



# Studying of the interaction between peat humic acids and metazachlor using spectroscopy methods

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Received: 30 September 2017 / Accepted: 8 January 2018 / Published online: 16 January 2018  
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## Abstract

**Purpose** The analysis covered the interaction of humic acids (HA) isolated from peats with the metazachlor using spectroscopic methods.

**Materials and methods** Five peatlands have been selected for the study in the southern and northern parts of Poland. Extraction of humic acids (HA1, HA2, HA3, HA4, and HA5) was performed using a procedure recommended by the International Humic Substances Society. Metazachlor 500 SC with metazachlor as a biologically active substance [2-chloro-N-(pyrazol-1-ylmethyl)acet-2',6'-xylidide] has been used. HA have been assessed on the basis of their elemental composition. Spectroscopic techniques have been used to study the HA structure and their interaction with metazachlor including: UV-visible spectroscopy, dynamic light scattering, and delayed luminescence (DL)

**Results and discussion** Based on their morphological and chemical properties, the studied peat soils can be classified as follows: (1) Eutric Murshic Sapric Histosols, (2) Eutric Sapric Histosols, (3) Eutric Hemic Histosols, (4) Eutric Fibric Histosols, and (5) Dystric Dranic Hemic Histosols according to the WRB guidelines (2015). Results showed that the largest particle size, measured by  $E_{4/6}$  coefficient, was found in HA2 sample, while the smallest in HA3 sample. The addition of metazachlor to HA solutions reduced the values of  $E_{4/6}$  coefficient by 33 to 72%, while the values of hydrodynamic diameter by 4 to 32%. No significant changes were found between  $E_{4/6}$  after adding of metazachlor to HA solutions. The largest changes in DL intensity, excited both by blue and red light after herbicide addition, were observed in HA2 sample, which is characterized by the largest particle size, the highest oxygen content and CQ value as well as the lowest “aromatization rate” value.

**Conclusions** The particle sizes of HA molecules measured by  $E_{4/6}$  coefficient do not impact on the particle sizes of HA-herbicide systems measured by the same ratio. The delayed luminescence may become valuable, because it is simple, fast, and sensitive. Additionally, the results show minor errors comparing with chemical methods. This method may provide information about structure and nature of humic acids, as well as their photoreactivity. The using of delayed luminescence in studies of HA-pesticides interaction may enable us to better understand the luminescence properties of HA.

**Keywords** Delayed luminescence · Herbicides · Humic substances · Peatlands

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Responsible editor: Jerzy Weber

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## 1 Introduction

For many years, despite a number of controversies around the negative impact on the environment, the application of pesticides has been the most effective and modern method protecting crops against various threats of biotic origin (Aktar et al. 2009). Since pesticides have been commonly used and their half-time is rather long, their residues can now be found in every segment of the natural environment, including water (Tankiewicz et al. 2010), soil (Aktar et al. 2009), bottom sediments (Erkmen et al. 2013), air (Zivana et al. 2016), plants (Fantke et al. 2011), and living organisms (Jayaraj et al. 2016). Apart from their direct threat, the fact that pesticides reside in

the environment, they can migrate within and between ecosystems. A natural storage of various organic pollutants in ecosystems, including pesticides, is the organic matter (OM). The adsorption of pesticides by the OM plays an important role by modifying their transport, orientation, bioavailability and toxicity in the natural environment (Aktar et al. 2009; Włodarczyk 2014; Włodarczyk and Buchwał 2015). The two processes are responsible for the sorption of xenobiotics by different OM fractions, namely physical and chemical adsorption (Oleszczuk 2007; Ukalska-Jaruga et al. 2015). These processes include ionic, hydrogen and covalent binding, van der Waal forces, electron donor-acceptor and charge-transfer mechanisms, as well as ligand exchange and hydrophobic binding (Gevao et al. 2000). However, it must be noted that not all mechanisms occur simultaneously. The one that is observed depends on the nature of the functional groups of the organic matter components and pH of the reaction medium. Surface sorption is not the only way to accumulating organic pollutants. They can be trapped in three-dimensional structures of organic matter (Oleszczuk 2007; Ukalska-Jaruga et al. 2015).

