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ORIGINAL PAPER

Sorption of pendimethalin by humin fraction isolated from the mollic horizon of Chernozems[*]

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Abstract

The aim of the research was to investigate interactions between pendimethalin (PE), an active substance of plant protection products, and the humin fraction (HM), which is the most recalcitrant component of soil organic matter. The soil material used for the study was collected from the mollic horizon of two Chernozems different in physicochemical properties. HM was obtained in the solid state after discarding humic acid (HA) and fulvic acid (FA) and digesting the mineral fraction in an HF-HCl mixture. Pure PE and two commercial products containing the substance (Penfox 330 EC and Stomp Aqua 455 SC), dissolved in hexane and added to the HM, were used in the research. The batch sorption experiment was carried out in accordance with OECD Guidelines for the Testing of Chemicals No.106. Spectroscopic methods (UV-Vis-nearIR and fluorescence) were used to assess the molecular characteristics of HM exposed to pesticides. The study showed significant differences in the molecular structures of the tested HM as a result of interactions with the pesticides used. The results revealed that PE had a different effect than the commercial products, and proved that the composition of commercial products significantly modified the strength and ability of organic matter to bind pesticides. This is probably related to the presence of adjuvants that are more competitive in forming bonds with the active sorption sites of HM, and thus strengthen or weaken the process of forming pesticide-HM complexes. As a result, the diversity of the molecular structure of HM and the presence of accompanying substances in commercial pesticide products interact, leading to different sorption mechanisms and durability of the resulting products.

Keywords: pesticides, pendimethalin, humin, batch sorption experiment, UV-Vis, Vis-nearIR, fluorescence

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INTRODUCTION

Modern agriculture uses a wide variety of synthetically produced chemicals including insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, and plant growth regulators to protect plants cultivation and support agricultural production (Gevao et al. 2000). Nevertheless, excessive use of pesticides poses direct and indirect risks for most of the soil ecosystem functions (Aktar et al. 2009). Among various agrochemicals, herbicides are useful compounds that limit weed growth to increase global crop yield and quality. Among the commercialized dinitroaniline herbicides, there are several active substances from this group, including pendimethalin (PE), that have been approved by EFSA for marketing in the EU countries.

Pendimethalin (PE) PE (3,4-Dimethyl-2,6-dinitro-N-(pentan-3-yl)aniline) is a selective, systemic herbicide used for weed control of many crop species (wheat, corn, soybeans, potatoes, cabbage, peas, carrots, and asparagus) and some ornamental plants. The mechanism of its action is to inhibit the formation and function of microtubules and mitotic cell divisions in weeds. PE is uptaken by seedlings of grasses and dicotyledonous weeds through the roots during application to the soil cover, or through the leaves directly after spraying on plants (Kulshrestha et al. 2000, Anyszka et al. 2011). PE is a highly hydrophobic compound ($\log K_{ow} > 5$), thus it is classified as a non-leaching compound with high sorption affinity to soil particles (Zheng et al. 1993, Chopra et al. 2010, Sondhia 2012). These properties shape its resistance to degradation (half-life of 72-172 days in soil) with persistence related to the: (1) soil factors – soil type, soil chemical diversity, soil organic matter (SOM) composition and microbial activity; (2) herbicide physico-chemical properties – water solubility, vapour pressure, susceptibility to biodegradation processes; (3) climatic conditions – humidity, temperature, sunlight irradiation (Pat et al. 1991, Zheng et al. 1993, Kulshrestha et al. 2000, Serrano et al. 2010, Bejger et al. 2014, Carpio et al. 2021). However, according to the Kulshrestha et al. (2000) and Sondhia (2012), it may be rapidly degraded under anaerobic conditions of flooded soils, and slowly degraded by some aerobic microorganisms in favourable soil agroecological conditions.

Recent studies have shown that the sequestration capacity of pesticides is strongly connected to the content and composition of SOM (Pignatelo 2012, Ukalska-Jaruga et al. 2023, Ćwieląg-Piasecka 2023). Soils with the same organic matter content may have different sorption affinity for pesticides and other organic contaminants. It has been reported that structure characteristics (aromaticity and aliphaticity), spatial arrangement, physical conformation and polarity of SOM strongly affect its sorption capacity (Pignatello 2012). SOM contains various components, mainly humic acids (HA), fulvic acids (FA), humin (HM), kerogen, bitumen and black carbon (Tan 2014, Hayes, Swift 2020). Different SOM components vary remarkably in structure and composition, and therefore show deviated sorption properties of organic contaminants. Compared with HA and FA, HM and kerogen are more enriched in crosslinked, condensed structures, resulting in higher sorption affinity for nonpolar solutes (Luo et al. 2008, Ukalska-Jaruga et al. 2023). Some studies proved that sorption of hydrophobic organic compounds on SOM is controlled by aromatic carbon (Hayes et al. 2017), while others showed that sorption was controlled by aliphatic carbon (Kang, Xing 2005). Nevertheless, the polarity of SOM was reported to be a limiting factor for the sorption of hydrophobic organic compounds (Kang, Xing 2005).

