

## Influence of photochemical reactions on the complexation of humic acid with europium(III)

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### Abstract

Photochemical reactions in the Eu(III)–humic acid system are investigated by fluorescence spectroscopy. For comparison, humic acid without europium is also studied. Irradiation is performed by high energy laser beam and a low pressure mercury lamp. The impact of photodegradation on spectroscopic properties, size and decomposition of humic acid is monitored by steady state and time-resolved fluorescence spectroscopy, UV–Vis spectroscopy, gel permeation chromatography (GPC), dissolved organic carbon (DOC) analysis and ultrafiltration. The different indicators for photodegradation show different sensitivity. The decrease in DOC content with increasing irradiation dose is lower than the decrease in UV/Vis absorption. The highest impact is found for the fluorescence intensity. At 3 kJ/mg humic acid absorbed energy and in absence of europium, fluorescence diminishes by more than 90%. In the presence of Eu(III), however, fluorescent groups are partly stabilized in this range of absorbed energy. Results from GPC show changes in the chemical structure, especially generation of smaller entities. The photodegradation of the humic acid leads to a decrease of the europium–humate complexation constant. Furthermore, europium is reduced to the divalent state. The present study shows that for metal ion humic acid complexation studies by laser fluorescence spectroscopy, great care is needed to avoid significant experimental artifacts, such as photodegradation and metal ion redox reactions. © 2001 Published by Elsevier Science B.V.

*Keywords:* Humic acid; Europium; Complexation; Photodegradation; Laser spectroscopy

### 1. Introduction

All natural waters contain dissolved organic substances in concentrations ranging from approximately 0.1 up to more than 100 mg dissolved organic carbon (DOC) per liter [1,2] depending on the geochemical surrounding. Between 50 and 90% of DOC consist of humic substances [2] which are macromolecules with a complex and heterogeneous structure [3,4]. These acids have a high density of proton exchanging groups varying between 1.5 and 11.2 meq/g [5]. The high functional group content gives them their strong affinity for metal cations, leading to complexation with metal cations, especially of higher charge [6].

Numerous investigations have been performed on the complexation behavior of humic acid with actinide ions. Different methods have been used such as gel permeation chromatography (GPC) [7], solvent extraction [8,9], UV

spectroscopy [10–16], ion exchange [17–19], laser induced photoacoustic spectroscopy (LPAS) [11], time-resolved laser fluorescence spectroscopy (TRLFS) [12,20–22], ultrafiltration [11,23,24] and dialysis [19,25]. Depending on the method, the results vary considerably. TRLFS has the advantage of direct speciation and allows measurements at the very low metal ion concentrations required for the low solubility of multivalent metal cations. Thereby, spectral information is obtained from excitation, emission and the lifetime of emission. When TRLFS is used to evaluate the metal ion complexation, it is generally assumed that no photodegradation accompanies the excitation of these multi-functional macromolecules. Such photodegradation, however, has been reported for excitation of the Eu– and Tb–humate at 308 and 394 nm using an excimer laser [21]. The objective of the present work is to evaluate photochemical reactions induced by UV and laser irradiation and their influence on complexation studies of the Eu(III)–humic acid system by fluorescence spectroscopy.

In this work, humic acid solution is irradiated with different light sources. For comparison between different sources

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and wavelengths, the irradiation is expressed in energy absorbed per unit weight humic acid (kJ/mgHA). The resulting photodegradation is measured at different absorbed energy by steady state and time-resolved fluorescence spectroscopy, UV–Vis absorption spectroscopy, DOC concentration and GPC. Furthermore, the influence of photodegradation of humic acid on the Eu(III)–humate complexation is determined by measuring the emission spectra of Eu with photodegraded humic acid. The complexation constant of Eu(III) with non-photodegraded and photodegraded humic acid is determined by means of ultrafiltration.

## 2. Experimental

### 2.1. Reagents

The humic acid investigated is Gohy-573(HA), which originates from a groundwater at 139 m depth of the Gorbelen aquifer system located in Northern Germany. The purification and characterization of Gohy-573(HA) can be found elsewhere [26]. Its proton exchange capacity (PEC) determined by pH titration under Ar atmosphere is  $5.38 \pm 0.20$  meq/g [26]. Stock solutions are prepared by dissolving a known amount of humic acid in 0.1 M NaOH rapidly followed by dilution with 0.1 M NaClO<sub>4</sub>. The pH is adjusted to 6.0 by addition of HClO<sub>4</sub>. With few exceptions,  $10^{-3}$  M MES buffer (2-mospholine–ethane sulfonic acid) is used for stabilization of pH. The molar humic acid concentration is obtained by multiplying a given weight concentration (g/l) by the PEC (meq/l) divided by the charge of the metal ion under investigation (*z*). Thus, for europium(III), the humic acid concentration is expressed as [HA(III)] [27].

### 2.2. Hg/UV irradiation

In the Hg/UV irradiation experiment, a 14 W low pressure mercury lamp (Katadyn GmbH, Germany) is used at an irradiation wavelength of  $\lambda = 254$  nm. The photon flux is determined to 9.91  $\mu$ Einstein/s by actinometry (with K<sub>3</sub>Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>) at a radiation power of  $4.7 \pm 0.5$  W.