Soil organic matter (SOM) is a non-homogeneous and complex mixture of macromolecular compounds. It consists of input matter of plant and animal origin at various decomposition stages, as well as organic substances of specific properties, i.e., humic substances (HS) (Kumada 1987; Stevenson 1994). The structure and chemical properties of HS vary depending on climatic geochemical conditions, whereas those conditions determine HS sorption capacity. The rate of sorption depends of HS origin, molecular mass and polarity (Senesi et al. 1995; Oleszczuk 2007; D’Orazio and Miano 2016). Humic substances such as humic acids (HA), fulvic acids (FA), and humins are generally dominant fractions of soil organic matter (Kumada 1987; Stevenson 1994). It is known that HA are heteropolycondensates of a ‘statistical’ structure, and they consist primarily of aromatic rings linked with  $-O-$ ,  $-(CH_2)_n-$ ,  $=NH$ , and  $-S-$  bridges that contain various functional groups (e.g.,  $-COOH$ ,  $-OH$ ,  $=C=O$ ,  $-OCH_3$ ) (Kumada 1987; Stevenson 1994). This “wealth” of active functional groups causes that HA are the most powerful reacting agents which are able to interact with, e.g., heavy metals (Boguta and Sokołowska 2016), aromatic compounds (Sun et al. 2008), organic acids (Cozzolino et al. 2001), herbicides (D’Orazio and Miano 2016), fungicides (Morales et al. 2013), and insecticides (Scaglia et al. 2016). The studies show a strong influence of HA on the uptake, transport, deposition, bioavailability, bioaccumulation, degradation, and toxicity of inorganic and organic pollutants.

Many different spectroscopic techniques have been used to study the HA structure and their interaction with xenobiotics such as: fluorescence spectroscopy (D’Orazio and Miano 2016), NMR (Huang et al. 2012), ESP (Pandey et al. 1999), infrared spectroscopy (Senesi et al. 1995), and UV-visible spectroscopy (Leita et al. 2009).

The delayed luminescence (DL) phenomenon involves quickly decaying luminescence of the material after its exposure to light has discontinued. DL is usually tested by the registration of the luminescence decay kinetic or the registration of its intensity in specific time sequences after the irradiation of the material (Prokowski and Mielnik 2012). DL provides information about the photophysical processes preceding the photochemical reactions. The photochemical reactions induced by HS involve the transfer of energy from excited  $HS^*$  to reactive species such as solvated electrons ( $e_{aq}$ ), hydroxyl radicals ( $\cdot OH$ ), singlet oxygen ( $^1O_2$ ), and reactive triplet states ( $^3HS^*$ ) etc. It is known that, HS act as photosensibilizers, which can activate many photochemical processes (Aguer et al. 1999; Nkhili et al. 2014). DL has been found as a sensitive and efficient method for monitoring of the aquatic environment state (Mielnik 2009; Prokowski and Mielnik 2012). So far, the studies of the interaction of humic acids with organic pollutants, using delayed luminescence, have not been conducted. Therefore, in this work, the interaction of humic acids isolated from peats with the herbicide using spectroscopic methods has been analyzed.

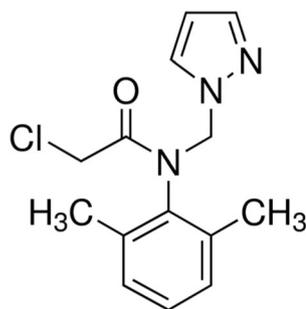
## 2 Material and methods

### 2.1 Materials

The five peatlands have been selected for the research in the southern and northern parts of Poland (1—drainage peatland located in the Orava-Nowy Targ Basin area, 2, 3—mountain fens located in the Babiogórski National Park area, and 4, 5—fen and raised bog, respectively, located in the Dolna Odra Valley area). Representative peat samples were collected from the surface layer (0–50 cm). The collected soil samples were transported directly to the laboratory, air-dried and milled.

Humic acids (HA1, HA2, HA3, HA4, and HA5) were isolated from studied peat samples according to the International Humic Substances Society procedure (Swift 1996). The extraction was performed in the following steps: (1) decalcitation of peat samples with HCl, (2) triple extraction with NaOH, (3) HA precipitation by HCl, (4) HA purification by redissolving in KOH with adding solid KCl, (5) HA reprecipitation by HCl, (6) washing out by redistilled water until the negative  $Cl^-$  test with silver nitrate  $AgNO_3$ , and (7) HA freeze-drying.

The study used Metazachlor 500 SC (*suspension concentrate*), a herbicidal preparation consisting of metazachlor [2-chloro-N-(pyrazol-1-ylmethyl)acet-2',6'-xylylide] as a biologically active substance (Fig. 1). It is a selective herbicide of soil and foliage application, designated to fight mono- and dicotyledon annual weeds in winter canola, spring canola, white head cabbage, red head cabbage, kale, and Brussels sprouts. The agent is absorbed by roots of



**Fig. 1** Chemical structure of metazachlor [2-chloro-N-(pyrazol-1-ylmethyl)acet-2',6'-xylylide]

germinating weeds and they are destroyed before emergence. It is also efficient in the case of weeds after emergence until the first pair of leaves appear. (Praczyk and Skrzypczak 2004; Włodarczyk 2014).