The chemical properties of pesticide active substances as well as their cooccurrence with other commercial preparation components, i.e. surfactants, coagulants, decomposition inhibitors, buffer and synergistic substances or adjuvants (Laha et al. 2009, Włodarczyk et al. 2009, Włodarczyk 2014) can significantly modify interactions with soil components. For example, adjuvants use in a pesticide's formulation can change the effectiveness and phytotoxicity of the final product. Moreover, the solvents and additives present in commercial products may also affect the environmental impact, as dispersion patterns may be altered and the functional activity period of the active ingredient may be extended or limited. In turn, the buffer substances are responsible for the pH maintenance of pesticide emulsion (Cycoń, Piotrowska-Seget 2006). Furthermore, components of commercial formulations may enter the aquatic environment, through direct runoff and leaching, and affect species from aquatic communities (Giglio and Vommaro 2022). The up-to-date environmental and ecotoxicological studies indicate that PE used in the form of a commercial product may exhibit severe toxic effects on animals, humans and ecosystems (Dimitro et al. 2006, Sondhia 2012, Giglio and Vommaro 2022, Wang et al. 2022). Therefore, it is essential to verify the environmental fate of this herbicide, also considering the other ingredients of a commercial preparation which substantially modulate the behavior of the active substance.

Kočárek et al. (2018) confirmed that the addition of adjuvants present in commercial products significantly increased the sorption and dissipation half-life time of pendimethalin in the topsoil layer. Oliveira et al. (2020) pointed out that even the addition of vegetable oil may significantly decrease pendimethalin retention in the soil and could significantly improve weed control by irreversible processes. Similarly, Khan et al. (2017) indicated highly significant effect of commercial formulation on the leaching behaviour of the herbicide relative to the pure active substance. The pesticide adsorption is a result of the physical and chemical properties of soil and pesticides (water solubility, half-life, distribution coefficient Koc, and the dissociation constant in the case of ionizable pesticides). Occurring processes may be also affected by soil moisture and temperature, and ultimately by the ionic strength due to the presence of another substance.

Sorption and desorption of organic compounds in soil are mainly regulated by SOM (Gunasekara, Xing 2003), whose different components can indicate different properties and sorption abilities. Among the SOM fractions, HM is considered to be the most important one for the accumulation of hydrophobic organic components. Several investigations deemed that as residence time increases, pesticides tend to be transferred from FA and HA to HM, where they are strongly retained as bound residue (Zhang et al. 2008). There are few studies discussing the characteristics of HM that contains a variety of functional groups, such as carboxyl, phenol-hydroxyl, quinone, and methoxy groups (Almendros, González-Vila 1987, Rice, MacCarthy 1988, Simpson et al. 2007, Song et al. 2011, Hayes et al. 2017, Hayes, Swift 2020). They provide multiple sites for incorporation of organic contaminants. However, the interaction of HM with pesticides is still not fully recognized. The aim of the research was to assess the interaction between PE and HM, which is the most abundant organic carbon pool in soil and represents the SOM fraction that is the most resistant to microbiological decomposition. For this purpose, a bath sorption experiment according to OECD guidelines no. 106 was carried out with the saturation of HM with PE, as well as its two commercial products (Penfox 330 EC and Stomp Aqua 455 SC). To better understand the processes occurring during the sorption of PE on HM and the stability of the interactions formed, the following spectroscopic methods were applied: fluorescence and ultraviolet-visible-near infrared (UV-Vis-nearIR).

MATERIALS AND METHODS

Soil samples

Soil samples were collected from the mollic horizon of two Chernozems derived from silt loam in different regions of Poland. Five soil samples were taken from randomly selected places of a given site, then mixed and treated as one composite sample. The bulk soil samples were air-dried, the remains of plants were removed, and then the material was sieved through a sieve with diameter of 2 mm. The basic properties of soils labelled as 9H and 7T are presented in Table 1.

Table 1

Basic properties of the mollic horizon of investigated soils

Soil	pH (KCl)	$CaCO_3$	TOC	TN	TOC/TN	CEC	HA	FA	HM	USDA textural class
		(g kg^{-1})					(% of C)			
9H	7.52	32.6	39.9	2.90	13.7	52.5	26.54	24.34	49.12	silt loam
7T	5.64	5.1	41.7	3.39	12.3	53.2	2TOC3.18	32.47	44.35	silt loam

TOC – total organic carbon, TN – total nitrogen, CEC – cation exchange capacity [cmol(+) kg^{-1}], HA – humic acids, FA – fulvic acids, HM – humin fraction

Isolation of HM

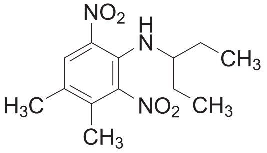
The isolation of HM was described in our previous publication (Weber et al. 2022). Briefly, HA and FA were extracted with NaOH, then the remaining material was digested with HF-HCl mixture to remove the mineral fraction. Finally, the material was neutralized, purified by dialysis and freeze dried. The HM obtained was a mixture of various groups of organic compounds strongly associated with the mineral fraction of the soil, highly resistant to decomposition processes.

