



# Humic acid and biochar as specific sorbents of pesticides

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Received: 26 December 2017 / Accepted: 13 March 2018 / Published online: 26 March 2018  
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## Abstract

**Purpose** The aim of the research was to compare the effect of two types of organic sorbents—humic acid (HA) and biochar (BC)—in sorption-desorption processes of different polar pesticides, which residues are commonly present in arable soils and are potentially harmful for the environment. It also aims to advance the understanding of behavior of both ionizable and nonionizable pesticides in the presence of BC and HA in soils.

**Materials and methods** Three different classes of pesticides were investigated: carbamates (carbaryl and carbofuran), phenoxyacetic acids (2,4-dichlorophenoxyacetic acid (2,4-D) and 4-chloro-2-methylphenoxyacetic acid (MCPA)), and aniline derivatives (metolachlor). Investigated humic acid was extracted by Shnitzer's method from topsoil horizon of arable Gleyic Phaeozem. Biochar was produced from wheat straw in gasification process at 550 °C, remaining 30 s in the reactor. To obtain the experimental goal structural properties of both sorbents were determined and sorption-desorption experiments conducted. To the investigated organic matter samples (HA or BC), 10 or 15 mg L<sup>-1</sup> pesticide solutions in 10 mM CaCl<sub>2</sub> were added and the mixtures were shaken for 24 h. Afterwards, the samples were centrifuged and supernatants analyzed by LC-MS/MS for the pesticide content. Analogous experiment was performed for desorption studies (samples refilled with 10 mM CaCl<sub>2</sub>).

**Results and discussion** Humic acids exhibited strong affinity for the ionic substances, for which high-percentage uptake (74.6 and 67.9% initial dose of 2,4-D and MCPA, respectively) was obtained. Retention of nonionic carbamates on HA was much weaker (35.4% of carbofuran and 10.2% of carbaryl sorbed). Sorption of carbamates to BC was significantly reduced (76.4–84.3%) by the alkaline hydrolysis. Metolachlor was bound comparably strong both by HA (72.9%) and BC (70.2%), although different mechanisms governed its sorption. Noticeable desorption occurred only in the case of 2,4-D bound to HA (over 50%), whereas other studied compounds were released from HA within the range of 4.4–10.8% of the dose sorbed. Oppositely to HA, desorption of all studied pesticides from BC was completely inhibited, except for 2,4-D (3.7% desorbed).

**Conclusions** Investigated humic acid has high affinity to polar, ionic pesticides of high water solubility, which are sorbed via specific interactions with HA functional groups. Studied biochar, due to its moderately hydrophobic character, preferentially attracts nonionic pesticides of relatively high log*P* values and low water solubility. Hydrophobic bonding is postulated as a main mechanism of their attraction to BC. Besides sorbent structural properties, pH is the main factor governing sorption equilibria in the studied mixtures.

**Keywords** Biochar · Desorption · Humic acid · Pesticides · Sorption

Responsible editor: Teodoro Miano

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## 1 Introduction

It has often been reported that soil organic matter (SOM) is actively involved in the binding of pesticides (Bollag et al. 1992; Pignatello 1998; André et al. 2005; Barriuso et al. 2011; Ćwieląg-Piasecka et al. 2017). Crucial role in this process is played by humic substances (HS), which represent the most ubiquitous and widespread natural nonliving organic materials in soil, as well as in all terrestrial and aquatic environments (Senesi 1992; Barriuso et al. 2011). Humic acids (HAs) are the most abundant and chemically and biochemically active

fractions of humified natural organic matter (Loffredo and Senesi 2008). The carboxylic and phenolic hydroxyl group content, the organic free radical concentration, and the aromaticity and humification degrees appear to be the most important chemical properties of HAs affecting adsorption of many organic xenobiotics in soil, including pesticides (Jeziński et al. 2000; Milori et al. 2002; Gennari et al. 2007; Witwicki et al. 2015; Klimkiewicz-Pawlas et al. 2017; Schellekens et al. 2017). Many of these mechanisms depend on molecular properties of pesticides. According to some studies, humic acids have lower affinity for neutral than for charged pesticides (Rosa et al. 2005). Moderately water-soluble and polar compounds are mainly adsorbed to HAs by multiple binding mechanisms, including hydrogen bonding, ionic, and charge-transfer processes (Senesi 1992). In case of the low water-soluble nonpolar compounds, hydrophobic bonding is suggested to be the preferential mechanism of their binding to HAs (Senesi et al. 2001). And in turn, the adsorption capacity of various organic matter fractions for the different pesticides will strictly vary upon their chemical composition, functionality, and structure (André et al. 2005; Bejger et al. 2014; Mayakaduwa et al. 2016). Previous research has established that the highly aliphatic, low humified HAs from organic amendments tend to bind pesticides by hydrophobic bonding, whereas the well-humified soil HAs would prefer chemical binding forms (Senesi et al. 2001).