## 2.2 Analytical methods

In the soil samples, the following properties were determined: (1) pH in a 1:2.5 (*w/v*) soil: water suspension and 1 mol dm<sup>-3</sup> KCl solution, using the potentiometric method (Tan 2005), (2) the ash content in a muffle furnace at 500–550 °C, (3) the content of organic carbon (*C<sub>org</sub>*) using Orłow and Grindel's spectrophotometric method (Orłow et al. 1969), and (4) the content of total nitrogen (*N<sub>tot</sub>*) using LECO CNS 2000 automatic analyzer (LECO 1996).

Elemental C, H, and N analyses were performed on VARIO EL III Analyzer. Before the analysis, the HA samples were air-dried at 105 °C. The atomic ratios were expressed on an ash and water-free basis. The percentage of oxygen was calculated by subtracting the sum of C, H, and N from 100%.

The hydrodynamic diameters (*d<sub>h</sub>*) range 0.6–6000 nm of HA particles dispersed in 0.01 mol L<sup>-1</sup> NaOH solution with and without metazachlor was determined. The studies were performed using the Dynamic Light Scattering (DLS) method with the ZetaSizer Nano ZS apparatus (Malvern Ltd., UK) which is equipped with the He-Ne laser (633 nm). The back scattering technique (173°) was applied (Zetasizer Nano Series User Manual 2004). Measurements were done by the use of the “Size & Zeta potential” capillary cell in three replications with 12 sub-runs at the 20 °C.

The limitation of this method is that large particles mask the presence of smaller ones in the polydisperse sample. The intensity of scattered light is inversely proportional to the sixth power of the radius of particles smaller than the laser wavelength. In a consequence, bigger particles scatter light stronger than smaller ones (Filella et al. 1997).

Spectrophotometric UV-Visible measurements were performed using SPECORD UV-VIS M-42, a computer-aided dual beam spectrophotometer with the START software by Carl Zeiss Jena. HA preparations were dissolved in the 0.01 mol L<sup>-1</sup> NaOH solution. The 0.01 mol L<sup>-1</sup> NaOH

solution was also used as reference. Before and after adding of metazachlor, HA solutions subjected to photometry, showed carbon concentration of 0.005 mgC mL<sup>-1</sup>. The concentration of metazachlor in HA solutions was 0.45 mg mL<sup>-1</sup>. Before measurements, each solution went through a 0.45 μm syringe filter. Cuvettes were used of 1 cm path length.

Delayed luminescence measurements of HA solutions used an excitement and DL continuous registration set. The set was developed by the Department of Physics and Agrophysics, the West Pomeranian University of Technology in Szczecin, Poland.

Special light sensitive flow cuvettes are the main and the most important components of the set. They enable simultaneous excitation and DL continuous registration (Prokowski 2009, Pat. No. 200390).

The solution in question is placed in a container, content of which flows through the cuvette exposed to light combined with a measurement cuvette. The cuvette is exposed to monochromatic light passing through a removable illuminator. The solution then flows through the measurement cuvette and returns to the container, whereas the peristaltic pump maintains the flow of the solution.

DL of HA solutions was induced by blue (465–485 nm) and red (620–630 nm) light with irradiation photon flux density 1500 (μmol(quanta)PAR·m<sup>-2</sup> s<sup>-1</sup>). DL was registered 0.10 to 0.35 s after excitation. DL intensity was measured in the spectral range from 185 to 850 nm. DL measurements for HA solutions were conducted at the same carbon content 30 mg C L<sup>-1</sup> in 0.01 mol L<sup>-1</sup> NaOH without and with metazachlor at the same temperature of 25 °C. The metazachlor concentration in HA solutions was 450 mg L<sup>-1</sup>.

All measurements of the HA-herbicide systems were performed after 24 h.

## 3 Results and discussion

Based on their morphological and chemical properties, the studied peat soils can be classified as follows: (1) Eutric Murshic Sapric Histosols, (2) Eutric Sapric Histosols, (3) Eutric Hemic Histosols, (4) Eutric Fibric Histosols, and (5) Dystric Dranic Hemic Histosols according to the WRB guidelines (2015).

Data from the selected chemical parameters of studied peat samples are presented in Table 1. The studied peat soils showed various total nitrogen and organic carbon contents as well as pH and C/N ratio values. It seems most probable, that the intensity and direction of transformation occurring in the peat deposit are different.

Humic acids are heterogenic compounds developed by specific structures. Thus, the analytical approach to examining of their chemical composition enables determining approximate content of certain parts of their structure or groups; sometimes, the latter is subject to major error. The presentation of HA

**Table 1** The selected chemical parameters of studied peat samples

Peat samples	pH		Ash content (% d.m.)	C <sub>org</sub> g kg <sup>-1</sup>	N <sub>tot</sub> g kg <sup>-1</sup>	C/N
	H <sub>2</sub> O	KCl				
1	5.9	5.1	39.3	352.1	20.3	17.3
2	6.3	5.7	39.8	349.0	21.7	16.1
3	5.6	5.6	24.4	422.2	14.9	28.3
4	5.7	5.1	8.8	462.0	25.2	18.4
5	3.7	3.1	1.5	468.0	15.2	30.7

