

## Humic acid and biochar as specific sorbents of pesticides.

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**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 logP 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.

#### Słowa kluczowe

Biochar, Desorption, humic acid, Pesticides, Sorption

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