### 2.3. Laser induced fluorescence spectroscopy

The laser system used for irradiation of humic acid solution and for laser fluorescence spectroscopy of complexed and non-complexed europium is an excimer pumped dye laser system (Lambda Physics, Compex 205 and Scanmate II). Dye-laser pulse at 394 nm (dye: Qui), 1 mJ pulse energy and a pulse duration of 25 ns at FWHM is used for irradiation of the sample solution. The sample cell is a rectangular silica cell (HELLMA). The fluorescence emission light is monitored perpendicular to the laser pulse, spectrally resolved by a polychromator (Acton Research, Spectra Pro 275; entrance slit width: 0.5 mm; grating: 300

lines/mm) and detected by an intensified time gated diode array detector (Princeton Instruments, OSMA IRY 700 GR, 1024 linear arranged Si photo diodes). The experimental equipment operates in a spectral window of 210 nm width with a wavelength resolution of about 1.1 nm. Using a beam splitter, a small fraction of the laser pulse is reflected onto a pyroelectric detector connected to a powermeter (Newport 1835C) to monitor the pulse energy. Reading out and digitizing the data from the diode array detector is controlled by an SII80 camera controller (Spectroscopy Instruments). The system components are synchronized by a digital delay/pulse generator (Stanford Research Systems: DG535) as a master trigger unit. With the software POSMA (Spectroscopy Instruments), a PC is used to control the system and analyze the data. Final emission spectra obtained are the results of 10–25 averaged single spectra. The resulting emission spectra are normalized to the average pulse energy.

### 2.4. Flashlamp induced fluorescence lifetime determination

Time-resolved humic acid fluorescence measurement is performed using an FL900CDT fluorescence lifetime spectrometer (Edinburgh Analytical Instruments, UK) in the time-correlated single photon counting mode. The instrumental set up is described in detail elsewhere [28]. An F900 nitrogen-filled (1 bar, 6.6 kV, 0.3 mm electrode separation) nanosecond flash lamp (Edinburgh Analytical Instruments) operated at 40 kHz is used as excitation light source. The excitation wavelength in the time-resolved fluorescence experiments is  $\lambda_{\text{ex}} = 314$  nm. The experiment is typically run at a time base of 100 ns with a 5 ns delay of the photomultiplier tube. The time calibration is 0.095 ns per channel. The emitted light is monitored at  $\lambda_{\text{em}} = 400$  and 500 nm using a spectral bandwidth of 9 nm. To prevent counting artifacts caused by excessively high photon loads, the counting rate is typically <1%. The fluorescence decay is evaluated with a commercial software package of Edinburgh Analytical Instrument based on the Marquardt algorithm which is described elsewhere [29]. The same spectrometer is used for the steady state fluorescence experiments. The instrument is set up in a T-format with two detection channels and operated in the single photon counting mode. A 450 W Xenon arc lamp is used for the excitation of samples. The slit width is 1  $\mu$ m in the excitation and emission path with a spectral resolution of 1.8 nm. The emission spectra are recorded for excitation wavelength range from 275 to 401 nm ( $\Delta\lambda = 3$  nm) in the emission range from 281 to 545 nm ( $\Delta\lambda = 1$  nm).

### 2.5. Ultrafiltration

Ultrafiltration is used to investigate the Eu complexation with photodegraded and non-photodegraded humic acid. This method allows the separation of the non-complexed

Eu ion from its humate complex by size fractionation [30]. The filtration system uses a membrane of nominal cut-off 1000 Da (Filtron, Microsep<sup>TM</sup> Microconcentrators). Europium concentrations in filtrates are quantified by ICP-MS. A correction is used for the partial retention of the non-complexed Eu ion, and possibly sorption on the membrane (at pH 6.0, 0.1 M NaClO<sub>4</sub>, 75% of the non-complexed Eu<sup>3+</sup> ion is found in the filtrate). The Eu species distribution is calculated by the total Eu concentration and the concentration in filtrate, applying the correction factor. Published results [30] show the validity of the method for non-photodegraded humic acid. Alteration of humic acid by photodegradation, including changes in size distribution, could introduce experimental artifacts. As shown in this work, however, this method can be applied also for photodegraded humic acid.

### 2.6. Gel permeation chromatography

The GPC is performed with on-line detection of fluorescence ( $\lambda_{\text{ex}} = 300 \text{ nm}$ ,  $\lambda_{\text{em}} = 400 \text{ nm}$ ), UV absorption at  $\lambda_{\text{abs}} = 254 \text{ nm}$  and DOC detection [31]. The column, packed with TSK HW 50 S (Toyopearl), has a length of 25 cm and an inner diameter of 2 cm. The exclusion volume is 19 ml, (determined with dextran blue) and the total volume is 46 ml. Phosphate buffer with  $c(\text{K}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}) = 1.25 \text{ g/l}$  and  $c(\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}) = 2.5 \text{ g/l}$ , pH = 6.8, is used as eluent at a flow rate of 1 ml/min. Samples are diluted with phosphate buffer ( $c(\text{K}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}) = 2.5 \text{ g/l}$  and  $c(\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}) = 5 \text{ g/l}$ ) the ratio of 1:1 to adjust the phosphate concentration of the sample and eluent. The system is integrated in an assembly for column experiments with additional detectors for electrical conductivity (LDM/S, WTW) and pH-value (Ingold).