SD did not exceed  $\pm 5\%$

C<sub>org</sub>, organic carbon content, N<sub>tot</sub> total nitrogen content

composition expressed in the weight and atom percentage structure of particular elements is the most frequent method applied to describe and compare HA of different origin. Calculation and comparison of H/C and C/N ratios provides information regarding proportions between aromatic, aliphatic and heterocyclic systems in HA molecule (Gieguzynska et al. 2009). Elemental composition, atomic ratio, and internal oxidation of studied HA samples are reported in Table 2. The results showed that studied HA samples elemental composition is characteristic for HA isolated from peats (Szajdak et al. 2007, 2016; Huang et al. 2012).

Based on the H/C ratio, we can estimate the HA molecule “aromatization rate.” The lower H/C values, the higher HA molecule “aromatization rate.” The values of H/C atomic ratio in studied HA samples are in the range from 1.03 to 1.36 (Table 2). According to van Krevelen (1950) H/C atomic ratios from 0.7 to 1.5 correspond to aromatic systems coupled with aliphatic chains and contain up to ten carbon atoms.

According to Kumada (1987), the C/N ratio is used as an indicator of decomposition degree of organic matter. The highest values of C/N ratio were obtained in HA5 sample, while the lowest in HA3 sample. The observed differences in C/N ratios and the absence of those differences in H/C ratios indicate that the nitrogen content is the main factor differentiating examined HA samples.

On the basis of elemental composition, the value of internal oxidation (CQ) according to Kumada (1987) was calculated

based on the following equation  $CQ = [4C/(4C + H + 3 N - 2O)]$ . The internal oxidation reflects proportions between the sum of C-H bonds and the sum of all C-X bonds (X-electronegative heteroatom) in the HA molecule based on the total carbon content (Gieguzynska et al. 2009). The highest values of CQ were found in HA2 samples and the lowest in HA5 sample (Table 2).

The studies by Szajdak et al. (2007, 2016) showed that, the elemental composition of peat humic acids depended on the geobotanical nature of peat.

The UV-visible spectroscopy is a non-destructive and simple method that for many years has been applied to determine properties of humic acids. The resulting HA absorption spectrums are monotonic, non-characteristic and very similar to each other (Kumada 1987; Stevenson 1994). For this reason, the spectral coefficient of  $E_{465/665}$  ( $E_{4/6}$ ) calculated as the ratio  $A_{465}/A_{665}$  has been used. The ratio has negative values correlated primarily with the sizes of HA molecules and their molecular weight and the ratio of carbon content in the HA aromatic nucleus and aliphatic carbon in HA and the total carbon (Chen et al. 1977).

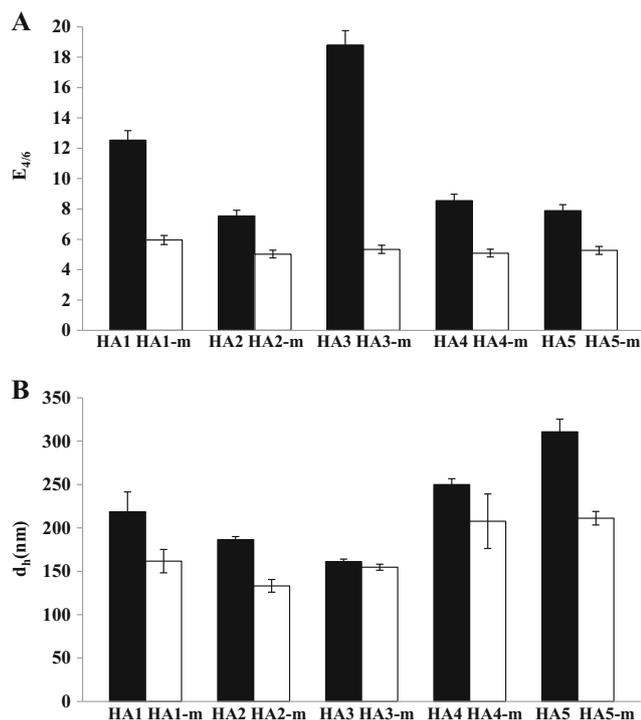
The obtained values of the spectral coefficient  $E_{4/6}$  ranged between 7.9 and 18.8 (Fig. 2). The largest particle size was found in the HA2 sample with the lowest  $E_{4/6}$  value, while the smallest particle size was found in the HA3 sample with the highest absorption coefficient value. The addition of metazachlor to HA solutions reduced the values of  $E_{4/6}$  coefficient by 33 to 72%. No significant changes were found between  $E_{4/6}$  after adding of metazachlor to HA solutions. Terschalk et al. (2004) also did not find statistically significant correlations between  $E_{4/6}$  of humic acids and adsorption of phenanthrene.