Pendimethalin chemical characterization

Pure pendimethalin (PE) and two different commercially available formulations of PE based-herbicide were used in the experiment: emulsifiable concentrate Penfox 330 EC (PFX) and concentrated suspension Stomp Aqua 455 SC (STQ). The reference analytical standard of PE of 99.8±0.1% purity was provided by Merck (Darmstadt, Germany). Selected physical and chemical properties of PE are presented in Table 2.

Table 2

Selected physical and chemical characteristics of PE (Kathleen et al. 2016)

Structure diagram	IUPAC name	N-(1-ethyloprophyl)-3,4-dimethyl-2,6-dinitroaniline
	physical state chemical formula molecular mass solubility in water octanol/water partition coefficient	orange-yellow crystals $C_{13}H_{19}N_3O_4$ 281.31 g mol^{-1} 0.33 mg dm^{-3} at 20°C $\log K_{ow}$= 5.4 at 20°C

Sorption/saturation experiment

The sorption/saturation experiment was carried out according to the OECD Guidelines for the Testing of Chemicals No. 106. PE and its two commercial formulations were dissolved in hexane and added to HM to obtain its 100% saturation with pesticides. All analyses were performed at a constant carbon concentration of the HM (C_{HM} = 0.5 g dm^{-3}) to ensure the same saturation conditions for each sample. The settings of the experiment were selected on the basis of the values of the K_{oc} coefficients of PE and its absorption potential on soil components given in the OECD Guidelines for the Testing of Chemicals No. 106. The experiment was performed at 20°C, under dynamic conditions, where the ratio of HM to the volume of the solution was 1:100. The samples were closed with corks and equilibrated in laboratory shakers for 24 h. After shaking, hexane was decanted and evaporated for 24 h to the dry weight of the sample. The saturation process was optimized according to the experiment presented previously by Ukalska-Jaruga et al. (2023*b*).

Spectroscopic characteristics

UV-Vis spectra

UV-Vis spectra were recorded using a Jasco 770 UV-VIS-NIR spectrophotometer. The spectra were recorded in the wavelength range from 220 nm to 760 nm and referred to as a blank spectrum, at a constant laboratory temp. of 20°C. Prior to analysis, HM samples were dissolved in DMSO+H_2SO_4 solution (vv 94%÷6%), while maintaining a constant HM carbon content at 10 mg dm^{-3}. The mixtures were pre-exposed to ultrasounds twice for 10 min to obtain homogeneous solutions, and then shaken on a horizontal shaker for 24 h. Each solution was pre-filtered through a pleated paper filter with a pore size of 0.2 mm, and then through a syringe filter with a pore size 0.45 µm. The absorption spectra obtained were used to calculate the values of selected optical parameters: e_{255}, e_{280}, e_{600}, E_{255}:E_{280}, E_{255}:E_{436}, E_{465}:E_{665}.

Vis-nearIR spectra

Spectral measurements were performed using a PSR-3500® spectroradiometer (Spectral Evolution, Lawrence, KS, USA) in the nearIR spectral range (700-2500 nm). The instrument worked in the mode of 2 nm sampling intervals and a spectral resolution of 3.5, 10, and 7 nm from 700 to 1000 nm, 1500 nm and 2100 nm, respectively. Data were interpolated to 1 nm. The scanning involved the use of a cuvette bundle for measurements (absorption – transmission mode). The calibration solution (used every 5 samples) was 0.01 M HCl. The cuvette was placed under a cover to avoid interferences with the outside light.

The Savitzky-Golay derivative procedure was applied to the spectra acquisition and to compute the first, second, third and fourth order derivatives. The Savitzky-Golay algorithm is based on performing a least squares linear regression fit of a polynomial around each point in the spectrum to smooth the data. The resulting derivative is then the derivative of the fitted polynomial at each point. The algorithm includes a smoothing factor that determines how many adjacent variables will be used to estimate the polynomial approximation of the curve segment. In the research, one transformation with the following steps: polynomial order = 2, left points = 2, right points = 2, range columns = 1-2151 was applied.

Fluorescence spectra

Fluorescence spectra were recorded using a Hitachi F 7000 spectrofluorometer. The solutions were placed in a non-fluorescent quartz cuvette with a path length of 1 cm and thermostated at 20°C. Fluorescence emission spectra were recorded for selected excitation wavelengths. The three-dimensional fluorescence excitation-emission matrix spectra (EEM) were collected with successive scanning emission spectra from 250 to 650 nm, varying the excitation wavelength from 200 to 600 nm. The width of the monochromators for the excitation and emission bands was 5 nm and 10 nm, respectively, and the scanning speed was 1200 nm min^{-1}. Solutions for measuring fluorescence spectra were prepared similarly to those for the UV-Vis analysis.

RESULTS AND DISCUSSION

UV-Vis spectra

A large number of types of chromophores, their individual/independent concentration and the lack of a unique absorption band mean that the UV-Vis spectra of SOM are usually broad and devoid of characteristic features (Hayes, Swift 1978, Pansu, Gautheyrou 2006, Giovanela et al. 2010, Mayhew et al. 2023). For this reason, molar absorption and absorbance coefficients are used in data interpretation.

