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# The role of humic substances in detoxification process of the environment

## Rola substancji humusowych w procesach detoksykacji środowiska

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### Abstract

Chemical pollution of anthropogenic origin such as heavy metals, pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls are some of serious threats to the environment. Their main sources are industry, transport, and agriculture. Chemical substances pollute the air, water and soil, where ultimately most of them reach and accumulate.

Soil constituent involved in the adsorption of impurities is organic matter (OM), the structure of which can be divided into three fractions: humic acids (HA), fulvic acids (FA) and humin (H). The impact of pollution with OM allows the presence of active functional groups, among others,  $-OH$ ,  $-COOH$ ,  $-NH_2$ ,  $-OCH_3$ . Strongly adsorbed contaminants are not available for soil microorganisms.

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## 1. INTRODUCTION

Soil is a biologically active part of the lithosphere and the first recipient of any contamination arising from various human activities [Oleszczuk 2007a]. Due to the sorption of contained therein humic substances (HS) it provides a natural protective barrier against pollution [COM 2002]. It reduces heavy metals in plants, prevents their introduction into the trophic chain, leaching and migration into groundwater [Kwiatkowska 2007, Malej 2009]. The main component of soil involved in the process of sorption is organic matter (OM), the structure of which should be distinguished in three fractions: humic acids (HA), fulvic acids (FA) and humin (H), which differ in solubility in water, acid and alkali, thereby characterised by varied properties [Zawadzki 1999].

An important role in the construction of HA – fulvic and HAs – play functional groups conditioning properties such as hydrophilic, acidic, ion exchange capacity. Among the most important functional groups, corresponding to the ion exchange properties of HA in relation to the metal, are:  $-OH$ ,  $-COOH$ ,  $>C=O$ ,  $-OCH_3$ . Thanks to them, the HA are capable of forming complexes of heavy metal ions, and the same ability to bind metal ions due

### Streszczenie

Zanieczyszczenia chemiczne pochodzenia antropogenicznego takie jak metale ciężkie, pestycydy, wielopierścieniowe węglowodory aromatyczne (WWA), polichlorowane bifenyle (PCB) stanowią jedno z poważnych zagrożeń dla środowiska przyrodniczego. Głównymi ich źródłami są przemysł, komunikacja, a także rolnictwo. Substancje chemiczne zanieczyszczają powietrze, wodę oraz gleby, do których ostatecznie trafia i ulega akumulacji większość z nich.

Składnikiem gleby uczestniczącym w sorpcji zanieczyszczeń jest materia organiczna (MO), w strukturze której można wyróżnić trzy frakcje: kwasów huminowych (KH), kwasów fulwowych (KF) i humin (H). Oddziaływanie zanieczyszczeń z MO umożliwia obecność aktywnych grup funkcyjnych m.in.  $-OH$ ,  $-COOH$ ,  $-NH_2$ ,  $-OCH_3$ . Silnie zaadsorbowane zanieczyszczenia nie są dostępne wówczas dla mikroorganizmów glebowych.

to the presence of carboxyl groups and hydroxy phenols [Kwiatkowska 2007].

The results of many studies [Pandey et al. 2000, Bejanaro et al. 2005, Kwiatkowska 2007, Oleszczuk 2007b, Pastuszko 2007, Malej 2009] indicate that HA strongly interacts with contaminants, including heavy metals, radioactive substances, pesticides and other organic hydrophobic compound taking part in the processes of detoxification of environment.

From the point of view of the role of HS in making the soil barrier limiting excessive consumption of inorganic and organic contaminants by plants and their migration into the soil profile to groundwater, it appears advisable to stabilise and increase the resources of OM (C org.) as a source of HS [Karczewska, Kabała 2010].

The aim of this study is to assess, on the basis of reports in the literature, the possibility of using HS in the processes of detoxification of the environment. The characteristic of OM has been presented in terms of the importance of detoxification processes with a special emphasis on the role of HS as a natural protective barrier for soil and water environment against pollution.

## 2. THE IMPORTANCE OF CONSTRUCTION OF ORGANIC MATTER IN THE PROCESS OF HEAVY METAL IONS SORPTION

The structure and chemical nature of the OM varies depending on the climatic and geochemical properties of the environment, which has a large impact on the process of sorption of organic and inorganic contaminants [Pastuszko 2007].