The detection limit of the DOC detector (determined with potassium hydrogen phthalate according to DIN 32645 (calibration curve method)) is 0.2 mg C/l. The eluent passes an UV reactor before use in order to decrease the background concentration of DOC. The irradiation time is approximately 8.5 h. The samples are injected by an autosampler (Gilson Abimed, Model 231 BIO with Dilutor 401), whose injection volume can be set within the range from 0 to 2000  $\mu\text{l}$ . In this work, 2 ml of sample is injected. To remove bicarbonate from the sample stream after passing through the column and before the DOC measurement, a continuous stream of diluted H<sub>3</sub>PO<sub>4</sub> together with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is added to lower the pH value to 1.5. Subsequently CO<sub>2</sub> is stripped with N<sub>2</sub>. The sample is then pumped through a capillary UV reactor, where the organic substances react with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and UV light to form CO<sub>2</sub>. The retention time within the reactor is about 14 s. The CO<sub>2</sub> is stripped by a N<sub>2</sub> stream. The gas stream is passed through a cooling module to remove water vapor in order to improve the signal-to-noise ratio in the IR absorption detector (Ultramat 3, Siemens). The data collected from all detectors are recorded on a PC.

## 3. Results and discussion

Humic acid has a broad UV/Vis absorption, increasing strongly towards shorter wavelength without distinct features. It has broad excitation and emission bands and a complex fluorescence decay time dependency. Part of the complexity in fluorescence properties has been attributed to excited state processes (e.g., intramolecular energy transfer) [28,32]. Due to irradiation, a number of different photochemical processes can be induced, including breaking of bonds, change in functional groups and structures that may also change intramolecular interactions. Through examination of UV/Vis absorption and fluorescence, including comparison of fluorescence decay between irradiated and non-irradiated humic acid, information is obtained on structural changes induced by photodegradation. Additional information is obtained by GPC with different detection methods.

### 3.1. Humic acid solution without europium

Humic acid solution is irradiated at wavelengths of 254, 308 and 394 nm. Continuous irradiation at 254 nm is done by a mercury lamp light source. Discontinuous irradiation at 308 and 394 nm is made by the pulsed laser system; 308 nm is chosen because at this wavelength the highest dose rate is achieved and 394 nm is chosen because of its relevance for Eu–humate interaction studies. For comparison, an absorbed energy of 3.0 kJ/mg HA reflects the typical situation for measurement of the Eu fluorescence lifetime for speciation purposes under these conditions.

#### 3.1.1. Influence on UV/Vis absorption

In Fig. 1, UV/Vis absorption spectra are shown for humic acid after irradiation at 308 nm with absorbed energy up

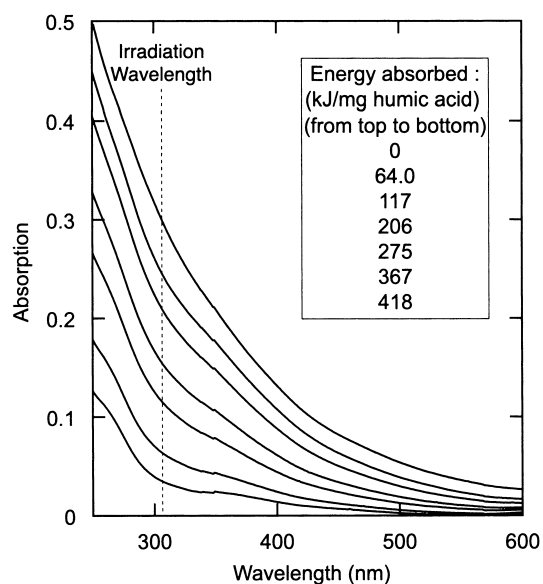


Fig. 1. UV/Vis absorption spectra of humic acid for different absorbed energy from pulsed laser irradiation at 308 nm.