In SOM molecules, the chromophores absorbing in the UV region are mainly aromatic groups with various degrees and types of substitution – e.g. mono- and/or polysubstituted phenols and/or various aromatic acids (Korshin et al. 1997, Enev et al. 2018). The absorption spectra of HM obtained in our research were distinguished by the presence of a unique broad band in the region of 245-310 nm with two specific peaks at wavelengths of 255 nm and 280 nm (Figure 1). In the UV region, both 7T and 9H samples showed similar absorbance, which was also reflected in the values of molar absorption coefficients ε_{255} and ε_{280} (Table 3). As the wavelength increased, the differences between 7T and 9H became more distinctive; 9H showed relatively higher absorbance in the Vis region than 7T (see ε_{600} values). Differences in the intensity of the occurring maxima resul-

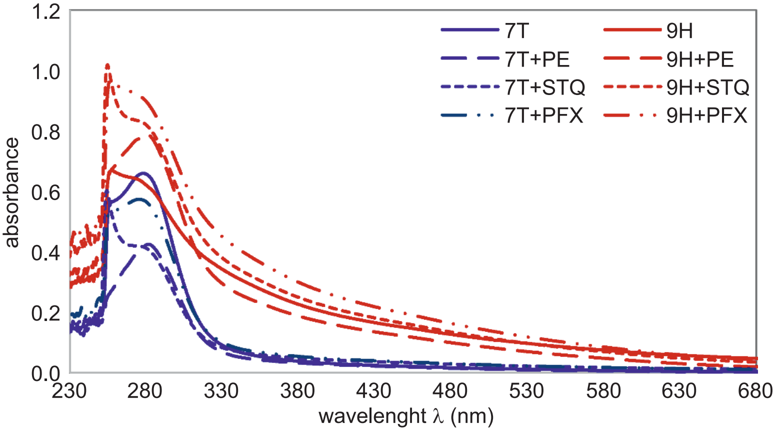


Fig. 1. UV-Vis spectra of the analyzed HM, and HM saturated with PE (7T+PE, 9H+PE), and its commercial preparations: Stomp Aqua 455 SC (7H+STQ, 9T+STQ) and PFX-Penfox 330 EC (7H+PFX, 9T+PFX)

Table 3

Values of the optical coefficients calculated from UV-Vis spectra

Specification	UV-Vis coefficient					
	ε_{255}	ε_{280}	ε_{600}	E_{255}:E_{280}	E_{255}:E_{436}	E_{465}:E_{665}
7T	55.6	65.7	0.68	0.65	23.7	4.82
7T+PE	26.2	42.2	0.48	0.57	12.3	8.56
7T+STQ	60.2	41.2	1.59	1.46	17.0	2.42
7T+PFX	53.4	56.6	1.59	0.83	13.9	2.77
9H	66.5	62.1	6.71	0.90	4.2	2.75
9H+ PE	65.9	78.8	4.02	0.74	5.1	4.98
9H+STQ	101.6	82.0	6.00	1.23	5.8	3.85
9H+PFX	96.4	89.8	7.35	0.94	4.6	3.81

ted from different properties of the HM themselves, as well as the sorption potential of the pesticides. Thus, they may indicate various content and/or arrangement of individual chromophore groups in the structure of the HM, which are responsible for the absorption of electromagnetic radiation in this area.

In general, the addition of pesticides reduced the absorption in the UV range, as it was observed in the 7T sample, while the effect was opposite in the 9H sample. This indicates differences in spectroscopic properties of both HM. The effect of the interaction of various formulations containing pendimethalin with HM, changing their absorption capacity, is reflected in the values of the calculated molar absorption coefficients (ε_{255}, ε_{280}, ε_{600}) and absorbance coefficients (E_{255}:$E_{280,}$ E_{255}:E_{365}) presented in Table 3. Changes in the values of these parameters suggest preferential modification (blocking or activation) of aromatic chromophores, depending on the properties of the HM themselves and the chemical composition of the applied commercial products. According to some studies (Korshin et al. 1997, Morán Vieyra et al. 2009, Enev et al. 2018), the addition of commercially available products can promote the substitution of aromatic rings with polar groups (hydroxyl, carbonyl, carboxyl groups), which causes a decrease in ε_{280} and consequently an increase in E_{255}:E_{280} coefficients.

However, the decrease in the ε_{255} value and consequently the E_{255}:E_{280} ratio in HM after the addition of PE may indicate the substitution of aromatic rings with aliphatic functional groups. In the Vis area, the addition of commercial PE preparations increased the absorbance in the case of both 7T and 9H samples, while the addition of PE decreased the absorbance in both HM over the entire visible range, with particularly high absorption losses observed in the long-wave region. The impact of the pesticides introduced into the sample matrix may influence changes in electronic interactions between chromophores, in particular between intramolecular charge transfer (CT) complexes, determining the absorbance in the range above ca 370 nm

(Sharpless et al. 2014). The observed changes in the values of the E_{255}:E_{436} ratios suggest that CT complexes were probably destroyed by the degradation of donor and/or acceptor groups under the influence of the additives used (and by reducing the molecular weight/size of the tested HM).