There is the assumption that amending soil with organic matter increases pollutant sorption and reduces efficacy of pesticides. Many different substances have been dedicated for this purpose (Wang et al. 2010; Bekier et al. 2011; Banach-Szott et al. 2014; Dechene et al. 2014; Matuszak-Slamani et al. 2017; Rosa and Debska 2017). However, in recent days, a lot of attention is paid to biochar (BC)—a carbonaceous material with similar properties to activated carbon, produced in incomplete combustion of biomass at temperatures between 200 and 800 °C, under limited oxygen conditions (Hunt et al. 2010; Kookana 2010). Biochar-derived organic carbon has similar properties to the native organic carbon in soil (Graber et al. 2015; Jiang et al. 2016). Type of feedstock and pyrolysis temperature are crucial factors which determine the biochar properties and hence their capability to sorb pollutants (Zhang et al. 2013a; Vithanage et al. 2016). Beesley et al. (2011) suggested that hardwood-derived high-temperature chars should be considered a material suitable for the retention and immobilization of organic contaminants, while grass-derived low-temperature chars were recommended as potential sorbents for inorganic contaminants (Beesley et al. 2011; Sun et al. 2012). Other studies have demonstrated that biochar production at lower temperatures results in a BC with more surface functional groups and higher cation exchange capacity, compared with biochar produced at higher temperatures (Lin et al. 2012; Taha et al. 2014). Thus, low-temperature biochars are considered to sorb polar and ionic organic compounds more efficiently due to a big share of residual amorphous organic matter in the carbonaceous matrix of BC (Li et al. 2013a; Kearns et al.

2014). According to other research, biochar produced at temperatures higher than 400 °C (with a more strongly condensed aromatic core) increases the sorption capacity of the soil in the case of the uncharged, polar compounds (Dechene et al. 2014; Cederlund et al. 2016).

Biochars are investigated mainly in terms of their use as a soil amendment or as a filter material in soil remediation (Schulz et al. 2012; Li et al. 2013a; Oleszczuk et al. 2014; Medyńska-Juraszek 2016; Godlewska et al. 2017; Hussain et al. 2017; Zhelezova et al. 2017). Various studies have documented that the increased sorption of pesticides by biochar-amended soils may result in a decrease of their degradation, desorption, leaching, and uptake by plants when compared with the nonamended soils (Mesa and Spokas 2011; Taha et al. 2014; Mandal et al. 2017). On the other hand, increased leaching and desorption of pesticides from BC-amended soils can be also found in the research papers (Cabrera et al. 2014; Delwiche et al. 2014).

Each particular BC has different surface area, porosity, and specific adsorption sites and hence, one can expect more selective interaction with pesticides, when testing series of distinct biochars produced in various conditions (Zhelezova et al. 2017). The extent to which biochar will adsorb the organic chemicals depends also on their own properties. According to the recent studies, many biochars possess even better sorption ability than the natural soil organic matter due to their greater surface area, negative surface charge, or porosity (Taha et al. 2014; Ren et al. 2016). The impact on the fate and dissipation of pesticides with BC additions is still a developing knowledge, with continuously growing number of biochars that have been evaluated to date (Sun et al. 2014; Khorram et al. 2016; Ren et al. 2016).

Both soil organic matter fractions (in particular humic acids) and biochars have been widely studied in terms of the role they play in the binding and transport of pesticides in soil. So far, however, to the best of our knowledge, there has been no research that would actually focus on comparison of their affinity to sorb pesticides. That is why in this paper, humic acid extracted from arable soil together with a wheat-straw biochar were investigated as potential, competitive sorbents of chosen classes of polar pesticides commonly used in agricultural practice. Thus, this work also aims to advance the understanding and prediction of the behavior of both ionizable and nonionizable pesticides in the presence of BC and humic acid (HA) in soils.

## 2 Material and methods

### 2.1 Chemicals

Carbaryl (1-naphthyl-*N*-methylcarbamate, 97%), carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol *N*-methylcarbamate, 98%), 2,4-dichlorophenoxyacetic acid (2,4-D, 98%), 4-chloro-2-methylphenoxyacetic acid (MCPA, 99%), and metolachlor

**Table 1** Properties of the model pesticides used in this study (IUPAC PPDB)

Pesticide	Chemical group	Use	Water solubility (mg L <sup>-1</sup> )	Octanol-water partition coefficient Log <i>P</i> at pH 7	p <i>K</i> <sub>a</sub> values
2,4-D	Phenoxyacetic acid	Herbicide	24,300	-0.82	3.40
MCPA	Phenoxyacetic acid	Herbicide	29,390	-0.81	3.73
Metolachlor	Chloroacetamide	Herbicide	530	3.4	n/a
Carbaryl	Carbamate	Insecticide	9.1	2.36	10.4
Carbofuran	Carbamate	Insecticide	322	1.8	n/a

n/a, not applicable; no dissociation

solution in acetonitrile 100 µg/mL (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide, 98%) were of analytical grade and were purchased from Sigma-Aldrich (Schnelldorf, Germany). Stock solutions of all pesticides were prepared in 10 mM CaCl<sub>2</sub>. Ultrapure water was supplied by a Merck Millipore DirectQ3 system (Warsaw, Poland). Argon at 99.995% was purchased from Messer (MESSER POLSKA Sp. z o.o.).

## 2.2 Pesticides under study

Five polar pesticides (both ionic and nonionic) were chosen for the studies because of their contrasting chemical properties and prior knowledge about diverse behavior in soils amended with organic matter (Jana and Das 1997; Raturi et al. 2005; Iglesias et al. 2009; Cabrera et al. 2011; Cederlund et al. 2016; Trigo et al. 2016b). Their basic chemical properties are described in Table 1.