A specific group of soil contaminants are heavy metals (e.g. Ni, Co, Zn, Cu, Cr, V, Ti, Cd, Hg, Mo and others), the positively charged ions may interact with the soil due to the presence of the so-called sorption complex – a highly dispersed colloidal fraction of the soil. Complex absorbent soil (soil colloid) is one of the most important structural units of the soil. Its construction affects the chemical and physicochemical properties of the soil including the buffer capacity, with respect to cation exchange capacity (CEC), soil water content, and stability of soil aggregates [Kwiatkowska 2007, Oleszczuk 2007b]. A characteristic feature of the soil colloids is that their surface has a negative relief charge. The elemental composition of the colloid particles of soil includes: soil mineral phase particles, mainly clay minerals, OM and mineral – organic complexes [Malej 2009].

The content of OM in soil can vary from 0.1% in desert soil to 90% in organic soil. It is an important component of soil sorption complex. A significant fraction of soil OM includes the so-called HS. They can be divided into nonspecific HS and soil-specific substances. Because of their functions, the presence of HS in the soil environment is very important. They represent an average of 80% to 90% of all of HS present in the soil [Zawadzki 1999, Pastuszko 2007].

HS are heterogeneous, three-dimensional structural complexes – with the properties of polydisperse macromolecules. They are composed of carbon, oxygen, hydrogen and small amounts of nitrogen, phosphorus and sulphur. From a chemical point of view, generally they described as clusters of aromatic and aliphatic units covalently linked together so-called bridging atoms (e.g. –O– oxygen, nitrogen –N=), having a plurality of carboxyl groups (–COOH), hydroxyl (–OH) phenols, methoxy (–OCH<sub>3</sub>), alcohol (–OH), amino (–NH<sub>2</sub>), and other parts attached to the aliphatic and aromatic parts. They are formed by the fermentation and transformation of plant residues (roots, stems, leaves) and other necrotic material and tissues. HS are traditionally defined by solubility and there are three fractions: HA, FA and H [Kwiatkowska 2007].

The presence of HS in soils has a significant impact on the sorption of chemicals. With respect to CEC for the HA and FA, it is very high in comparison with other soil components as shown in Table 1. This is due to the presence of negative charge on the surface of the particles of HA and FA [Zawadzki, 1999]. The main reason for the presence of these charges is dissociated functional groups: carboxyl (–COOH) and hydroxyl (–OH) phenols [Oleszczuk 2007a].

Carboxyl functional groups of HA and FA can form cations, for example, heavy metal complexes and chelates, which results in soil detoxification (permanent immobilisation of heavy metals) and increase in the availability of nutrients for plants [Mocek-Plóćiniak 2011].

The mechanism of forming complex or chelate connections involves the displacement of metal cations of hydrogen from a part of the functional groups of HA. Oleszczuk [2007a] reports that chelate structures are characterised by greater durability than complex ones.

A decisive factor in the durability of connections organometallic reaction is the environment in which it occurs. There are two types of organometallic complexes: labile complexes that decompose during the acidification of the environment and more stable complexes that are nondegraded during the change of pH [Kwiatkowska 2007].

In acidic environment metals may be in the form of soluble hydro complexes and free ions, and with the increase of the pH sparingly soluble compounds are generated, mainly hydroxides and carbonates. The deposits of alkaline give rise to ion exchange of metal forms, for example, copper, manifested by the formation of hydroxide anion in the form of Cu(OH)<sub>3</sub><sup>-</sup>, Cu(OH)<sub>4</sub><sup>2-</sup>, Cu(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> [Pandey et al. 2000, Baker, Khalili 2005, Xiaoli et al. 2012].

In addition to reaction, among the factors determining the mobility of heavy metals, include: the origin and original form of chemical pollutant, soil sorption capacity, oxidation-reduction potential and the creation of complex connections with OM. In the case of migration of heavy metals in soil and the aquatic environment, their content and form of migration potential accessible to plants and soil microorganisms are of particular importance [Stern et al. 2014].

Schnitzen and Hansen [cit. by Pastuszko 2007] appointed the so-called constant stabilities of metal-FA and created a number of metal forming complex compounds by increasing the durability of HS: Fe<sup>3+</sup> > Al<sup>3+</sup> > Cu<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Pb<sup>2+</sup> > Zn<sup>2+</sup> > Fe<sup>2+</sup> > Mn<sup>2+</sup> > Mg<sup>2+</sup> > Hg<sup>2+</sup>.