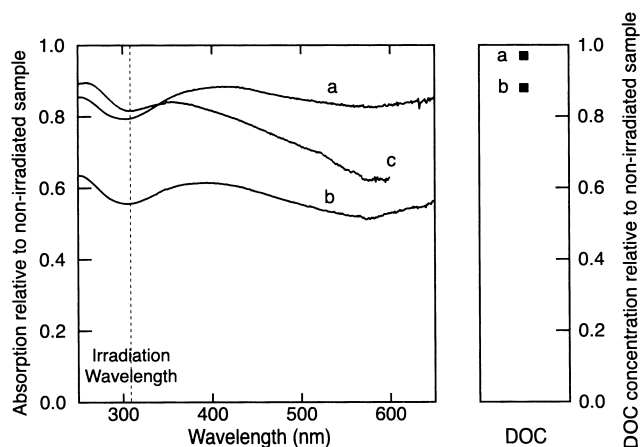


Fig. 2. UV/Vis absorption and DOC concentration relative to non-irradiated samples of humic acid for different absorbed energy from pulsed laser irradiation at 308 nm. Samples a and b are without MES buffer and 28.1 and 66.8 kJ/mg humic acid absorbed irradiation energy, respectively. Sample c is with  $10^{-3}$  mol/l MES buffer and 64.0 kJ/mg humic acid absorbed irradiation energy.

to 418 kJ/mg humic acid. The UV/Vis absorption decreases over the entire wavelength range and for the highest dose the absorption decreases with almost 80%.

In Fig. 2, the absorption relative to non-irradiated samples is shown for irradiation doses of 28.1 and 66.8 kJ/mg humic acid, with and without presence of MES buffer. The decrease in absorption is higher around the irradiation wavelength than at shorter and longer wavelengths. Nevertheless the decrease in absorption is relatively uniform and also takes place at shorter wavelengths than that of irradiation. In the presence of MES buffer, the decrease in UV/Vis absorption is lowered compared to samples without the buffer. This indicates that the organic buffer acts as a scavenger for photochemically generated reactive species.

A key question is to which extent UV/Vis absorption can be used as an indicator for decomposition of humic substances. As seen in Fig. 2, the decrease in DOC concentration with increased absorbed irradiation dose is lower than the decrease in UV/Vis absorption. This shows that the decrease in UV/Vis absorption is the result of a variety of photochemical reactions including modification of the electronic structure and bond-breakage. As seen below, this includes the generation of smaller entities.

### 3.1.2. Influence on fluorescence spectrum

The decrease in fluorescence intensity with irradiation is much stronger than the decrease in UV/Vis absorption. In Fig. 3, the fluorescence spectra of humic acid are shown for irradiation at 394 nm. In Fig. 4, the fluorescence emission intensity at 500 nm is shown as a function of the absorbed energy. The fluorescence intensity decreases with increasing absorbed energy. At an absorbed energy of approximately 3.0 kJ/mg HA, the fluorescence intensity is decreased by approximately 95%, compared to an only marginal decrease

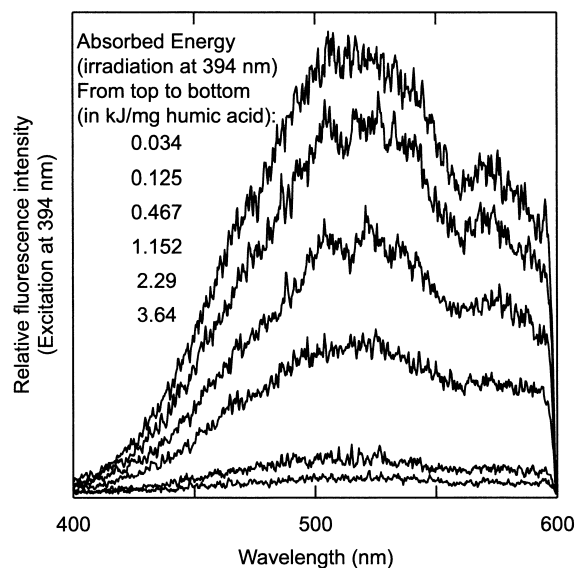


Fig. 3. Influence of irradiation by laser at 394 nm on the fluorescence of humic acid. Fluorescence spectra from excitation at 394 nm are shown for different absorbed irradiation energy.

in the UV/Vis absorption for the same irradiation dose (cf. Fig. 1).

### 3.1.3. Influence on fluorescence decay time

The fluorescence decay can be evaluated by different approaches. On the one extreme, the decay can be seen as a continuum with certain features. On the other hand, one may also represent the fluorescence decay by a limited number of operational components. The latter approach is guided

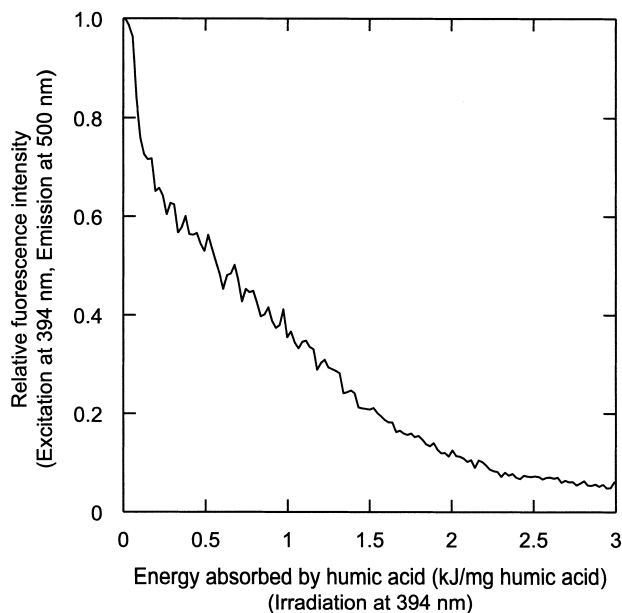


Fig. 4. Influence of irradiation by laser at 394 nm on the fluorescence of humic acid. Fluorescence at 500 nm from excitation at 394 nm is shown as a function of the absorbed irradiation energy.