## 2.3 Sorbents characteristics

HA utilized in the studies was extracted from the topsoil horizon of Gleyic Phaeozem (IUSS Working Group WRB 2014) derived from loam, located in the area of Domaniów (near Wrocław, Poland, (Kabała 2015)) according to the Schnitzer's method, recommended by the International Humic Substances Society (IHSS) (Spark 1996). The extract was treated with a mixture of 0.1 M HCl and 0.3 M HF in purification step. It was left overnight and then centrifuged. Humic acid precipitate was placed in a dialysis tube (Spectra/Por® 7 MWCO 10,000, Spectrum Europe B.V., The Netherlands) and dialyzed with distilled water until chlorides were removed. Afterwards the HA was freeze dried.

BC was produced from the wheat-straw pyrolyzed under the oxygen-limited conditions at 550 °C for 30 s. After the process, it was allowed to cool overnight at room temperature. The material was milled to pass through 2 mm sieve, obtaining the fine powder consistence. Then it was sealed in a glass bottle and stored at room temperature until use.

## 2.4 Evaluation of basic properties of tested sorbents

Both sorbents were characterized for their physical and chemical properties. The pH of BC was conducted by soaking the sample with deionized water and 10 mM CaCl<sub>2</sub> at a 1:20 solid/liquid ratio for 24 h with agitation (Zhao et al. 2013). It was then measured using the pH meter (Mettler Toledo, Warsaw, Poland). Additionally, the pH of HA and BC mixtures in 10 mM CaCl<sub>2</sub> used in the experiment was also determined with a potentiometric method to monitor its effect on pesticides sorption. The specific surface area of the biochar sample was measured with glycol adsorption method (Madsen 1977). Wettability of a biochar was determined by the water drop penetration time (WDPT) assay (Letey et al. 2000). Measurements were done in triplicate.

Bulk elemental compositions of HA and BC were measured on the CE Instruments EA 1110 CHNS (Tables 2 and 3). The O content was calculated from the mass difference (O% = 100 - C% - H% - N%). Ash content in all the investigated samples was measured by heating the sample at 550 °C for 6 h (Kearns et al. 2014). The H/C, N/C, O/C, and (O + N)/C atomic ratios and ω (internal oxidation degree) were calculated for both sorbents (Table 4). The latter parameter (ω) was evaluated according to the formula:

$$\omega = (2O + 3N - H) : C;$$

**Table 2** Basic properties of wheat straw biochar

Surface area (m <sup>2</sup> g <sup>-1</sup> )	pH (H <sub>2</sub> O/CaCl <sub>2</sub> )	Ash content 550 °C (% w/dw)	Carbon (% w/dw)	Hydrogen (% w/dw)	Nitrogen (% w/dw)	Oxygen (% w/dw)	H/C ratio (molar)	O/C ratio (molar)
237.39	9.9/9.6	28.08	55.65	1.78	0.66	13.83	0.38	0.25

**Table 3** Functional groups, ash content and bulk elemental composition of the studied humic acid

Total acidity (meq g <sup>-1</sup> )	Phenolic OH (meq g <sup>-1</sup> )	Carboxyl COOH (meq g <sup>-1</sup> )	Ash content 550 °C (% w/dw)	Carbon (% w/dw)	Hydrogen (% w/dw)	Nitrogen (% w/dw)	Oxygen (% w/dw)
5.46	3.76	1.70	1.19	52.42	4.09	3.97	38.33

where O, N, H, and C contents were expressed in atomic percent (Banach-Szott et al. 2014).

In humic acid sample, the total acidity (Ba(OH)<sub>2</sub> method) and the carboxylic acidity (Ca-acetate method) were determined (Schnitzer and Gupta 1965). Phenolic acidity was calculated from the difference between total and carboxylic acidity (Busato et al. 2017).

Additionally, the humic acid and biochar functional groups were determined using a Fourier transform infrared (FTIR) Bruker spectrophotometer (Verter 70). The samples for FTIR analysis were prepared as pellets with fused KBr. The infrared spectra were collected in 400 and 4000 cm<sup>-1</sup> region.

## 2.5 Sorption and desorption experiments

Sorption of the investigated pesticides on the wheat-straw biochar and humic acid was determined using a simplified batch equilibrium method (OECD 2000). To compare the effect of the two sorbents, adsorption was measured using only the single concentration of the selected agrochemicals (15 mg L<sup>-1</sup> for carbofuran, 2,4-D and 10 mg L<sup>-1</sup> for MCPA, carbaryl, and metolachlor).