In the literature discussing SOM, the most commonly used coefficient is E_{465}:E_{665}. The detailed study carried out by Chen et al. (1977) showed that the E_{465}:E_{665} ratio depended mainly on the molecular size. The PE saturation resulted in an increase in E_{465}:E_{665} values in both samples, while the addition of its commercial products caused different effects; increase in 9H and decrease in 7T samples. This phenomenon is difficult to explain unambiguously, but it may suggest different directions of changes in the molecular size or molecular weight of both HM.

Vis-nearIR spectra

The results indicated that the sorption potential of pesticides towards HM varied depending on the HM properties as well as the chemical composition of commercial products (Figure 2). The higher sorption effects of PE was observed in 9H sample, for which the reflectance was achieved at 35%, compared to the 7T with reflectance at the level not exceeding 26%. Generally, the sorption capacity of the pesticide varied depending on the accompanying substances occurring in the STQ and the PFX added, compared to the pure substance and HM without pesticide addition. Saturation with the STQ caused an increase in the spectral parameters of 7T sample, while the same effect in 9H sample was observed only in the first range of wavelength (from 3500 to 1800 nm). The PFX reduced reflectance only in the 7T sample, compared to PE effect. Nevertheless, the addition of commercial products did not significantly change the shape of the spectrum with maintaining the observed band fluctuations, but affected only their intensity. Thus, STQ and PFX modified vibrations in aromatic structures and C-H symmetric and asymmetric stretching of aliphatic groups at 1st overtone region (>2000 cm^{-1}). Moreover, small fluctuations were recorded at 2nd overtone region (12 000-1500 cm^{-1}) within the vibration bands for symmetric C-O stretching in celluloses, hemicelluloses and lignin groups CxHy aliphatic and cyclic, Si-O-Si asymmetric vibration, C-OH stretching in phenols, ethers and alcohols (Mortimore et al. 2004, Vaz 2018). Therefore, not every single relationships can be recognized, especially in the aspect of diffusion and mutual agglomeration of the analyzed molecules.

Fluorescence spectra

Fluorescence analysis can provide important information about similarities or differences in the structure and function of an organic substance. This technique can also be used to understand the mechanisms of intramolecular and intermolecular interactions between organic chemicals occurring in SOM (Boguta et al. 2016). Figure 3 shows the EEM spectra, which reveal