Table 1

Selected results for fluorescence lifetime of humic acid, described by three individual components (excitation wavelength 314 nm)

Humic acid	Emission wavelength (nm)	Fluorescence lifetime (ns) of operational decay components		
		1	2	3 <sup>a</sup>
Non-photodegraded	400	1.7	5.0	8
	500	1.6	4.8	12
Photodegraded	500	1.6	4.8	10

<sup>a</sup> The contribution of this component to the total fluorescence is approximately 15%. Due to the low contribution and low intensity at long delay time, the error of this component is larger than that of the other ones.

by the perception that different distinguishable fluorescent entities are present. It furthermore allows better visualization of the fluorescence decay process. Results show that the humic acid fluorescence decay can be well represented by three operationally defined individual decay components ([32], Table 1).

For the first two operationally defined fluorescence decay components, no significant difference is found for different degrees of photodegradation. The third component with the longest decay time represents only approximately 15% of the total fluorescence. Due to the delay and low intensity, the error in evaluation of this component is larger than for the other two. Also for this component, however, no major impact of photodegradation is seen.

### 3.1.4. Gel permeation chromatography of UV-irradiated HA

GPC in aquatic media separates substances according to their hydrodynamic size, charge and gel surface sorption properties. In Fig. 5, GPC chromatograms of humic acid are shown before and after irradiation at 254 nm with the low pressure mercury lamp. One main peak is observed by UV and fluorescence detection. Chromatograms from absorption detection at 254 nm fall mainly within the working range of the column (between dotted vertical lines), however, tailing beyond the total volume is also observed. For the fluorescence detection (excitation at 300 nm and emission at 400 nm), this tailing is more pronounced. With increasing irradiation dose the peak maximum is shifted to larger elution volume, indicative for a change in charge/sorption properties, but especially smaller size. The main part of non-irradiated humic acid is eluted between 22 and 38 ml. With increasing irradiation dose, the amount eluted in this region is decreased. Integration of the chromatograms, however, reveals that at 8.05 kJ/mg humic acid absorbed dose, the total area of the absorption chromatogram decreases only by 10%. This shows that the main effect at this dose is not oxidation to CO<sub>2</sub>, but rather fragmentation of humic acid.

The gel permeation chromatograms with DOC detection (Fig. 5) are strongly influenced by the signal from the MES buffer. In addition to the large signal from the buffer, three peaks can be seen, at around 35, 70 and 80 ml elution volume. With increasing irradiation, the first peak decreases where this decrease is less pronounced for entities of larger apparent size. The peaks at 70 and 80 ml elution volume, i.e.

beyond the total volume, are hardly visible in the original humic acid, but become more intense with increasing irradiation dose. These entities show no significant absorption or fluorescence signals.

In summary, the results from GPC verify findings discussed above (cf. Fig. 2). Photodegradation results in changes in the humic acid with emphasis on generation of smaller molecular size and small fragments with no measurable absorption and fluorescence.

## 3.2. Irradiation of a humic acid solution containing Eu

### 3.2.1. Influence on the emission spectrum of Eu and humic acid

When exciting a non-complexed Eu<sup>3+</sup> ion solution at 394 nm, two main bands (<sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>1</sub> and <sup>5</sup>D<sub>0</sub>–<sup>7</sup>F<sub>2</sub>, at 592 and

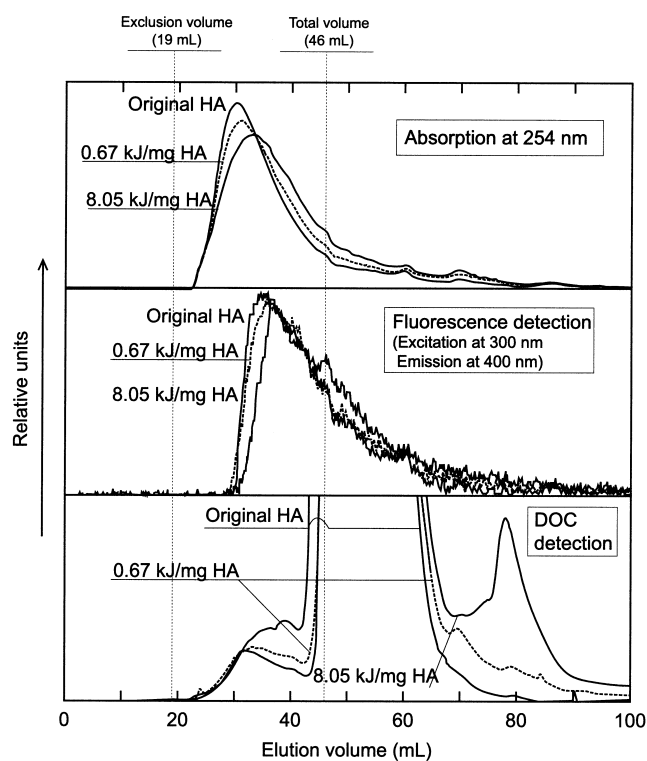


Fig. 5. GPC of original and photodegraded humic acid (HA) applying different detection methods, namely absorption at 254 nm, fluorescence (excitation at 300 nm, emission at 400 nm) and DOC.