Briefly, 10 mL of each pesticide solution and 100 mg of the humic acid or biochar were placed in 15 mL volume polypropylene falcon centrifuge tubes. Aqueous 10 mM CaCl<sub>2</sub> was used as a background solution to maintain the constant ionic strength. For HA and BC a pre-study was conducted to estimate the sorbent: solution ratio of 1:100 (*m/v*). In the next step, all sealed samples were agitated on a rotary shaker (Biosan, Multi RS-60) at 80 rpm and 22 ± 0.5 °C for 24 h. Preliminary tests showed that sorption equilibrium was reached for all the investigated pesticides within less than 24 h. Then samples were centrifuged for 25 min at 10,000 rpm followed by the solution prefiltration and a subsequent filtration through a 0.45-μm membrane prior to LC-MS/MS analysis. The amount of pesticide sorbed to the HA and BC was calculated from the difference between the initial and final concentrations of the pesticide in the solution phase. A preliminary experiment showed that no sorption occurred on the Falcon tube wall (control samples containing only

pesticide solutions in 10 mM CaCl<sub>2</sub>, in the concentrations tested). To determine the probable hydrolysis during the investigations, additional control samples without the tested sorbents were prepared. They consisted only of the pesticide solutions in 10 mM CaCl<sub>2</sub> (15 mg L<sup>-1</sup> for carbofuran, 2,4-D and 10 mg L<sup>-1</sup> for MCPA, carbaryl, and metolachlor) with pH adjusted to 2.9 and 9.6 (pH value obtained for experimental mixtures containing HA and BC, respectively). All experiments were carried out in triplicate.

Desorption experiment was conducted immediately after the taking up of the solutions for sorption studies, according to the procedure described in the literature (Spark and Swift 2002). After the removal of 7.5 mL of supernatant, the same volume of fresh background solution containing no pesticide was added and the mixtures were agitated for additional 24 h, centrifuged, and sampled as described before. The procedure was repeated three more times for suspensions containing BC to check the persistence of inhibitory effect that occurred towards the investigated pesticides already during the first desorption cycle, oppositely to HA. Measured pesticide concentration in the solution after the desorption cycle was the sum of pesticide amount remaining in the solution (2.5 mL of supernatant after the sorption experiment) and the amount of the investigated compound that desorbed from the BC or HA back to the solution (Tatarková et al. 2013). The amount of pesticide present in the remaining 2.5 mL was accounted for in the calculation of desorption magnitude (Cederlund et al. 2016) which was estimated with respect to the pesticide dose that was initially sorbed by HA or BC. The magnitude of pesticide sorption on both sorbents (BC and HA) was expressed as the percentage (%) adsorption and desorption estimated for each of the investigated pesticide (Table 5).

The equilibrium concentrations of pesticides (both after the sorption and desorption step) were analyzed immediately after the filtration, using high-pressure liquid chromatography coupled with tandem mass spectrometer (LC-MS/MS, Thermo Scientific TSQ Quantum Access MAX). The chromatographic conditions were a Thermo Scientific Hypersil GOLD column (50 mm × 2.1 mm) with 1.9 μm particle size, flow rate of 0.50 mL min<sup>-1</sup>, sample injection volume of 10 μL

**Table 4** Elemental composition (atomic percent) of HA and BC, the values of their atomic ratios, and the degree of internal oxidation

Sample	C	H	N	O	H/C	N/C	O/C	(O + N)/C	ω
HA	39.31	36.56	2.55	21.58	0.93	0.065	0.55	0.61	0.363
BC	42.31	37.09	1.77	18.83	0.88	0.042	0.445	0.49	0.139

(with loop), gradient elution with eluent A being deionized water with a trace of formic acid (0.1%), and eluent B consisting of acetonitrile (90%), deionized water (10%), and trace of formic acid (0.1%). The analysis started with 100% of eluent A from the first minute, which was being replaced linearly up to 100% by eluent B in 20 min. This composition was held for further 3 min before being returned to 100% of eluent A, followed by a re-equilibration time of 7 min, to give a total run time of 30 min. The mass spectrometer was run in single reaction monitoring (SRM) mode. Argon 99.995% was used as collision gas with a pressure of  $1.87 \times 10^{-3}$  mbar in the collision cell. Capillary voltage of 4 kV was used both in positive ionization mode (carbofuran, carbaryl, and metolachlor) and negative ionization mode (2,4-D and MCPA). The ion transfer capillary temperature was set to 380 °C and the vaporizer temperature of ESI probe to 400 °C.

### 3 Results and discussion

#### 3.1 Properties of the investigated sorbents

The basic characteristics of the BC and HA are summarized in Tables 2 and 3, respectively. Studied biochar was highly alkaline with the pH value of 9.9 which might be influenced by the separation of alkali salts from the organic matrix in the input material. Relatively high ash content (28.08% w/dw) may be attributed to the combustion of cellulose, hemicellulose, and removal of the volatile material at the pyrolysis temperature. The investigated wheat-straw biochar had a high specific surface area of  $237.39 \text{ m}^2 \text{ g}^{-1}$ .