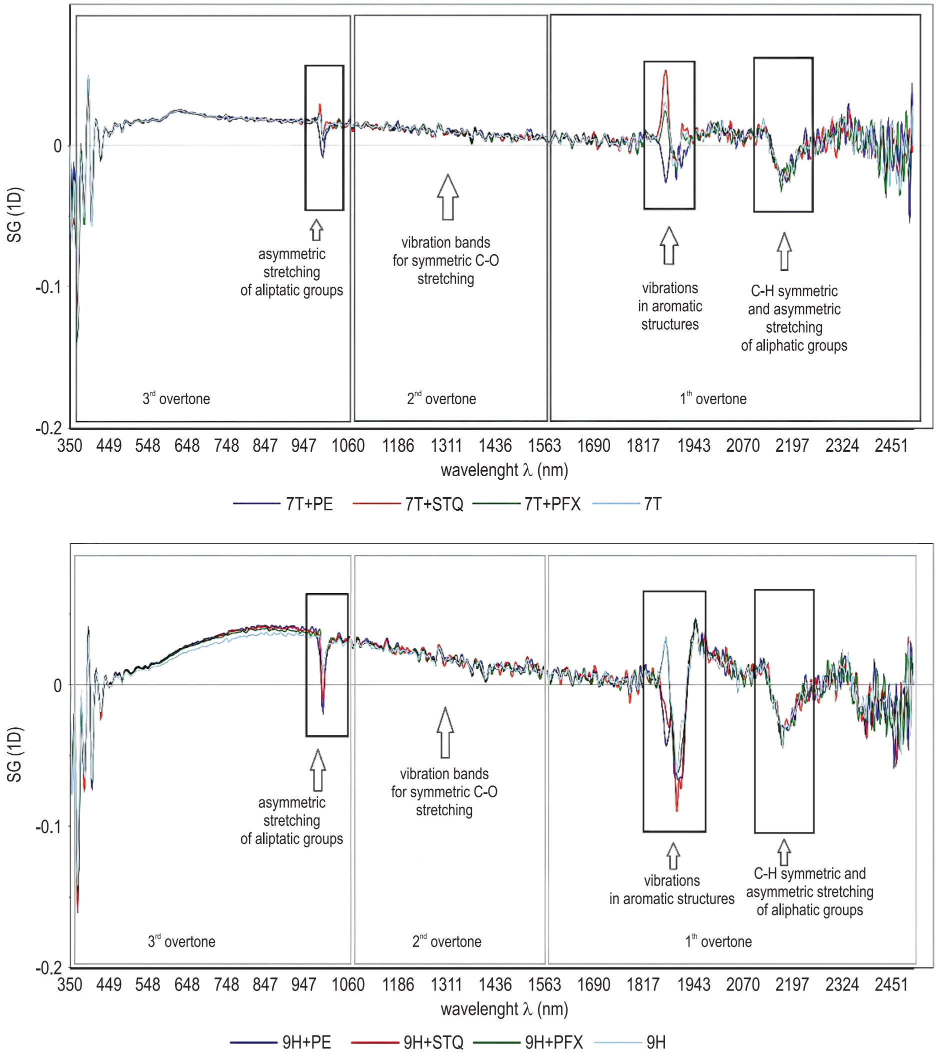


Fig. 2. Reflectance spectra of non-contaminated HM (7H, 9H), and HM saturated with PE (7T+PE, 9H+PE), and its commercial preparations: Stomp Aqua 455 SC (7H+STQ, 9T+STQ) and PFX-Penfox 330 EC (7H+PFX, 9T+PFX), after Savitzky-Golay derivative procedure

the presence of various fluorophores and, consequently, enable the observation of changes in the structures of the studied HM. The fluorescence features of the HM indicated their different origins as well as the nature of interactions with the PE formulations studied. The EEM contours showed the presence of four main fluorescence regions at the following excitation and emission wavelengths $\lambda_{ex}/\lambda_{em}$: 280-340/350-420 (peak A), 350-380/400-460 (peak B), 310-340/480 -520 (peak C) and 430-460/490-540 (peak D) corresponding to the presence of different, similar to humus-like structures, types

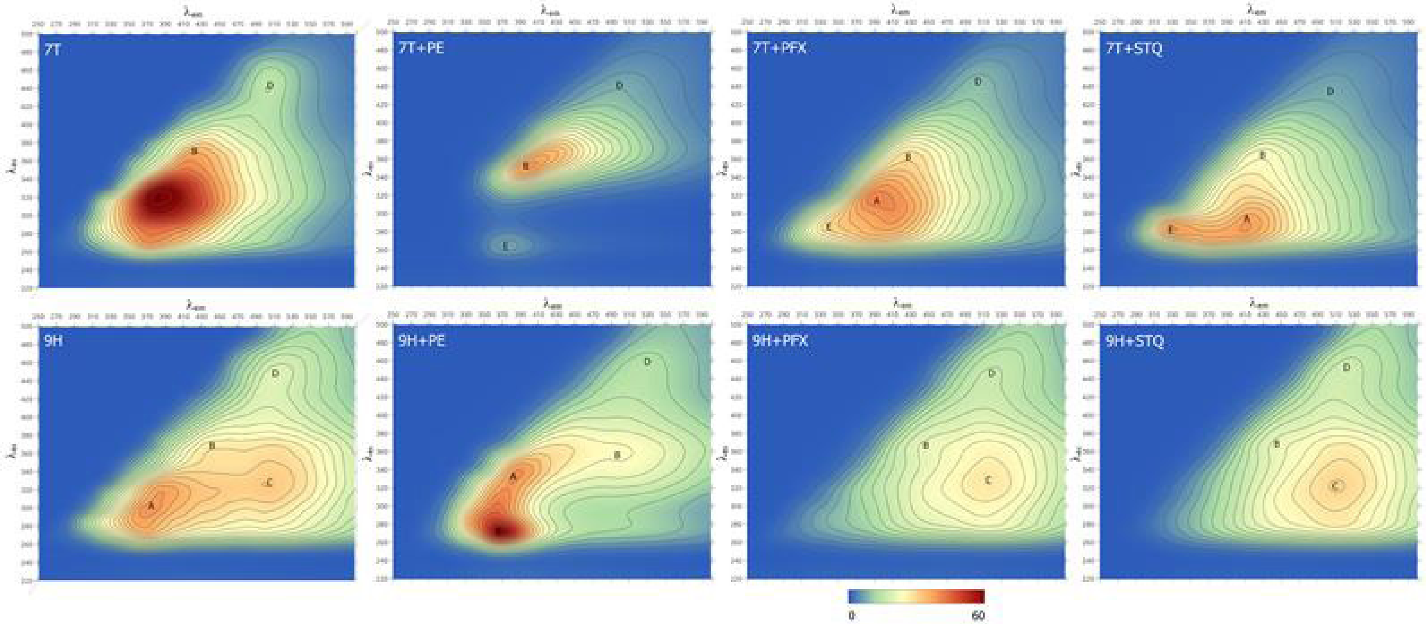


Fig. 3. EEM spectra non-contaminated HM (7H, 9H), and HM saturated with PE (7T+PE, 9H+PE), and its commercial preparations: Stomp Aqua 455 SC (7H+STQ, 9T+STQ) and PFX-Penfox 330 EC (7H+PFX, 9T+PFX).