Table 1. Characteristics of soil sorbents [Zawadzki 1999]

Characteristics	Montmorillonit	Illit	Kaolinit	Hydrated oxides Fe and Al	HA	FA
CEC cmol (+)/kg	80-120	20-50	1-10	4	485-870	900-1400
Specific area (×10 <sup>3</sup> m <sup>2</sup> /kg)	600-800	70-120	10-20	–	800-900	
Dependence of charge on pH	weak	medium	strong	strong	strong	strong

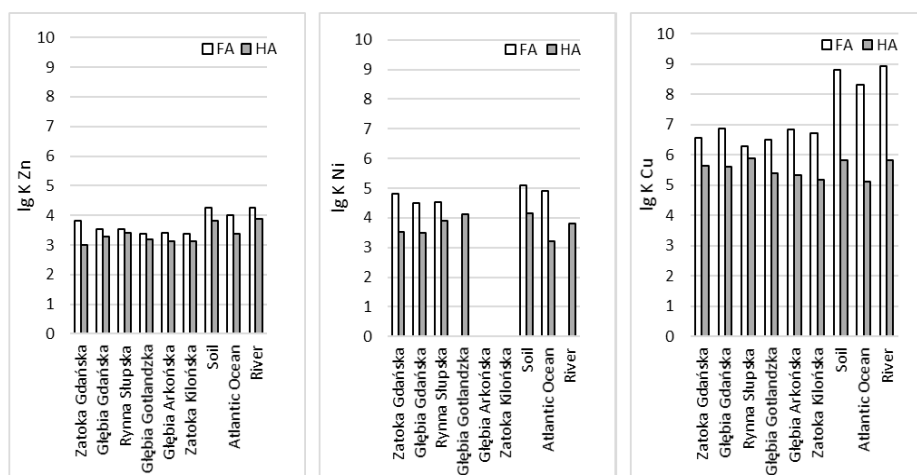


Fig. 1. The values of logarithms of stability of HA complexes (lg K) from the Baltic Sea bottom sediments of heavy metal ions selected. Own study on the basis of [Malej 2009]

The assessment of the degree of metal binding with HS also allows for dependency on van Dijk [cit. by Malej 2009]:  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+} > Zn^{2+} > Fe^{2+} > Ni^{2+} > Co > Mn > Mg > Ca > Ba$ . Van Dijk [cit. by Pastuszko 2007] also demonstrated no significant differences in the strength of metal binding by HA of different origins.

The literature emphasises that HA also helps to detoxify the land and marine systems. The formation of complexes with HS with heavy metal cations plays a significant role in their accumulation in sediments and affects the processes of migration and the redistribution of metals in the aquatic environment. Constant heavy metal complexation with HS has a high value, which prevents the uptake of these metals by the cells in water and soil [Karczewska, Kabała 2010, Mocek-Płóćiniak 2011].

The results of research on creating organometallic complexes in the Baltic Sea water conducted at the Institute of Sciences indicate a large percentage of these complexes in seawater. The research of the Baltic Sea bottom sediments indicates that the content of heavy metals, that is, of Cu, Ni, Zn, Cd, Co, Pb correlates with the content of OM and plays a significant role in the transfer of heavy metals from seawater to the bottom sediments [Pempkowiak, cit. by Malej 2009]. The values of the logarithms of stability constants of complexes (lg K) with metal ions HA and FA isolated from the Baltic Sea bottom sediments, sediment river, ocean and soil, illustrated in the graphs in Figure 1, clearly show the higher values of lg K FA compared with HA [Malej 2009].

Therefore, it is right to say that a higher ability to form metal complexes is possessed by a fraction of FA rather than HA [Paney et al. 2000]. Pempkowiak [cit. by Malej 2009] reports that the value of constant stability of zinc complexes with HA increases with the content of functional groups, and decreases with increasing molecular weight.

### 3. SORPTION OF ORGANIC POLLUTION BY HS

Hydrophobic binding processes of organic pollutants contained in soil or water by HS are not fully understood, but Bejanaro et al.