Humic acids have an amphiphilic nature, that is why they spontaneously form micelle-like structures in aquatic solutions, which are rather a variety of species of different molecular size (Palmer and von Wandruszka 2001; Chilom et al. 2009). Numerous studies have shown that the extent and type of HA aggregation depends on HA components, pH, ionic strength, type of electrolyte, and temperature (Palmer and von Wandruszka 2001; Terashima et al. 2004; Chilom et al. 2009; Wang et al. 2013). The obtained values of the

**Table 2** Elemental composition, atomic ratio, and internal oxidation of studied HA samples

HA samples	C In atomic %	N	H	O	H/C Atomic ratio	C/N	CQ
HA1	32.13 $\pm$ 0.30	1.84 $\pm$ 0.01	42.03 $\pm$ 0.60	23.99 $\pm$ 0.30	1.31 $\pm$ 0.03	17.44 $\pm$ 0.05	1.10 $\pm$ 0.01
HA2	30.94 $\pm$ 0.25	1.75 $\pm$ 0.02	42.04 $\pm$ 0.56	25.27 $\pm$ 0.29	1.36 $\pm$ 0.03	17.64 $\pm$ 0.03	1.13 $\pm$ 0.01
HA3	38.12 $\pm$ 0.26	2.84 $\pm$ 0.03	41.31 $\pm$ 0.05	17.73 $\pm$ 0.26	1.03 $\pm$ 0.01	13.43 $\pm$ 0.05	1.02 $\pm$ 0.01
HA4	38.23 $\pm$ 0.21	2.21 $\pm$ 0.02	41.66 $\pm$ 0.62	17.89 $\pm$ 0.42	1.09 $\pm$ 0.02	17.29 $\pm$ 0.19	1.00 $\pm$ 0.01
HA5	38.34 $\pm$ 0.42	1.29 $\pm$ 0.07	43.54 $\pm$ 0.24	16.83 $\pm$ 0.89	1.14 $\pm$ 0.04	29.92 $\pm$ 1.95	0.96 $\pm$ 0.02

CQ internal oxidation acc. Kumada (1987)— $[4C/(4C + H + 3 N - 2O)]$

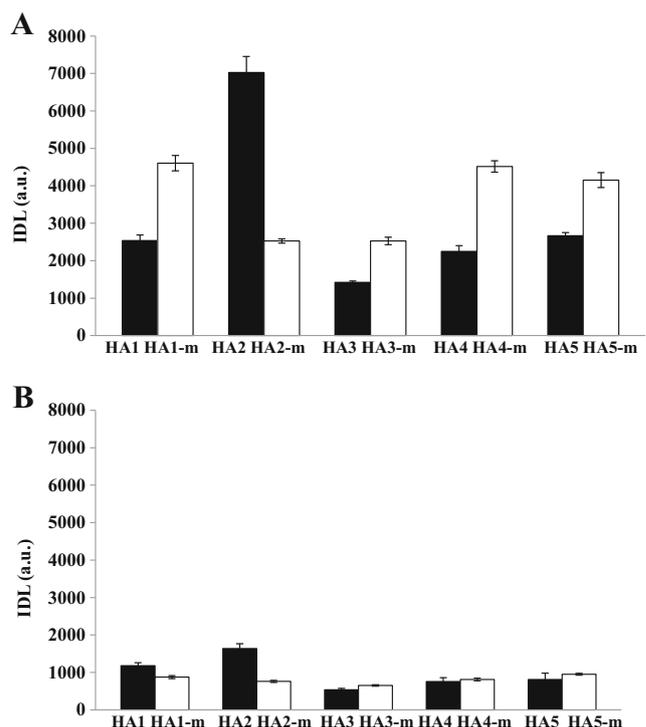


**Fig. 2** Values of  $E_{4/6}$  (a) and  $d_h$  (b) of studied humic acids solutions (HA1, HA2, HA3, HA4, HA5) and after adding of metazachlor (HA1-m, HA2-m, HA3-m, HA4-m, HA5-m)

hydrodynamic diameter ranged between 133.2 and 218.6 nm (Fig. 2). It was found that HA5 sample was characterized by the smallest hydrodynamic diameter, while the HA3 sample the largest. The addition of metazachlor to HA solutions reduced the values of  $d_h$  by 4 to 32%. The largest changes in hydrodynamic diameter value was observed in HA5 sample, which is characterized by the lowest nitrogen and oxygen content as well as CQ value, and the highest C/N ratio value.