Table 4

Characteristic EEM maxima and intensity of the fluorescence (IFl)

Specification	A		B		C		D		E	
	$\lambda_{ex}/\lambda_{em}$	IFl	$\lambda_{ex}/\lambda_{em}$	IFl	$\lambda_{ex}/\lambda_{em}$	IFl	$\lambda_{ex}/\lambda_{em}$	IFl	$\lambda_{ex}/\lambda_{em}$	IFl
7T	320/385	66.0	370/420	37.8	-	-	440/505	15.0	-	-
7T+PE	-	-	355/400	39.0	-	-	440/503	7.8	266/376	6.7
7T+STQ	285/410	38.5	365/430	24.0	-	-	440/505	7.0	285/335	38.0
7T+PFX	315/395	41.0	370/425	28.8	-	-	440/505	9.4	290/345	31.3
9H	315/370	38.5	370/440	27.2	320/500	32.5	440/510	19.8	-	-
9H+PE	335/385	40.0	360/500	24.5	-	-	455/530	13.4	275/370	60.0
9H+STQ	-	-	370/435	20.0	320/510	30.5	450/520	17.2	-	-
9H+PFX	-	-	370/435	19.5	330/515	27.7	440/515	16.6	-	-

of fluorophores. The location of the characteristic fluorescence maxima and their intensity for individual samples are presented in Table 4.

The positions of the observed peaks showed a shift in the long-wave direction (red-shift), which is typical for “mature” SOM with a relatively high degree of transformation. They can be attributed to the increased range of the π-electron system and the presence of heterocyclic N-atrazine atoms (D ‘Orazio, Miano 2016). Peak A and peak B can be attributed the presence of simple structural components with high molecular heterogeneity and low degree of aromatic polycondensation (Plaza et al. 2006). In turn, peaks C and D may indicate the participation of more stable forms of terrestrial humus-like structure. Long-wave emission can be attributed to the presence of an extended, linearly condensed network of aromatic rings and other unsaturated bond systems capable of a high degree of conjugation in high molecular weight and well humified units (Plaza et al. 2006). Interestingly, peak C is only observed in the fluorescence of 9H samples.

The EEM spectra obtained indicate that the investigated HM do not exhibit short-wave excitation fluorescence (λ_{ex} = 220-240 nm), which is characteristic for other organic matter fractions, especially for ones originating from the aquatic environment (Hur, Kim 2009, Mielnik, Kowalczuk 2018). Upon the addition of PE and commercial preparations, the maximum fluorescence in the area of $\lambda_{ex}/\lambda_{em}$ = 285-290/335-370 nm (peak E) appeared, which may indicate the modification of HM structure towards its opening (Gosh, Schnitzer 1980). Discussed fluorophore groups may constitute specific “fingerprints” that may reflect differences in HM structure and mechanisms of interaction with organic pollutants.

For better visualization of the results, monodimensional fluorescence emission spectra for λ_{ex} = 310 nm, λ_{ex} = 370 nm and λ_{ex} = 460 nm were analyzed (Figure 4). The main feature of organic matter emission spectra is the

