

Photochemical Activity of Aqueous Solutions of Humic Acids Extracted from Soil within Horizon A, Studied by Means of Luminescence

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(Received August 28, 2003)

Abstract

The photochemical stability of aqueous solutions of humic acids (HA) extracted from black soil and from solonetz soil from different depth R is studied by means of luminescence for the first time. It is shown that the photochemical activity of both HA samples extracted from the sub-surface soil layers is higher. The method of photochemical probing is concluded to have advantages over other methods for discrimination of the sorts of HA molecules.

INTRODUCTION

Humus and humic acids (HA) in particular play a crucial part in the formation of agrochemically significant soil structure and to a high extent define physical and chemical properties of soil. Agricultural soil is always affected by direct sunlight, so HA as the components of soil undergo substantial photochemical transformations [1, 2]. Photochemical activity of HA notably depends on types of soil from which HA have been extracted [1, 2]. Recently, urgency of the investigation of photochemical activity of HA has grown substantially in connection with the problem of soil degradation under the action of various pollutants [3]. The aspects of photochemical activity are directly linked with the problems of energy redistribution in an excited molecule. Because of this, investigation of the regularities of redistribution of the energy of photo-excitation in HA molecules is one of the most important fundamental problems, since the problem concerning

redistribution of photo-excitation energy between various groups of fluorophors in HA acids goes out of the limits of consideration of these objects only; it is one of the central aspects for the investigation of numerous photochemical and photophysical processes in complicated molecular ensembles (rhodopsin, laser media, photosynthesizing molecules, *etc.*) [4]. Finally, a separate task and correspondingly a separate object of investigation is photochemistry of aqueous solutions of HA in connection with transformations of organic molecules under the action of sunlight in natural water [5, 6].

As a rule, photochemical activity of HA was studied for samples extracted from horizon A (depth $R = 0-15$ cm); methods of investigation included absorption spectroscopy (electron [1], IR [5], pulsed photolysis [6]) or chromatography [7]. It was implied that the chemical properties of soil are the same over the entire depth of horizon A. However, it has been reported recently that the electron properties of HA molecules undergo noticeable changes within

this horizon [8, 9]. It follows from those results that the photochemical activity of HA can undergo changes within horizon A, too. However, there are no data on the photochemical activity of HA sampled from the same soil with a step of several centimeters.

The goal of the present work was to study photochemical activity of aqueous solutions of HA sampled from horizon A of the same soil but from different depth R with a step of 2–3 cm. Analysis of the photochemical activity was carried out by means of luminescence; this method is one of the most sensitive and intensively used during the recent years to study the chemical structure of HA molecules [3, 9–11]. Light source was natural solar radiation. As a result, it was established that the photochemical activity of HA decreases with an increase in R .

EXPERIMENTAL

Samples to be investigated were taken from weakly leached black soil formed under the meadow steppe of the steppe-forest region of the Altay Territory and from the meadow-steppe medium-columnar solonetz soil of the solonetzic motley grass fescue couch-grass steppe of the Barabinsk lowlands.

Standard methods of HA extraction previously described in [9] were used. The concentration of the aqueous solutions of HA was 100 mg/l. For better solubility and increase in photochemical activity, alkaline medium (pH 12.3) was used [1]. The solutions were kept in the light for 3 days. Experiments were carried out during March and April 2002. Reference samples were stored in the dark. Fluorescence spectra were obtained with a N_2 laser spectrometer [12] in standard quartz cells with a volume of 4 cm³. Air was not removed from the samples. Absorption spectra were recorded with a Bruker spectrometer.

Photochemical activity of HA sample from the depth R was characterized quantitatively by k_R value:

$$(\alpha_{b,g}^{\text{exp}} / \alpha_{b,g}^{\text{exp}}) (K_{OA}^R)^{-1} \quad (1)$$

Here $\alpha_{b,g}^{\text{exp}} = (I_{\lambda=450 \text{ nm}} / I_{\lambda=490 \text{ nm}})_{\text{irrad}}$, $\alpha_{b,g}^{\text{exp}} = (I_{\lambda=450 \text{ nm}} / I_{\lambda=490 \text{ nm}})_{\text{init}}$, where $(I_{\lambda=450 \text{ nm}})_{\text{irrad}}$,