Calculated H/C and O/C molar ratios are the indicators of BC aromaticity and polarity, respectively. It is assumed that BCs produced at the temperature higher than 400 °C should be characterized by the H/C ratio lower than 0.5 and decrease with the raising pyrolysis temperature below 0.3, which is an indicator of highly aromatic ring systems (Cely et al. 2014). In the case of the investigated BC, produced at 550 °C, H/C ratio falls within the 0.3–0.5 range which might indicate a decreased fraction of original wheat residues. Obtained BC molar ratios (Table 2) emphasize the presence of aromatic structural features and (similar to other biochars produced at that temperature; Mayakaduwa et al. 2016) reduced content of O-containing polar functional groups on BC surface (low molar O/C ratio and polarity index). Also Monterumici et al. (2015) observed that biochar samples obtained at high temperatures (650 °C) were reach of aromatic C. Moreover, they found differences in aromatic ring condensation between biochars derived from different sources (Monterumici et al. 2015). BC hydrophobicity was measured in the water drop penetration test. WDPT result (time necessary for the drop of water to be soaked into the sorbent) was in the range of 120–180 s. It places the investigated BC in the

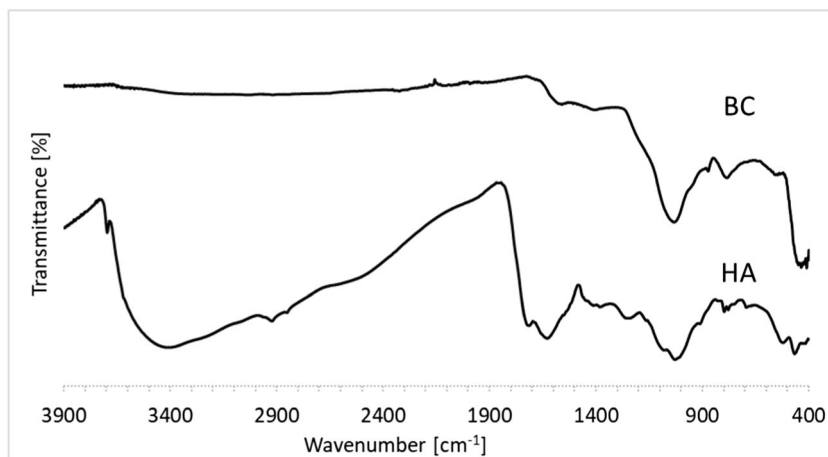
moderately hydrophobic sorbents group. It is consistent with the literature according to which the heat treatment of the chars at temperatures between 400 and 500 °C increases BC wettability through the removal of aliphatic domains from its surface (Gray et al. 2014).

The investigation of the acidic functional groups in the HA sample revealed the presence of total acidity of  $5.46 \text{ meq g}^{-1}$  (Table 3). Most of this acidity (69%) is due to phenolic groups presence ( $3.76 \text{ meq g}^{-1}$ ), while the carboxylic groups were responsible for the remaining 31% ( $1.70 \text{ meq g}^{-1}$ ).

Elemental composition of humic acid and biochar (expressed in atomic percent) is presented in Table 4. According to the van Krevelen diagram, the investigated HA and BC samples can be classified into the same region of lignin-like compounds ( $\text{H/C} = 0.7\text{--}1.5$ ,  $\text{O/C} = 0.1\text{--}0.67$ ), based on their H/C and O/C atomic ratios (Rosell et al. 1989; Aranda and Oyonarte 2006; Ohno et al. 2010; Li et al. 2013b; Lu et al. 2015; Barančíková et al. 2018). This BC characteristics is in accordance with thermal resilience of lignin, as opposed to hemicellulose and cellulose that decompose at temperatures lower than 400 °C (220 to 315 °C and 315 to 400 °C, respectively) (Yang et al. 2017). Nevertheless, the pyrolysis temperature (550 °C) was not sufficiently high to place BC into the condensed aromatic ring structure (CAS) region ( $\text{H/C} = 0.2\text{--}0.7$ ;  $\text{O/C} = 0\text{--}0.67$ ). Obtained HA atomic ratios were typical for the humic acids extracted from topsoil horizons of Gleyic Pheozems located in the Wrocław district (Łabaz 2010). They are higher than in BC sample which might suggest the bigger number of oxygen-containing functional groups in HA. It is supported by the higher polarity index ( $(\text{O} + \text{N})/\text{C}$ ) and over two times higher internal oxidation degree ( $\omega$ ) of HA than the one calculated for BC (Table 4).

FTIR analysis revealed significant differences between BC and HA in the types and relative abundances of functional group peaks observed on the spectra (Fig. 1). As it can be seen, HA is more abundant in hydroxyl groups (vibrational band from –OH groups at  $3409 \text{ cm}^{-1}$ ) in comparison with BC. The latter exhibits only a trace band at this region corresponding probably to the stretching vibrations of –OH group of bonded water (Ahmad et al. 2012). The bands at 2922 and  $2854 \text{ cm}^{-1}$  observed in the HA spectrum were assigned to asymmetrical and symmetrical stretching of –CH<sub>2</sub> groups, respectively (Giovanela et al. 2004), whereas absorption band at  $1384 \text{ cm}^{-1}$  is assigned to COO or C–H bending of CH<sub>2</sub> group in the aliphatic chain (Banach-Szott et al. 2014). Since those three bands are not present in the spectrum of BC sample, it might suggest the absence of labile aliphatic groups on the char surface. The sharp peak present on HA spectrum at  $1619 \text{ cm}^{-1}$  and a very weak one on BC spectrum at about  $1600 \text{ cm}^{-1}$  are ascribed as stretching vibration of C=C or C=O in the aromatic ring (Fang et al. 2015). Additional weak band at  $1714 \text{ cm}^{-1}$ , present on the HA spectrum corresponds to carboxyl stretching absorption peak (Giovanela et al. 2004).