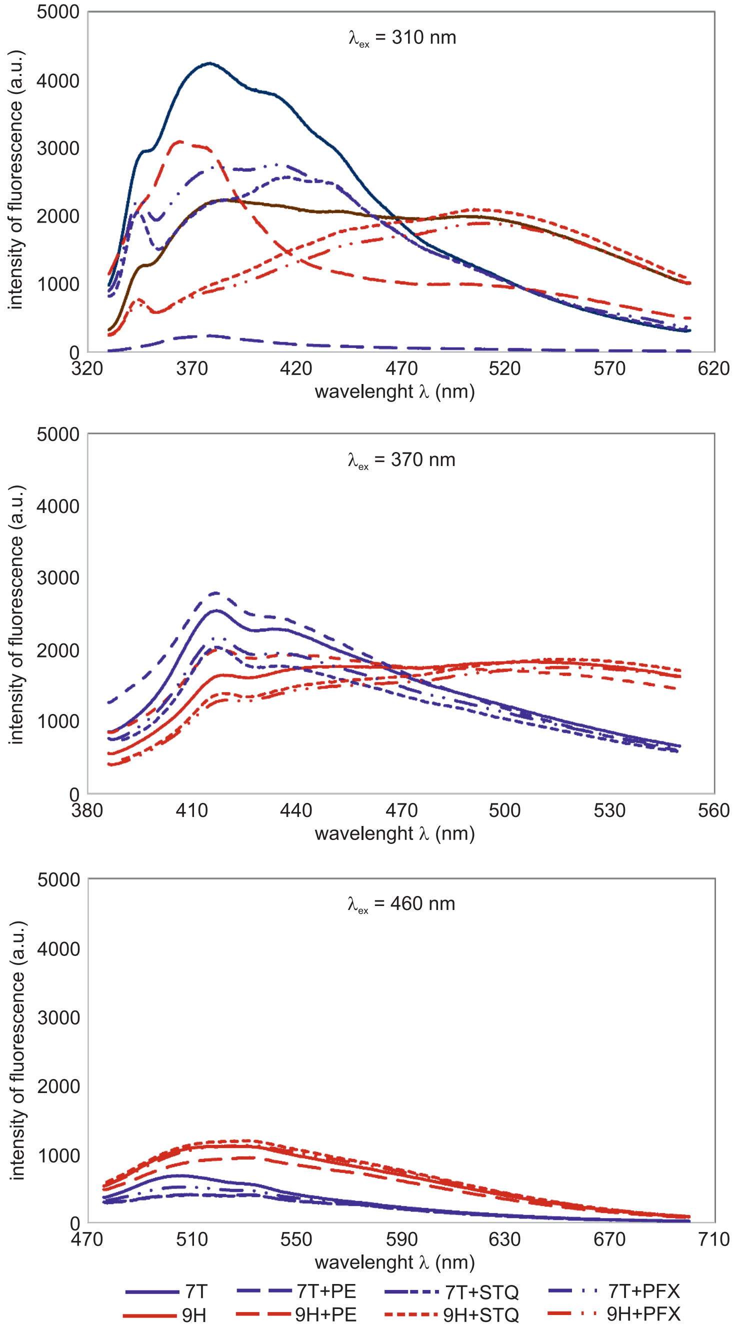


Fig. 4. The emission fluorescence spectra obtained with 310 nm, 370 nm and 465 nm excitation wavelength of investigated non-contaminated HM (7H, 9T), and saturated with PE (7T+PE, 9H+PE) and its commercial preparations: STQ (7T+STQ, 9H+STQ) and PFX (7+PFX, 9T+PFX)

broadband maximum. Short-wave excited emission spectra (λ_{ex} = 310 nm and λ_{ex} = 370 nm) differ in shape, fluorescence intensity and the location of the main maxima. The differences observed indicate differences in the structure of the tested HM and a different nature of the interactions between the HM and the pesticide products. The higher fluorescence emission of non-contaminated 7T is due to their less complex molecular structure and/or greater symmetry (Senesi et al. 1991, Mielnik et al. 2021), compared to non-contaminated 9H. Moreover, the presence of the main fluorescence peak in 7T in the shorter wavelength region suggests the presence of simple structural components with high molecular heterogeneity in non-contaminated HM, as well as a low level of conjugated fluorophores (Pedra et al. 2008). In turn, the fluorescence maximum for non-contaminated 9H, appearing in the region of longer wavelengths, indicates the presence of a highly condensed aromatic ring and other unsaturated bond systems, and a high degree of conjugation. These differences may result from different structure packing density, average macromolecule size, number and composition of fluorophores, and possible intramolecular energy transfer routes.

The addition of commercial products, both STQ and PFX, evoked significant fluorescence decrease within the wavelength range of 330-470 nm of both HM. A different interaction effect was observed in the case of PE. This almost completely quenched fluorescence within the entire recorded spectrum range of 7T+PE. In the case of 9H+PE, a significant increase in fluorescence intensity with a broad band with a maximum at 370 nm in the short-wave part of the spectrum was observed, while in the long-wave part of the spectrum the fluorescence was quenched. Fluorescence quenching may result from the formation of a non-fluorescent ground state complex due to the interaction between the fluorophore and the quencher (Pan et al. 2021).

The long-wave excited spectra (λ_{ex} = 460 nm) obtained were similar in shape, which indicates a strongly shaped aromatic core of the molecule. Long-wave induced fluorescence is characteristic of a more stable internal structure. According to Milori et al. (2002), at λ_{ex} = 465 nm primarily semiquinone-type radical structures, which constitute the core of the molecular structure of humic substances, are excited. The main differences between the spectra obtained concerned primarily the fluorescence intensity and the location of the main maxima. The spectra of 9H showed greater intensity, and their maxima were slightly shifted towards longer wavelengths compared to 7T.

CONCLUSIONS

The results provided the key information useful for predicting the interactions of HM and pesticides, which can be considered in terms of their potential transformation and migration in the environment. They proved that the composition of commercial products significantly determines the strength and ability of stable organic matter to bind pesticides. The analyses of the spectroscopic properties of PE saturated HM, which is the most abundant organic carbon pool in soil and represents the most resistant to microbiological decomposition SOM fraction, showed a significant effect of hydrophobic pesticides on molecular structure of SOM. This effect differed clearly, depending on the interactions with the pure active substance of this pesticide or its commercial preparation.

Moreover, the research results pointed out that the composition of commercial products significantly modifies the strength and ability of organic matter to bind PE. The interaction of the pure active substance of this pesticide with HM turned out to be different than in the case of PE commercial products, which is due to the presence of different adjuvants. They are more competitive in forming bonds with HM active sites, and thus enhance or weaken the process of forming pesticide-HM complexes or mediate these relationships. As a result, the diversity of the molecular structure of HM and the presence of accompanying substances in commercial pesticide products interact, leading to different sorption mechanisms and durability of the resulting products.

Author contributions

L.M. – writing – original draft preparation, methodology, results and discussion, R.B. – writing – review & methodology, A.U-J. – writing methodology, results & discussion, I.Ć-P. – writing – review & editing, preparation of references, J.W. – writing – review & editing, M.J. – chemical analyzes, A.K. – soil sampling & humin isolation, E.J. – humin isolation, M.D. – humin isolation, J.B. – humin isolation, M.P – graphical preparation of results, G.D – spectroscopic analyzes. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest. The authors ensure that they have neither professional nor financial connections related to the manuscript sent to the Editorial Board.

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