$(I_{\lambda=490 \text{ nm}})_{\text{irrad}}$, $(I_{\lambda=450 \text{ nm}})_{\text{init}}$, $(I_{\lambda=490 \text{ nm}})_{\text{init}}$ are experimentally observed intensities for λ equal to 450 and 490 nm, in the fluorescence spectra of the irradiated and initial samples, respectively;

$$K_{OA}^R = (OA_{\lambda_i})_R / (OA_{\lambda_i})_0 \quad (2)$$

where $(OA_{\lambda_i})_R$ and $(OA_{\lambda_i})_0$ are absorption coefficients for $\lambda = \lambda_i$ for the initial HA samples taken at a depth of $R = 6-9, 14-17$ cm and $R = 0-3$ cm, respectively. The contour shape parameter $a_{b,g}$ in fluorescence spectra can be considered as an analogue of the generally accepted parameter E4/E6 to characterize the absorption spectra of HA [2] (the ratio of absorption coefficients for the wavelengths of 450 and 650 nm, respectively). A principal advantage of the introduction of parameter $a_{b,g}$ is that its use for calculating k_R value does not require taking into account spectral sensitivity of the spectrometer and re-absorption of light emitted as fluorescence (see Supplement).

The contours of fluorescence spectra shown herein were obtained by diving experimentally observed intensities in the fluorescence spectra at $\lambda = \lambda_i$ by the intensity of the line of Raman spectrum of water (internal standard, taking into account absorption of light at $\lambda = 381.6$ nm).

RESULTS AND DISCUSSION

No changes in the fluorescence spectra of reference samples were observed during storage for 3 days. Fluorescence spectra of the initial and irradiated aqueous solutions of HA extracted from black and solonetz soil at $R = 1-3$ cm and $0-3$ cm are shown in Fig. 1. One can see that irradiation causes noticeable changes in the shape of fluorescence contour for both samples. Changes in k_R value *versus* R are shown in Fig. 2. It follows from these data that for HA extracted from both types of soil k_R values decrease with an increase in R . Substantial degree of transformation of the fluorescence spectra of samples extracted from the subsurface horizons in comparison with the samples from deeper ones means higher photochemical activity of these samples and therefore higher photostability of HA samples taken from deeper soil layers.

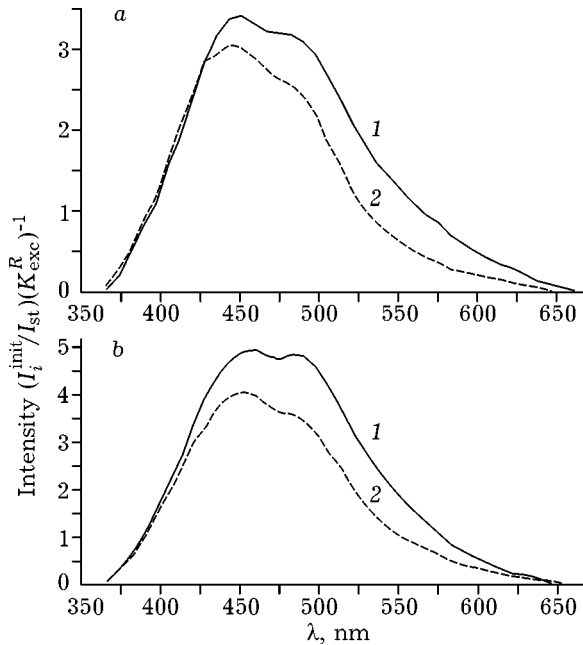


Fig. 1. The dependence of fluorescence spectra of the aqueous solutions of HA on irradiation: *a* - black soil, $R = 1-3$ cm, *b* - solonetz soil, $R = 0-3$ cm; 1 - fluorescence of the initial solution, 2 - fluorescence of the solution irradiated for 3 days.

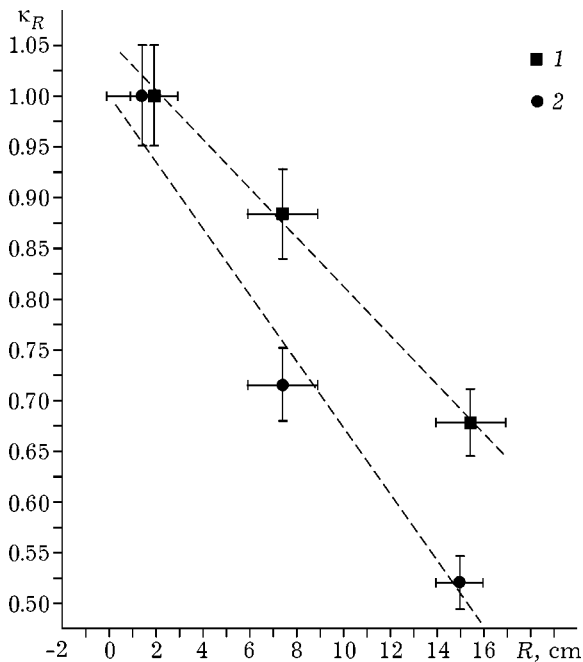


Fig. 2. The dependence of photochemical activity factors for the aqueous solutions of HA extracted from soil at different depth on sampling depth: 1 - black soil, 2 - solonetz soil; "whiskers" along the abscissa indicate the soil sampling step.