Humic acids show their ability to emit electromagnetic radiation as delayed luminescence (e.g., Bejger et al. 2011; Mielnik 2013). Studies by Mielnik (2009), Mielnik (2013) and Prokowski and Mielnik (2012) showed that DL intensity of HA solutions depends on the excitation light wavelength and the quantity and quality of active centers (luminophores) in molecules of those substances. Humic substances are polyphenol-nitrogen polycondensates. Nitrogen-containing polycondensates may be systems characterized by the possibility of intramolecular energy transport, due to the fact that nitrogen is an element that has the capability of the  $\pi$ -charge accepting, and the  $\sigma$ -charge removing, with an unchanged total charge. Energy transport is also possible due to the presence of double bonds in HA molecules (Lakowicz 2006).

Figure 3 presents values of delayed luminescence intensity of HA solutions and after adding of metazachlor excited by blue (A) and red (B) light with irradiation photon flux density 1500 ( $\mu\text{mol}(\text{quanta})\text{PAR}\cdot\text{m}^{-2}\text{s}^{-1}$ ). Among studied HA, the highest value of DL intensity, excited both by blue and red



**Fig. 3** Values of delayed luminescence intensity (IDL) of studied humic acids solutions (HA1, HA2, HA3, HA4, HA5) and after adding of metazachlor (HA1-m, HA2-m, HA3-m, HA4-m, HA5-m) induced by blue (a) and red (b) light with irradiation photon flux density 1500 ( $\mu\text{mol}(\text{quanta})\text{PAR}\cdot\text{m}^{-2}\text{s}^{-1}$ )

light, in HA2 sample was observed. According to Mielnik (2009), the presence of the more aliphatic groups in the HA molecule, increased DL intensity.

It was noted that HA solutions excited by blue light (of the higher energy level  $E_{hv} = 2.69\text{ eV}$ ) showed higher DL intensity comparing to HA solutions excited by red light (with and without metazachlor). The addition of metazachlor to HA solutions increased delayed luminescence intensity induced by blue light, except the HA2 samples in which the addition of metazachlor reduced DL intensity. In the case of DL intensity of HA solutions excited by red light, addition of metazachlor increased delayed luminescence intensity in HA3, HA4, and HA5 samples, while in HA1 and HA2 samples, reduced.

The largest changes in DL intensity, excited both by blue and red light after herbicide addition, were observed in HA2 sample, which is characterized by the largest particle size, the highest oxygen content and CQ value as well as the lowest “aromatization rate” value.

### 4 Conclusions

The particle sizes of HA molecules measured by  $E_{4/6}$  coefficient do not impact on the particle sizes of HA-herbicide systems measured by the same ratio.

The delayed luminescence may become valuable, because it is simple, fast, and sensitive. Additionally, the results show minor errors comparing with chemical methods. This method may provide information about structure and nature of humic acids, as well as their photoreactivity. The using of delayed luminescence in studies of HA-pesticides interaction may enable us to better understand the luminescence properties of HA.

**Acknowledgments** Special thanks to Professor Andrzej Bieganski and Dr. Jolanta Cieřla from Institute of Agrophysics PAS, Lublin, Poland, for enabling me to make measurements of hydrodynamic diameter of HA solutions.

**Funding information** This research was supported by the National Centre of Sciences (NCS), Poland, projects no. N N305 396838 and N N305 107540.