617 nm, respectively) are observed. Another weak band can also be seen ( $^5D_0-^7F_4$  at 697 nm), whereas the other transitions ( $^5D_0-^7F_3$ ,  $^5D_0-^7F_5$  and  $^5D_0-^7F_6$ ) are very weak. For the non-complexed  $\text{Eu}^{3+}$  ion, the band at 592 nm is the most intense. Upon complexation, the peak positions do not change, but the relative intensity of the different bands change and for  $\text{Eu(III)-humate}$ , the  $^5D_0-^7F_2$  (617 nm) band becomes the most intense.

Humic acid is complexed with europium at pH 6.0 (buffered with  $10^{-3}$  mol/l MES) in 0.1 mol/l  $\text{NaClO}_4$ . The europium concentration equivalent to 20, 40 and 65% of the fraction of humic acid functional groups that can be complexed under these conditions (the loading capacity) [27]. This ensures that the concentrations of non-complexed europium are negligible in the starting solutions. The solutions are equilibrated for 48 hours prior to irradiation experiments. Fig. 6 shows the europium and humic acid fluorescence as a function of the absorbed energy at 40% europium loading. The irradiation energy is delivered by the laser source used for the fluorescence measurements (394 nm). The fluorescence intensities of both europium bands and that of humic acid decrease with increasing irradiation dose.

The ratio between the two bands at 592 and 617 nm for different absorbed energies is shown in Table 2. Irrespective of the absorbed energy, this ratio remains basically constant ( $2.36 \pm 0.17$ ). This observation suggests that during pho-

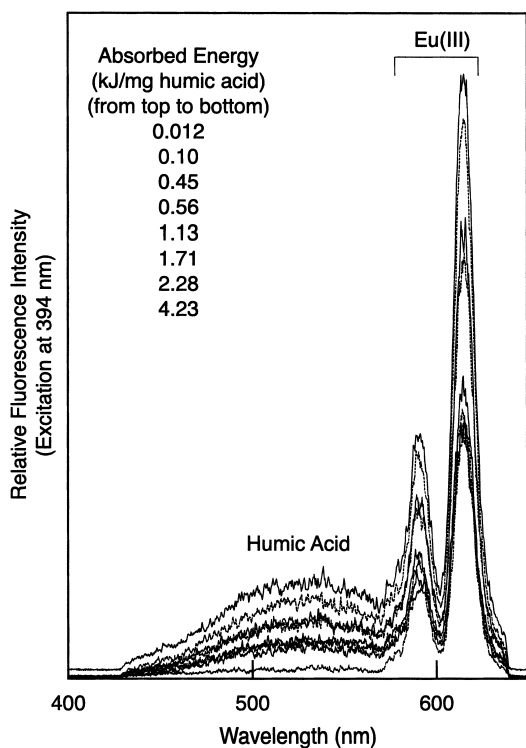


Fig. 6. Fluorescence of europium complexed with humic acid and that of humic acid (500 nm) as a function of absorbed irradiation energy by laser at 394 nm. The europium concentration is equivalent to occupation of 40% of the fraction of humate sites that can be complexed (loading capacity) under these conditions (pH 6.0,  $I = 0.1$  ( $\text{NaClO}_4$ )).

Table 2

Europium fluorescence intensity ratio of bands at 617–592 nm as a function of absorbed energy by laser irradiation at 394 nm<sup>a</sup>

Absorbed energy (kJ/mg HA)	Ratio FI 617 nm/ FI 592 nm
0.012	2.39
0.10	2.32
0.45	2.38
0.56	2.33
1.13	2.25
1.71	2.10
2.28	2.40
4.23	2.69
	$2.36 \pm 0.17^b$

<sup>a</sup>The europium concentration is equivalent to 40% of the loading capacity of humic acid; FI: fluorescence intensity.

<sup>b</sup> Mean value.

to degradation, the ratio of free Eu/complexed Eu is not affected. However, the fluorescence intensity of free Eu being much smaller than that of Eu–humic acid complex, a small change in the free Eu concentration is difficult to observe by the Eu emission spectrum (cf. Fig. 9). Furthermore, to which extent the mode of complexation between humic acid and  $\text{Eu(III)}$  is affected by degradation of humic acid cannot be determined.