Absorption spectra of the initial solutions of HA extracted from black and solonetz soil (Fig. 3) are the functions monotonously decreasing with an increase in wavelength. The shape of spectrum does not change with an increase in R ; only absorption increases. No changes were observed in the absorption spectra during irradiation time. Changes in the absorption spectrum (a decrease in intensity) can be observed only after 7 days of irradiation.

The quantum yield of any photochemical reaction j_{chem} can be represented as [13]

$$j_{chem} = K_{chem}/(K_{chem} + K_{n/chem}) \quad (3)$$

where K_{chem} and $K_{n/chem}$ are the probabilities (constants) for an excited molecule to undergo chemical and non-chemical transformations, respectively. A sum of several relaxation processes is usually considered as $K_{n/chem}$. These processes include fluorescence K_{fl} (radiative transition $S_1 @ S_0$), intersystem crossing $K_{i/cr}$

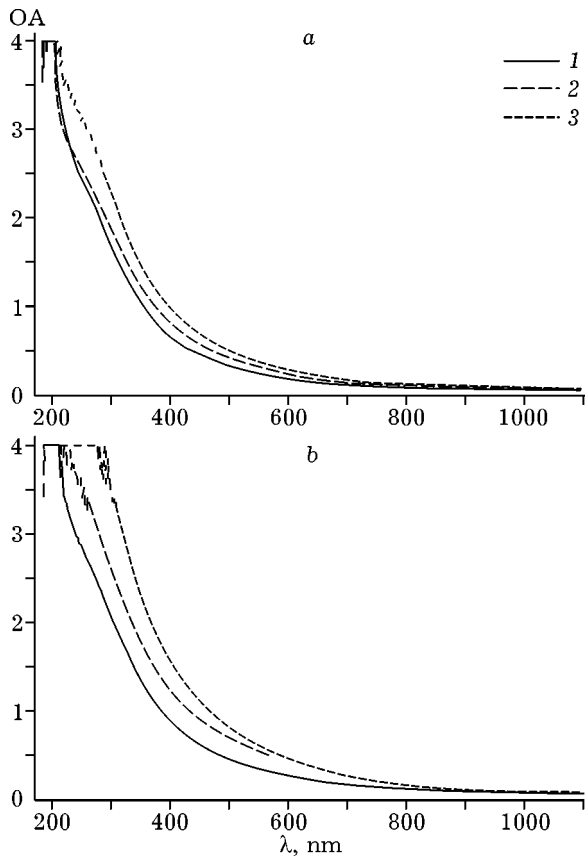


Fig. 3. Absorption spectra of the aqueous solutions of HA versus R : *a* - black soil, *b* - solonetz soil; R , cm: 0-3 (1), 6-9 (2), 14-17 (3).

($S_1 \otimes T_1$), internal conversion $K_{i/\text{con}}$ ($S_1 \otimes S_0$), non-radiative transition. So,

$$K_{n/\text{chem}} = K_{\text{fl}} + K_{i/\text{cr}} + K_{i/\text{conv}} \quad (4)$$
 These possible (competitive) transitions are presented for the case when a chemical process occurs from the excited singlet state.

For both HA samples, an increase in the first momentum of the fluorescence spectrum M_1 occurs with an increase in R [9]. This means that HA molecules sampled from a deeper horizon have lower first excited electron level S_1 and a correspondingly smaller energy gap $D = S_1 - S_2$. It was established experimentally for simple molecules that for unsaturated bonds (if we assume that fluorescence of HA is due to this type of fluorophores) K_{fl} increases (the quantum yield of fluorescence increases) with a decrease in the energy gap ($S_1 - S_2$) [13]. If we accept that such a regularity is true for HA molecules, it follows from the available data on changes in M_1 that K_{fl} should increase with an increase in R . Indeed, our preliminary data on direct observations of K_{fl} (measurement of quantum yield) showed that this value increases with an increase in R .

An additional confirmation can also be the data on the dependence of absorption (OA) on R (see Fig. 3). For simple molecules, $OA \sim \tau^{-1}$ (here τ is the radiative lifetime) [14]. Accepting this relation to be true also for HA molecules and taking into account the fact that $\tau^{-1} \sim K_{\text{fl}}$ [13, 14], we finally conclude that K_{fl} increases with an increase in R .