[2005] and Arias-Estévez et al. [2008] indicate that the factors that may play an important role are hydrogen bonding, covalent, van der Waals forces, ion exchange, adsorption, ligand exchange and chemisorption. According to literature [Chefetz et al. 2000, Jones, Huang 2003, Arias-Estévez et al. 2008] HS can, among others, increase the solubility of nonpolar compounds in water, cause the hydrolysis of certain pesticides, fotosensibilise degradation of organic matter and reduce the bioavailability of PAHs by aquatic organisms.

It is assumed that in the structure of HA and FA there are active sites capable of binding the organic xenobiotics and the intensity of the sorption process depends on the origin, molecular weight and polarity of the HS. HS characterised by poor polarity, thus with a low ratio of oxygen to carbon (O/C) and the aromatic fraction predominantly have a high affinity for hydrophobic organic pollutants [Seibel et al. 1996].

Arias-Estévez et al. [2008] show that the polarity is not always the determining factor in sorption and intensity of this process depends on the soil properties and the type of contamination. Schoone et al. [1997] in this study observed sorption pyrene increase with the decreasing polarity of the OM, while in phenanthrene, there was no such relationship. The sorption of pyrene by OM showed correlation between the increasing number of alkyl groups and the severity of the process. Studies by Chefetz et al. [2000] show that in the process of sorption of organic xenobiotics, the most important role is played by the presence and the relationship of functional groups rather than aliphaticism or aromatics of soil OM.

The reduction of toxicity of the compounds present in the soil over time is observed in the case of insecticides, herbicides, PAHs, 1,2-dibromomethane, and petroleum hydrocarbons. This is called the aging of pollution and what plays an important role is the processes such as sorption, diffusion and distribution of equilibrium (collectively referred to as sequestration). There are two explanations of the process of sequestration of organic contaminants in soils and sediments: diffusion into the OM retained within nano- and micropores soil [Jones, Huang 2003, Trubetskaya et al. 2006].

The sequestration of pollutants depends on the amount, type, properties, age and origin of organic substances. Seibel et al. [1996] in the studies presented a different effect of HA on the degree of degradation of naphthalene, phenanthrene, and pyrene. It was shown that the degree of degradation of naphthalene decreased in the presence of HA, and it was observed that the mineralisation of phenanthrene and pyrene was accelerated. The positive effect of HA on the scope of the degradation of phenanthrene was also found by White et al. [1999].

HS can also connect ammonium salts, urea or phosphorus compounds. Connections arise that can be polymerised and change the properties of HS. This happens usually by HS complexed with  $\text{Fe}^{3+}$  ions,  $\text{Al}^{3+}$  or  $\text{Mn}^{2+}$ . Such combinations make it possible for attachment of phosphorus via an ester  $\text{PO}_4^{3-}$ , or other portions of organophosphates. Attached in this way phosphorus can be partially consumed by the flora present in the water [Malej 2009].

The fraction of OM that may affect the degradation and accumulation of hydrophobic organic impurities is dissolved organic carbon (DOC). The soil can increase the rate of sorption of persistent organic pollutants (i.e. benzo[a]pyrene, tetrachlorobiphenyl) by the DOC with increasing its molecular weight and aromaticity. DOC particles comprise hydrophobic groups that interact with the hydrophobic organic pollutants. Studies on the effects of DOC on the accumulation of persistent organic pollutants by aquatic organisms and soil indicate a reduction of

accumulation of hydrophobic organic pollutants in the presence of DOC. This is explained by the formation of complex bonds between DOC and xenobiotic. The size and polarity of the formed complexes with DOC xenobiotic do not allow for diffusion through the cell membranes of organisms [Akkenen al. 2001 Akkenen and Kukkonen 2001, 2003].

## 4. CONCLUSION

HS in the soil provides a natural barrier to pollution of anthropogenic origin. Due to the presence of active functional groups they are involved in the sorption of pollutants, and thus the detoxification environment. HS improves the physical, physico-chemical and biological soil, they are a source of nutrients, regulate the concentration of soil solution by sorption and release to the solution of various ions and compounds. They have an impact on soil environment protection, on the protection of water and ecosystems against the effects of heavy metal pollution, thanks to their sorption and creating complexes with metal ions, as well as the binding of organic compounds (including pesticides) and increasing their biodegradability.

From the point of view of the role of HS in the making of the soil barrier limiting excessive consumption of contaminants (heavy metals) by plants and migration into the soil profile to groundwater, it seems appropriate to stabilise and/or increase resources of OM as a source of humic compounds.

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