaviour. This fact led us to the conclusion that the different parts of DOM participate in absorption and fluorescence processes. Probably, some special groups of fluorophores exist in natural organic matter. These groups form the fluorescence band and constitute a small part of DOM. Photo-physical processes of intra- and inter-molecular interactions of these fluorophores are complex and remain to be studied in more detail.

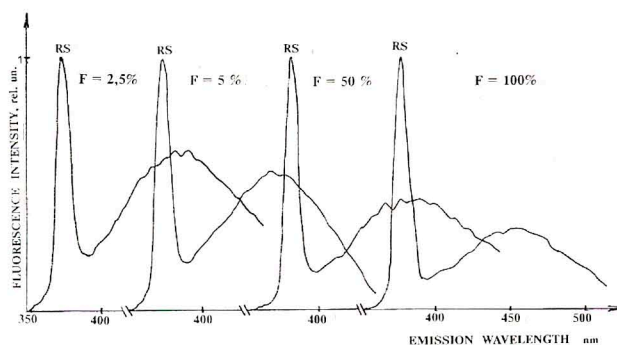


Fig. 5 - The DOM fluorescence spectra with various attenuations of laser pulse power F . All spectra are normalized by Raman scattering of water and illustrate the effect of fluorescence saturation.

ACKNOWLEDGEMENTS

This work was carried out at the General Physics Division, Laboratory of Molecular Spectroscopy (Sections 3-4) and the Quantum Radiophysics Division, Laboratory of Laser Spectroscopy of Water Media (Section 5) of the Physics Department of Moscow State University.

The author appreciates the helpful discussions with Professor V.V.Fadeev and Professor V.I.Yuzhakov. The author thanks senior engineer V.V.Chubarov and postgraduate student E.M.Filippova for technical assistance during the experimental studies.

REFERENCES

- Bristow M., Nielsen D., Bundy D., Furtek R., 1981. Use of water Raman emission to correct airborne laser fluorosensor data for effects of water optical attenuation. *Appl. Opt.* 1981, 20, 2887.
- Ekimov A.I., Samokhina I.A., Tibilov A.S., 1989. Changes of the fluorescence of sea water organic substance under the influence of solar radiation. *Izvestiya of Academy of sciences, USSR, Atmospheric and Oceanic Physics*, 25, 221.
- Klyshko D.N., Fadeev V.V., 1978. Remote measurements of the concentrations of admixtures in water by laser spectral method with calibration on Raman scattering signal. *Doclady Akademii Nauk, USSR*, 238, 2. 320.
- Patsayeva S.V., Fadeev V.V., Filippova E.M., Chubarov V.V., 1991. Laser diagnostics of natural dissolved organic matter and oil products in water. *Proc. of the 12-th Asian Conf. on Remote Sensing*. 30 Oct -5 Nov 1991. Singapore. P.Q12.1-Q12.3.
- Patsayeva S.V., Fadeev V.V., Filippova E.M., Chubarov V.V., Yuzhakov V.I., 1991. Temperature and ultraviolet radiation influence on luminescence spectra of dissolved organic matter Moscow Univ. *Physics Bull.* 32, N.6, 71.
- Patsayeva S.V., Filippova E.M., Chubarov V.V., Yuzhakov V.I., 1991. Fluorescence spectra changes of natural dissolved organic matter under influence of laser ultraviolet radiation. *Moscow Univ. Physics Bull.* 32, N.4, 76.
- Patsayeva S.V., Fadeev V.V., Filippova E.M., Chubarov V.V., Yuzhakov V.I., 1992. The saturation effect of dissolved organic matter fluorescence. *Moscow Univ. Physics Bull.* 33, N.5, 38.
- Philpot W.D., Vodacek A., 1989. Laser-induced fluorescence: limits to the remote detection of hydrogen ion, aluminum, and dissolved organic matter. *Remote Sensing of Environment*. 29, 51.
- Samokhina I.A., Tibilov A.S., 1989. The Variation of the attenuation index of the sea water under the effect of solar ultraviolet radiation. *Izvestiya of Academy of sciences, USSR, Atmospheric and Oceanic Physics*, 25, 98.
- Smart P.L. et al, 1976. The relation of fluorescence to dissolved organic carbon in surface waters. *Water research.*, 10, 805.
- Vodacek A., Philpot W.D., 1987. Environmental effects on laser-induced fluorescence spectra of natural waters. *Remote Sensing of Environment*, 21., 83.