In Fig. 7, the relative fluorescence intensities of humic acid with and without europium as well as the two europium emission bands are shown. As shown in Table 2, the relative fluorescence intensity ratio of the two europium emission bands remains virtually constant with increasing irradiation dose. In absence of europium, the humic acid fluorescence diminishes rapidly and, as discussed above, decreases by approximately 95% at an absorbed irradiation dose of 3 kJ/mg humic acid (cf. Fig. 4). In the presence of europium, the humic acid fluorescence becomes stabilized for absorbed doses

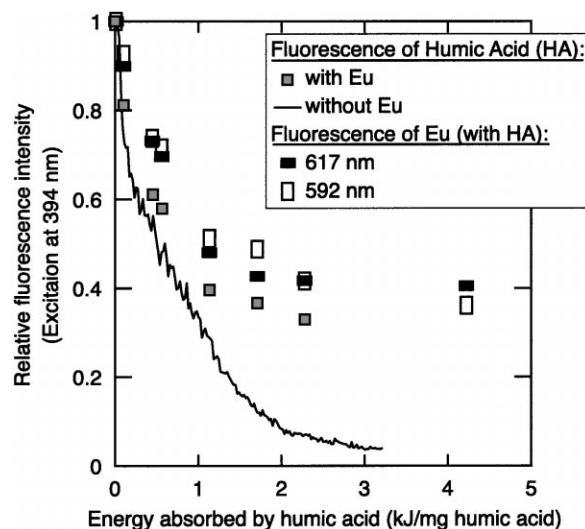


Fig. 7. Decrease in europium fluorescence bands (592 and 617 nm) and humic acid fluorescence at 500 nm with and without europium as a function of absorbed irradiation dose (cf. Figs. 4 and 6).

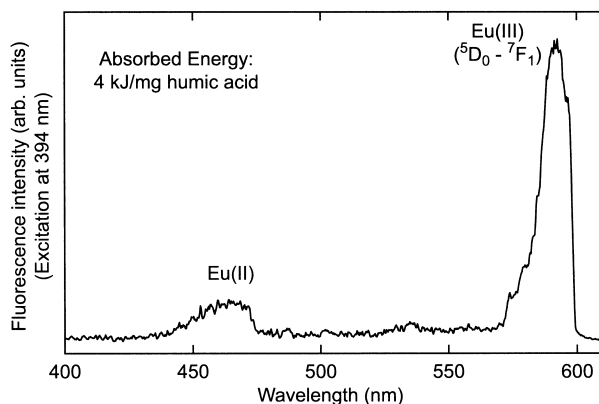


Fig. 8. Photolytic generation of  $\text{Eu}^{2+}$  in humic acid solution irradiated by laser at 394 nm (4 kJ/mg HA). The europium concentration is equivalent to 65% of the loading capacity of the humic acid.

above approximately 1 kJ/mg humic acid. The reason for the stabilization of humic acid fluorescence by europium in this range of absorbed energy is not yet clear.

### 3.2.2. Photolytic generation of $\text{Eu(II)}$

Irradiation with laser light at 394 nm not only leads to changes in the absorption, fluorescence, size distribution and functional group content of humic acid but also leads to the generation of divalent europium. In Fig. 8, the  ${}^5\text{D}_0-{}^7\text{F}_1$  transition (592 nm) of  $\text{Eu(III)}$  is shown for photodegraded humic acid in the presence of europium. This spectrum is

recorded for the highest europium concentration, i.e. 65% of the humic acid europium loading capacity and photodegradation by an absorbed energy of 4 kJ/mg humic acid. Around 460 nm a band corresponding to  $\text{Eu(II)}$  is observed.

### 3.2.3. Influence on the $\text{Eu}$ –humate complexation

Stability constants of europium with non-photodegraded and photodegraded humic acid are determined by the ultrafiltration method at pH 6.0 and  $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ). Degradation of humic acid is done by laser irradiation at 308 nm with an absorbed energy of 80 kJ/mg HA. After laser irradiation, europium is added in concentrations equivalent to 20 and 65% of the humic acid europium(III) loading capacity. The stability constants are evaluated by the charge neutralization model [27]. The results are shown in Table 3. For the investigation on the non-photodegraded humic acid, as expected, no influence of the loading is found. The overall average of the europium–humate stability constant is found to be  $6.37 \pm 0.10$ , which is in good agreement with values determined for different trivalent f-elements by ultrafiltration and spectroscopic methods ( $\log \beta = 6.24 \pm 0.28$  [27]). For the photodegraded humic acid results are different. Again, no significant influence of the loading of humic with europium is found, however, the overall average of the stability constant is much lower, namely  $5.19 \pm 0.12$ .

