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The role of humic acids and biochar as specific sorbents of pesticides in soil

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Pesticides are widely used in agriculture to prevent or control different pests and increase yield as well as products quality. Despite of the strict regulations concerning sustainable use of plant protection products, their residues are very often present in soil. Depending on their chemical and physical properties, they undergo various transformations in the soil. This results in their retention on different sorbents, degradation by microorganisms or leaching to the groundwater. Biochar is a carbon-rich byproduct of thermal biomass conversion, and due to its high sorption properties can be an efficient sorbent for pesticides in soil.
The aim of the research was to compare the effect of two types of organic sorbents – humic acids (HA) and biochar (BC) – in sorption-desorption processes of different pesticides, which residues are commonly present in arable soils and thus are potentially harmful for the environment.
The humic acids were extracted from topsoil horizon of arable cambisoil derived from loam (Lower Silesia, Poland) by Shnitzer's method, then purified using XAD resin and freeze-dried. Biochar was produced from wheat straw in gasification process at 550˚C, remaining 30 minutes in the reactor. Investigated pesticides belong to three different chemical classes: carbamates (carbaryl and carbofuran), phenoxyacetic acids (2,4-D and MCPA) and aniline derivatives (metolachlor), and are active substances of commonly used plant protection products in agriculture.
To obtain the experimental goal the sorption experiment was conducted. To the investigated organic matter samples (HA or BC) aliquots of pesticides solutions in 10M CaCl2 were added and the mixtures were shaken for 24h. Afterwards the samples were centrifuged and supernatants analyzed by LC-MS/MS for the pesticides content. After that the same samples were refilled with CaCl2 and analyzed in the same way for desorption studies.
Humic acids exhibited strong affinity for the ionic substances (2,4-D, MCPA), for which high percentage uptake was obtained (about 70% of the compound sorbed). Retention of carbamates on HA were much weaker, on contrary to their behavior towards BC – the uptake of carbamates on BC was nearly total (in the range from 90 to nearly 100%). Metolachlor was sorbed comparably strong both by HA and BC. Noticeable desorption occurred only in case of 2,4-D bound to HA, which might suggest the moderately strong bonding type. On the other hand, in case of BC desorption was completely inhibited due to stronger type of interaction with investigated substances.
The obtained results indicate that the sorption behaviour of HA and BC is completely different, depending on the chemical structure both of the organic sorbents and pesticides used. Hydrophobic surface of adopted BC may preferentially attract pesticides of nonpolar and nonionic structural features. Soil humic acids, which are main sorbents of organic pollutants in soil, bind chemicals through the ionic, hydrogen and covalent bonding as well as hydrophobic bonding or van der Waals forces, which in some cases may result in a weaker pesticide retention.