**Fig. 1** FTIR spectra of investigated biochar (BC) and humic acid (HA) samples



Intense, sharp band at 1035 and at 1029  $\text{cm}^{-1}$  observed on BC and HA spectrum, respectively, can be assigned to C–O stretching vibrations of carboxylic groups (Trigo et al. 2014) or of alcohols on ligno-cellulosic polymers (Li et al. 2013a; Jamroz et al. 2014). BC in comparison with HA tend to contain less oxygen- and hydrogen-containing functional groups, while the presence of these groups in the HA sample (namely phenolic and carboxylic) was additionally confirmed by the titration procedure (Table 3). Thus, according to the experimental results from FTIR and elemental analysis (Table 4) BC seems to be more aromatic and less polar than the investigated HA. These findings are in agreement with the studies of Chun who discovered that under high temperature (500–700 °C) the biochar derived from wheat is well carbonized and has a relatively high surface area and low oxygen content (Chun et al. 2004; Yu et al. 2009). Also, Ahmad et al. (2013) observed that decrease of atomic ratios (H/C and O/C) in the case of high-temperature chars was attributed to the removal of H- and O-containing functional groups resulting in the formation of high aromaticity and low polarity biochars (Ahmad et al. 2013).

### 3.2 Sorption of pesticides on biochar and humic acid

Percentage adsorption and desorption yields obtained in the sorption experiment for the investigated pesticides are presented in Table 5 and Fig. 2. The adsorption affinity of the humic acid for the pesticides varied greatly and decreased in the order 2,4-D > metolachlor > MCPA > carbofuran > carbaryl. Obtained data clearly show that humic acids sorb investigated phenoxyacetic acids and metolachlor more preferentially than the carbamates. What is interesting about the data in Table 5 is that the wheat-straw biochar reveals different affinity towards studied pesticides than HA. BC attracts carbamate pesticides to the highest extent (98.9 and 92.1% of carbofuran and carbaryl sorbed, respectively). Metolachlor sorption by BC (70.2%) is comparable with the one observed for HA (72.9%), whereas phenoxyacetic acids is a group of pesticides that are sorbed to the least extent among investigated

compounds (sorption of approximately 40% of the dose introduced to BC sample).

#### 3.2.1 Sorption of phenoxyacetic acids on HA and BC

Sorption of phenoxyacetic acids was much higher in the case of the humic acid (74.6 and 67.9% for 2,4-D and MCPA, respectively) than the studied wheat-straw biochar (Table 5). Investigated HA is abundant in oxygen containing functional groups such as carboxylic or phenolic (Fig. 1; Table 3) which may serve as a sorption site for binding of organic molecules. It may be the reason why the probability of electrostatic interactions between 2,4-D or MCPA and polar moieties on the HA surface increases, which results in higher adsorption of phenoxyacetic acids on HA. Another factor influencing their sorption might be a very low experimental pH (2.9) of the humic acid suspensions. It has been proven before that adsorption of ionic pesticides, particularly phenoxyacetic acids, may occur via formation of negative charge-assisted H-bonds in the presence of carboxylic or similar in structure groups on the sorbent surface, particularly at pH values below their  $\text{pK}_a$  (Khan 1973; Senesi et al. 1986; Li et al. 2013b). Thus, the relatively high 2,4-D and MCPA uptake by HA might be attributed to the specific interaction with active HA groups (Spurlock and Biggar 1994; Chiou 2002).

The percentage adsorption values for biochar sorbent were 42.3 and 37.6% for 2,4-D and MCPA, respectively. This relatively low sorption extent may be partly ascribed to electrostatic attraction between herbicides and small number of polar functional groups on BC surface or to a nonspecific interaction with the sorbent. Increased pH in samples containing BC (pH of 9.6 after 24 h of equilibration) may have resulted in their decreased sorption (Fig. 2) as in the experimental conditions (mixtures containing BC) both 2,4-D and MCPA occur predominantly in anionic form. Hence, the negative charge of both BC and phenoxyacetic acids may increase, which leads to enhanced repulsion and thus the weaker adsorption in

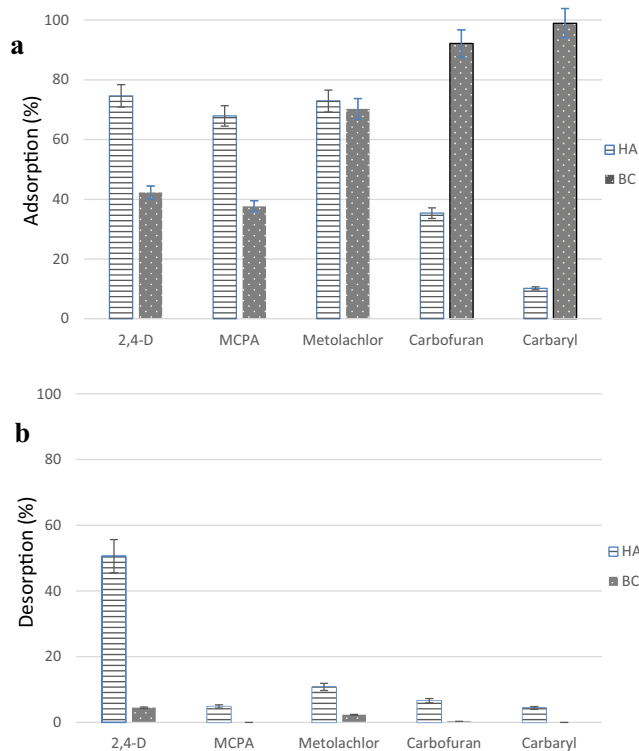
**Table 5** Sorption and desorption magnitude of the investigated pesticides, calculated for both sorbents (HA and BC)