The lower values for the stability constants found for photodegraded humic acid, could be the result of ultrafiltration artifacts. If humic acid entities decrease in size with photodegradation, the filter membrane could be partly

Table 3  
Europium–humate complexation results at pH 6.0 ( $I = 0.1 \text{ M}$  ( $\text{NaClO}_4$ ))<sup>a</sup>

Total	[Eu] ( $\mu\text{mol/l}$ )		[HA(III)] <sub>free</sub> ( $\mu\text{mol/l}$ )	$\log \beta$ (l/mol)	$\log \beta$ (average)
	Non-complexed	Humate complex			
<i>Non-photodegraded humic acid (20% europium loading)</i>					
2.32	0.10	2.22	9.38	6.37	
2.32	0.13	2.19	9.41	6.25	$6.31 \pm 0.06$
<i>Photodegraded humic acid (20% europium loading)</i>					
2.32	0.81	1.51	10.09	5.27	
2.32	0.90	1.42	10.18	5.19	
2.32	1.18	1.14	10.46	4.97	
2.32	1.04	1.28	10.32	5.08	$5.13 \pm 0.11^b$
<i>Non-photodegraded humic acid (65% europium loading)</i>					
7.54	0.55	6.99	4.61	6.44	
7.54	0.44	7.10	4.50	6.55	
7.54	0.72	6.82	4.78	6.30	
7.54	0.69	6.85	4.75	6.32	$6.40 \pm 0.10$
<i>Photodegraded humic acid (65% europium loading)</i>					
7.54	3.24	4.30	7.30	5.26	
7.54	2.85	4.69	6.91	5.38	
7.54	3.53	4.01	7.59	5.18	
7.54	3.45	4.09	7.51	5.20	$5.26 \pm 0.08^b$

<sup>a</sup> The effective humic acid concentration equals  $11.6 \mu\text{mol/l}$ , taking into account the loading capacity under these experimental conditions. Concentrations of the non-complexed europium ion and europium–humate are determined via species separation by ultrafiltration, taking into account partial retention of the non-complexed europium ion at this pore-size (1000 Da). Non-photodegraded and photodegraded humic acid is investigated for europium concentrations equivalent to 20 and 65% of the effective humic acid concentration.

<sup>b</sup> No correction is made for the impact of photodegradation on the functional group content.

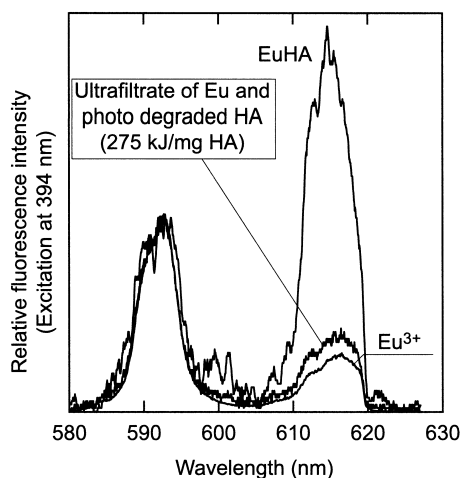


Fig. 9. Emission spectra of the Eu(III) ion in the non-complexed form as well as complexed with photodegraded and non-photodegraded humic acid (HA).

permeable for the europium complex. The composition of the filtrate was measured by taking an emission spectrum of this filtrate and comparing to the emission spectra of free Eu and complexed Eu. The  ${}^5D_0-{}^7F_2$  transition for Eu (617 nm) is sensitive to the complexation by humic acid and would increase drastically if smaller size europium humic acid entities would pass through the filter. In a good approximation, it is possible to estimate the amount of complexed Eu going through the filter by normalizing the intensity of the  ${}^5D_0-{}^7F_1$  (592 nm) transition for the different solutions and comparing directly the intensity of the  ${}^5D_0-{}^7F_2$  transition (Fig. 9). By this method, less than 8% of Eu in the filtrate is found to be complexed. Taking this correction value into account, the stability constant of photodegraded humic acid does not change significantly ( $\log \beta$  becomes  $5.33 \pm 0.08$  instead of  $5.26 \pm 0.08$  at 65% Eu loading of the humate ligand). Thus, the lowering of the stability constant by photodegradation is not a consequence of ultrafiltration artifacts.

Photodegradation leads to changes both in the functional group content of humic acid and decrease in molecular size. Investigations on different size fractions of humic acid show that with decreasing size the complexation strength decreases [33]. Comparison of the metal ion complexation with humic and with fulvic acid also shows lower complexation strength for the smaller fulvic acid [12]. Simultaneously, photodegradation results in modification of the functional group content. Delineation of the impacts from decrease in the molecular size and change in the functional group content, cannot be performed by the present data.

#### 4. Summary and conclusions

The sensitivity of different properties of humic acid towards photodegradation varies strongly. Photodegradation leads to generation of smaller entities. The decrease in DOC is lower than the decrease in UV/Vis absorption. The

decrease in fluorescence intensity, however, is much more pronounced than the former two decomposition indicators. Addition of europium leads to stabilization of humic acid towards photodegradation.

Application of laser induced fluorescence spectroscopy for studying the europium–humate interaction may be subject to considerable experimental artifacts through photochemically induced reactions. These artifacts are due to changes in functional group content and lowering in molecular size of humic acid. Simultaneously, photolytic reduction of europium from the trivalent to the divalent state takes place. Due to the relatively low fluorescence efficiency of europium, significant photolytic impact can occur. This is especially true for high absorbed irradiation doses, for example where europium lifetime measurements are conducted. Therefore, great care is needed to ensure that significant experimental artifacts are avoided where the europium humic acid system is studied.

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