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## References

- Aguer JP, Richard C, Andreux F (1999) Effect of light on humic substances: production of reactive species. *Analisis* 27(5):387–390. <https://doi.org/10.1051/analisis:1999270387>
- Aktar MW, Sengupta D, Chowdhury A (2009) Impact of pesticides use in agriculture: their benefits and hazards. *Interdiscip Toxicol* 2(1):1–12. <https://doi.org/10.2478/v10102-009-0001-7>
- Bejger R, Gołębiewska D, Nicia P (2011) The presence of humic-like substances in peat forming plants. *Water-Environ-Rural Areas* 11(33):21–29
- Boguta P, Sokołowska Z (2016) Interactions of Zn(II) ions with humic acids isolated from various type of soils. Effect of pH, Zn concentrations and humic acids chemical properties. *PLoS One* 11(4):e0153626. <https://doi.org/10.1371/journal.pone.0153626>
- Chen Y, Senesi M, Schnitzer M (1977) Information provided on humic substances by E4/E6 ratios. *Soil Sci Soc Am J* 41(2):352–358. <https://doi.org/10.2136/sssaj1977.03615995004100020037x>
- Chilom G, Bruns AS, Rice JA (2009) Aggregation of humic acid in solution: contributions of different fractions. *Org Geochem* 40(4):455–460. <https://doi.org/10.1016/j.orggeochem.2009.01.010>
- Cozzolino A, Conte P, Piccolo A (2001) Conformational changes of soil humic substances induced by some hydroxy-, cheto-, and sulphonic acids. *Soil Biol Biochem* 33(4-5):563–571. [https://doi.org/10.1016/S0038-0717\(00\)00196-6](https://doi.org/10.1016/S0038-0717(00)00196-6)
- D’Orazio V, Miano T (2016) Fluorescence properties of humic acid interaction products with s-triazine and bipyridilium herbicides and their Cu complexes: a multivariate approach. *J Soils Sediments*. <https://doi.org/10.1007/s11368-016-1611-2>
- Erkmen B, Yerli SV, Erk’akan F, Kolankaya D (2013) Persistent organochlorine pesticide residues in water and sediment samples from Lake Manyas, Turkey. *J Environ Biol* 34(2):171–176
- Fantke P, Charles R, Felipe de Alencastro L, Friedrich R, Joliet O (2011) Plant uptake of pesticides and human health: dynamic modeling of residues in wheat and ingestion intake. *Chemosphere* 85(10):1639–1647. <https://doi.org/10.1016/j.chemosphere.2011.08.030>
- Filella M, Zhang J, Newman ME, Buffle J (1997) Analytical applications of photon correlation spectroscopy for size distribution measurements of natural colloidal suspensions: capabilities and limitations. *Colloids Surf A Physicochem Eng Asp* 120(1-3):27–46. [https://doi.org/10.1016/S0927-7757\(96\)03677-1](https://doi.org/10.1016/S0927-7757(96)03677-1)
- Gevao B, Semple KT, Jones KC (2000) Bound pesticide residues in soils: a review. *Environ Pollut* 108(1):3–14. [https://doi.org/10.1016/S0269-7491\(99\)00197-9](https://doi.org/10.1016/S0269-7491(99)00197-9)
- Gieguzynska E, Amine-Khodja A, Trubetskoy OA, Trubetskaya OE, Guyot G, ter Halle A, Golebiowska D, Richard C (2009) Compositional differences between soil humic acids extracted by various methods as evidenced by photosensitizing and electrophoretic properties. *Chemosphere* 75(8):1082–1108. <https://doi.org/10.1016/j.chemosphere.2009.01.047>
- Huang SW, Chiang PN, Liu JC, Hung JT, Kuan WH, Tzou YM, Wang SL, Huang JH, Chen CC, Wang MK, Loeppert RH (2012) Chromate reduction on humic acid derived from a peat soil—exploration of the activated sites on HAs for chromate removal. *Chemosphere* 87(6):587–594. <https://doi.org/10.1016/j.chemosphere.2012.01.010>
- Jayaraj R, Megha P, Sreedev P (2016) Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdiscip Toxicol* 9(3–4):90–100. <https://doi.org/10.1515/intox-2016-0012>
- Kumada K (1987) Chemistry of soil organic matter. Japan Scientific Societies Press, Tokyo. Elsevier Scientific Publishing Company, Amsterdam Oxford New York
- Lakowicz JR (2006) Principles of fluorescence spectroscopy. Third Edition, Springer, New York. <https://doi.org/10.1007/978-0-387-46312-4>
- LECO (1996) CNS-2000 elemental analyzer—instruction manual. LECO Corp, St. Joseph
- Leita L, Margon A, Pastrello A, Arcón I, Contin M, Mosetti D (2009) Soil humic acids may favour the persistence of hexavalent chromium in soil. *Environ Pollut* 157(6):1862–1866. <https://doi.org/10.1016/j.envpol.2009.01.020>
- Mielnik L (2009) Application of photoinduced luminescence in research of humic substances of various origins. *Oceanol Hydrobiol Stud* 38(3):61–67
- Mielnik L (2013) Characterization of organic matter of lake sediments using photoluminescent methods. Habilitation thesis. Polish Humic Substances Society, Wrocław (in Polish)
- Morales J, Manso JA, Cid A, Mejuto JC (2013) Stability study of iprodione in alkaline media in the presence of humic acids. *Chemosphere* 92(11):1536–1541. <https://doi.org/10.1016/j.chemosphere.2013.04.020>
- Nkhili E, Boguta P, Bejger R, Guyot G, Sokołowska Z, Richard C (2014) Photosensitizing properties of water extractable organic matter from soils. *Chemosphere* 95:317–323. <https://doi.org/10.1016/j.chemosphere.2013.09.023>
- Oleszczuk P (2007) Organic pollutants in sewage sledge-amended soil. Part II Fate of contaminants in soils. *Ecol Chem Eng* 14(S2):185–198
- Orłow DS, Grisina LA, Jerosicewa HJ (1969) A guide-book of humus biochemistry. MGU, Moskwa (in Russian)
- Palmer NE, von Wandruszka R (2001) Dynamic light scattering measurements of particle size development in aqueous humic materials. *Fresenius J Anal Chem* 371(7):951–954. <https://doi.org/10.1007/s002160101037>
- Pandey AK, Pandey SD, Misra V, Viswanathan PN (1999) Role of free radicals in the binding of organochlorine pesticides and heavy metals with humic acids. *Sci Total Environ* 231(2-3):125–133. [https://doi.org/10.1016/S0048-9697\(99\)00090-X](https://doi.org/10.1016/S0048-9697(99)00090-X)
- Praczyk T, Skrzypczak G (2004) Herbicides. National Agricultural and Forestry Publishing House, Poznań (in Polish)
- Prokowski (2009) Integrated flow cell for determination of luminescence of liquids and suspensions Patent No 200390 (in Polish)