Pesticide	Humic acid		Biochar	
	Sorption (%)	Desorption (%)	Sorption (%)	Desorption (%)
2,4-D	74.6	50.6	42.3	3.7
MCPA	67.9	4.9	37.6	<dl
Metolachlor	72.9	10.8	70.2	<dl
Carbofuran	35.4	6.6	98.9 (14.6) <sup>a</sup>	<dl
Carbaryl	10.2	4.4	92.1 (15.7) <sup>a</sup>	<dl

dl, detection limit

<sup>a</sup> Sorption magnitude with the extent of the compound hydrolysis included

comparison with HA (Table 5). It is in agreement with some findings according to which an elevated pH of biochar may be negatively correlated with adsorption of some ionic agrochemicals, i.e., glyphosate (Herath et al. 2016) and MCPA (Trigo et al. 2016a). On the contrary, Tatarkova and Cabrera (Cabrera et al. 2011; Tatarková et al. 2013) observed an increased sorption of MCPA in the presence of biochar. Nevertheless, the effect was observed for soil amended with various biochars and was attributed to the general increase in carbon content and distinct surface affinities of the studied biochar for the herbicide.

**Fig. 2** Comparison of the effect of different sorbent (HA and BC) on: **a** adsorption and **b** desorption of 2,4-D, MCPA, metolachlor, carbofuran and carbaryl. Desorption is expressed as a percentage of dose that desorbed from HA or BC samples. Error bars represent standard deviation of triplicate samples

### 3.2.2 Sorption of metolachlor on HA and BC

Both sorbents attracted metolachlor comparably strong (72.9 and 70.2% of the applied pesticide dose for humic acid and biochar, respectively). According to the literature, metolachlor adsorption mechanism to humic acids is based on two types of interactions that is ionic and hydrogen bonding (Senesi 1993). The first one involves the electrostatic interaction of cationic amine group with carboxylic or phenolic groups at the surface of humic acid. Second type of interaction, namely hydrogen bonding is also a path of metolachlor interaction with HA, predominantly at acidic conditions (Senesi 1993). The probability of the described interaction is even higher when one takes into account the fact that based on the FTIR spectrum of HA (Fig. 1) and the results of functional groups determination (Table 3), it was clearly shown that the studied humic acid is relatively abundant in polar regions.

Metolachlor sorption on BC cannot be explained by the same mechanism as above mentioned due to the moderately hydrophobic nature of BC and its lower polarity in comparison with HA. It is also connected with the chemical properties of metolachlor, which exhibits relatively high value of  $\log P$  (3.4 at pH 7, Table 1) making it less polar than the other pesticides under study. According to the rule “like dissolves like,” congruent properties of both sorbent and the sorbate enables the hydrophobic effect to occur in the case of metolachlor sorption to biochar. Similar adsorption mechanism was proposed for phenylurea herbicide diuron (Fontecha-Cámara et al. 2007), which  $\log P$  equals to 2.87 and is similar to the octanol-water adsorption coefficient of metolachlor. This pesticide property may also at least partially explain much lower sorption of the studied phenoxyacetic acids on BC, due to their high, negative  $\log P$  values (Table 1).

### 3.2.3 Sorption of carbamates on HA and BC

Humic acid does not sorb studied carbamates as strong as the other pesticide classes under investigation. Approximately 10.2 and 35.4% of the introduced carbaryl and carbofuran dose,

respectively, were efficiently sorbed by HA. This limited magnitude of sorption may be attributed to hydrophobic interactions between carbamates that can occur with nonpolar regions of HA moieties. But more importantly, recently, we have proven that the studied carbamates are capable to react with the indigenous radicals of humic acids, decreasing the semiquinone radical spin concentration (Ćwiela-Piasecka et al. 2017). According to that finding, structural differences between carbaryl and carbofuran (presence of the furanyl moiety in carbofuran) were responsible for the higher reactivity of the latter in radical reactions. This finding also supports results of the sorption experiment presented here, according to which carbofuran is 3.5 times more extensively sorbed than carbaryl (Table 5).

On the contrary, calculated sorption of the carbamates on biochar was nearly total (92.1 and 98.9% of the introduced dose sorbed for carbaryl and carbofuran, respectively). It is in agreement with other studies which showed that biochar amendment to soil enhances the sorption of carbaryl (Ren et al. 2016) and carbofuran (Mayakaduwa et al. 2017). Hydrophobic effect together with van der Waals interactions may explain sorption of carbamates to BC due to their non-ionic nature and relatively high  $\log P$  values (Table 1). Recently, it was also postulated that the ester functional groups of carbaryl (of electron-withdrawing nature), makes the associated aromatic ring an electron acceptor thus it is expected to interact with the aromatic carbons on the BC surface through  $\pi$ - $\pi$  interactions (Ren et al. 2016). Nevertheless, one has to bear in mind that carbamates are very prone to chemical hydrolysis, which is enhanced at pH above 7 (Ren et al. 2016). Since the pH in the experimental conditions was estimated to be even higher (pH 9.6 in the sample containing 100 mg of BC and 10 mL of  $\text{CaCl}_2$ ), there are two scenarios of BC influence on pesticides fate that need to be taken into account when considering the extent of carbamates sorption. First one assumes enhance in hydrolysis by the catalytic effect of pH, whereas the second—reduction of carbamates hydrolysis by enhanced sorption.