While D decreases, the energy gap $D_1 = S_1 - T_1$ decreases, too [15]. The value of $K_{i/\text{cr}} \sim \exp(-D_1/(kT))$ [15]. So, $K_{i/\text{cr}}$ increases with an increase in R (decrease in D_1).

The $K_{i/\text{conv}}$ value is determined by the density of vibrational levels r of S_0 state at the "height" of S_1 ($K_{i/\text{conv}} \sim r$ [15]). For complicated molecules including HA, r is a quasi-continuum at the "height" of S_1 [15] and is almost independent of the position of S_1 which changes only slightly in the case under our consideration (~2%). Therefore, it may be accepted that $K_{i/\text{conv}}$ remains almost unchanged with a decrease in S_1 .

So, $K_{n/\text{chem}}$ in denominator of eq. (3) increases with an increase in R . Hence, k_R (an analogue of j_{chem} in (3)) should decrease with an increase in R , which is observed experimental-

ly. In principle, it is this result that could be expected *a priori*: the higher is the possibility for a molecule to participate in photochemical processes, the lower is the probability of its participation in radiative transitions (the quantum yield of fluorescence decreases) [13]. So, the photochemical activity of HA is described in the framework of generally accepted notions for simple molecules about the relations between the quantum yields of decomposition and fluorescence.

Photochemical probing can turn out to be useful for quantitative differentiation of HA. For example, if the data shown in Fig. 2 are approximated by a function of the type $y = a + bx$, each HA sample can be characterized by individual a and b parameters. It should also be noted that the sensitivity of photochemical probing can be made arbitrarily high because the degree of transformation of the initial solution can be varied due to variations in the intensity of excitation light and irradiation time. From the viewpoint of differentiation of HA kinds, this circumstance undoubtedly ensures advantages of this method over other ones the sensitivity of which is constant and may turn out to be insufficient for revealing small differences in the characteristics of HA.

CONCLUSIONS

1. It is proposed to characterize the photochemical activity of HA samples by changes in the ratio of intensities in their fluorescence spectra at 1 equal to 450 and 490 nm (I_b/I_g).

2. Photochemical activity of HA extracted from horizon A decreases with an increase in sampling depth and with an increase in absorption efficiency.

Acknowledgement

The investigation has been in part supported by RFBR, projects Nos. № 01-03-32448 and № 01-04-49513.

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SUPPLEMENT

In eq. (1), when determining k_R value, there are no corrections for absorption of luminescence K_{abs} and spectral sensitivity $K_{s/s}$. One should not introduce these corrections when determining k_R value for the reasons outlined below. Indeed, the true intensity I_{tr} of fluorescence at a definite wavelength should be obtained by multiplying the intensity observed experimentally I_{exp} by correction factors K_{abs} and $K_{s/s}$:

$$I_{\text{tr}}^{450} = I_{\text{exp}}^{450} K_{\text{abs}}^{450} K_{s/s}^{450}; \quad I_{\text{tr}}^{490} = I_{\text{exp}}^{490} K_{\text{abs}}^{490} K_{s/s}^{490} \quad (5)$$

According to the definition of $a_{b,g \text{ tr}}$, we obtain

$$a_{b,g \text{ tr}} = I_{\text{tr}}^{450} / I_{\text{tr}}^{490} = \frac{I_{\text{exp}}^{450} K_{\text{abs}}^{450} K_{s/s}^{450}}{I_{\text{exp}}^{490} K_{\text{abs}}^{490} K_{s/s}^{490}} \quad (6)$$

Correspondingly, we obtain for k_R :

$$k_R = \frac{\alpha_{b,g \text{ irradi}}^{\text{tr}}}{\alpha_{b,g \text{ tr}}^{\text{exp}}} = \frac{(I_{\text{exp}}^{450} K_{\text{abs}}^{450} K_{s/s}^{450})_{\text{irrad}}}{(I_{\text{exp}}^{490} K_{\text{abs}}^{490} K_{s/s}^{490})_{\text{irrad}}} \frac{(I_{\text{exp}}^{490} K_{\text{abs}}^{490} K_{s/s}^{490})_{\text{init}}}{(I_{\text{exp}}^{450} K_{\text{abs}}^{450} K_{s/s}^{450})_{\text{init}}} \\ = \frac{\alpha_{b,g \text{ irradi}}^{\text{exp}}}{\alpha_{b,g \text{ init}}^{\text{exp}}} \quad (7)$$