- Prokowski Z, Mielnik L (2012) Application of the long-term delayed luminescence for study of natural water environments, oceanography. In: Marcelli M (ed) InTech. <https://doi.org/10.5772/28478>
- Scaglia B, Baglieri A, Tambone F, Gennari M, Adani F (2016) Chlorpyrifos-methyl solubilisation by humic acids used as bio-surfactants extracted from lignocelluloses and kitchen wastes. *Chemosphere* 159:208–2013. <https://doi.org/10.1016/j.chemosphere.2016.06.008>
- Senesi N, D'Orazio V, Miano T (1995) Adsorption mechanisms of s-triazine and bipyridylum herbicides on humic acids from hop field soils. *Geoderma* 66(3–4):273–283. [https://doi.org/10.1016/0016-7061\(94\)00083-M](https://doi.org/10.1016/0016-7061(94)00083-M)
- Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions. John Wiley & Sons, New York
- Sun H, Zhu D, Mao J (2008) Sorption of polar and nonpolar aromatic compounds to two humic acids with varied structural heterogeneity. *Environ Toxicol Chem* 27(12):2449–2456. <https://doi.org/10.1897/08-124.1>
- Swift RS (1996) Organic matter characterization (chap 35). In: Sparks DL et al (eds) Methods of soil analysis. Part 3. Chemical methods. Soil Sci. Soc. Am. Book Series: 5. Soil Sci. Soc. Am. Madison, pp 1018–1020
- Szajdak L, Brandyk T, Szatyłowicz J (2007) Chemical properties of different peat-moorsh soils from the Biebrza River Valley. *Agron Res* 5(2):165–174
- Szajdak LW, Lapshina ED, Gaca W, Styła K, Meysner T, Szczepański M, Zarov EA (2016) Physical, chemical and biochemical properties of Western Siberia Sphagnum and Carex peat soils. *Environ Dyn Glob Clim Chang* 7(2):13–25. <https://doi.org/10.17816/edgcc7213-25>
- Tan KH (2005) Soil sampling, preparation and analysis. Taylor & Francis Group, Boca Raton, London, New York, Singapore
- Tankiewicz M, Fenik J, Biziuk M (2010) Determination of organophosphorus and organonitrogen pesticides in water samples. *TrAC Trends Anal Chem* 29(9):1050–1063. <https://doi.org/10.1016/j.trac.2010.05.008>
- Terashima M, Fukushima M, Tanaka S (2004) Influence of pH on the surface activity of humic acid: micelle-like aggregate formation and interfacial adsorption. *Colloids Surf A* 247(1–3):77–83. <https://doi.org/10.1016/j.colsurfa.2004.08.028>
- Terschalk JA, Henrichs SM, Shaw DG (2004) Phenanthrene adsorption and desorption by melanoidins and marine sediment humic acids. Final Report, OCS Study MMS 2004-001, Coastal Marine Inst., Univ. of Alaska Fairbanks, Fairbanks, AK
- Ukalska-Jaruga A, Smerczak B, Klimkiewicz-Pawlas A, Maliszewska-Kordybach B (2015) The role of soil organic matter in accumulation processes of persistent organic pollutants (POPs) in soils. *Polish J Agron* 20:15–23 (in Polish)
- van Krevelen D (1950) Graphical-statistical method for the study of structure and reaction processes of coal. *Fuel* 29:269–284
- Wang LF, Wang LL, Ye XD, Li WW, Ren XM, Sheng GP, Yu HQ, Wang XK (2013) Coagulation kinetics of humic aggregates in mono- and di-valent electrolyte solutions. *Environ Sci Technol* 47(10):5042–5049. <https://doi.org/10.1021/es304993j>
- Włodarczyk M, Buchwał A (2015) The behavior of metazachlor and clomazone immobilized in alginate matrix in water/soil and water/bottom sediment systems. *Przem Chem* 94(6):989–993
- Włodarczyk M (2014) Influence of formulation on mobility of metazachlor in soil. *Environ Monit Assess* 186(6):3503–3509. <https://doi.org/10.1007/s10661-014-3633-9>
- WRB (2015) World reference base for soil resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. World Soil Resources Reports No. 106, FAO, Rome
- Zetasizer Nano Series User Manual, MAN0317 (2004) Issue 1.1 Malvern Instruments Ltd., England
- Zivana O, Segal-Rosenheimer M, Dubowski Y (2016) Airborne organophosphate pesticides drift in Mediterranean climate: the importance of secondary drift. *Atmos Environ* 127:155–162. <https://doi.org/10.1016/j.atmosenv.2015.12.003>