In the studied BC mixtures, the pH value of suspensions containing BC was very alkaline. To confirm the effect of elevated pH on carbamates degradation, their hydrolysis (in concentrations used in the sorption experiment) was examined in a background solution with pH adjusted to 9.6. After 24 h, both pesticides were decomposed to the extent of 76.4 and 84.3% in the case of carbaryl and carbofuran, respectively. It is in good agreement with other studies where the decomposition of one of the carbamates, namely carbaryl at pH of 9.1 and in the presence of 500 mg of biochar pyrolyzed at 700 °C was equal to 86.5% (Zhang et al. 2013b). Indeed, biochars produced at higher temperatures (about 700 °C) may enhance the chemical hydrolysis of carbaryl in soil due to their strong liming effect. However, in the presence of biochar, hydrolysis of the carbamate may also be lowered due to the reduced availability of sorbed pesticides for the chemical reaction.

Based on that, it can be assumed that both hydrolysis and sorption contribute to the obtained high value of carbamates uptake on BC in our study. Hydrolysis process presumably prevails in the suspensions of carbamates with the studied BC. Taking that into account, we can estimate the effective sorption magnitude of the carbamates to be much lower (approximately 15.7 and 14.6% for carbaryl and carbofuran, respectively) than the one calculated based only on the sorption experiment results (Table 5).

### 3.2.4 Desorption of pesticides under study from HA and BC

Although the adsorption capability of investigated humic acid or biochar is considered to be a key factor that controls the environmental fate of pesticides, desorption of pesticides from the sorbents should be carefully investigated due to its association with the bioavailability and efficacy of pesticides (Khorram et al. 2016). Generally, pesticides desorb more readily from low temperature chars (Li et al. 2013a) while high temperature ones exhibit a substantial desorption hysteresis (Ahmad et al. 2012). Results of our study (Table 5) suggest that the wheat-straw biochar under investigation exhibits no significant desorptive properties. Studied biochar suspensions with adsorbed pesticides were subjected to desorption procedure four times and each time there was no pesticide release observed except for the first desorption cycle where 2,4-D was quantitatively estimated in the solution (Table 5). However, a correction should be made for the studied carbamates, where hydrolysis may contribute to the vastly reduced concentration of the insecticides after desorption. The inhibitory effect has been observed in other studies of polar organic compounds, suggesting that various pyrolytic carbon materials significantly reduces pesticide bioavailability and hence risk of its leaching (Kookana 2010).

Noticeable desorption occurred only in the case of 2,4-D bound to HA (over 50%), indicating its weak interaction with humic acid. Other studied compounds were released from HA within the range of 4.4–10.8% of the sorbed pesticide dose. These findings are in agreement with the recent work of Ozbay et al. (2017), who attributed the rapid 2,4-D desorption to soft carbon fraction of SOM (humic/fluvic acid and lipids) (Ozbay et al. 2017).

## 4 Conclusions

This research evaluated the impact of different structural properties of humic acid and a high-temperature wheat-straw biochar on the sorption behavior of five pesticides (2,4-D, MCPA, metolachlor, carbaryl, and carbofuran). Investigated HA exhibited very strong affinity to phenoxyacetic acids which are polar, ionic pesticides of high water solubility. It was attributed to the specific interactions of 2,4-D and MCPA



with active HA functional groups. The same interaction was postulated to explain metolachlor sorption on HA. On the contrary, studied biochar revealed a great affinity for nonionic pesticides studied due to their high  $\log P$  values and low water solubility. Moderately hydrophobic surface of biochar and low content of oxygen functional groups on its surface was ascribed as main structural features governing its interaction with the studied pesticides. The pH of HA and BC sorbent suspensions exerted a great influence on the fate of both, ionic and nonionic pesticides under study. Acidic conditions in HA mixtures favored phenoxyacetic acids sorption, whereas the elevated pH of BC samples enhanced repulsion of their deprotonated molecules and negatively charged BC surface, resulting in their decreased retention. In alkaline conditions enhancement of carbamate hydrolysis occurred in BC suspensions, having impact on the apparent magnitude of carbaryl and carbofuran sorption on biochar. Thus, both processes need to be taken into consideration when predicting fate of carbamates in soil amended with high-temperature chars, with potential of liming effect.

Important conclusion can be also deduced from the desorption experiment. It revealed a reduced availability of phenoxyacetic acids and metolachlor in the presence of BC sorbent. That is why the utility of the investigated high-temperature wheat straw BC as a filter material that can be deployed at hotspots for pesticides leaching, should be considered.

**Funding information** The research was supported by the National Science Center with grant number DEC-2012/05/D/ST10/02223.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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