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The Impact of Humic Substances as Remediation Agents to the Speciation Forms of Metals in Soil

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Abstract

Humic substances (HS) are the most widespread group of organic substances in natural environment and have high stability. The main terrestrial reserves are found in the form of naturally occurring ore, peat or lignite. The aim of this paper is to study possibilities to use HS as agents for remediation of contaminated with heavy metals soil and impacts of HS of metal speciation forms in it. It has been proved that HS are able to bind to metal ions and change their speciation forms in soils. The ability to form complexes with metal ions depends on the type of soil, type of metal, as well as concentrations of HS in soil. The study was carried out in experimental conditions and Andre Tessier's analytical method to determine availability of metals to living organisms was used for spiked soils. Remediation by using HS has shown good result for diminishing the content of biologically available copper and lead.

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1. Introduction

Humic substances (HS) are one of the most important groups of biomolecules [1] and do not belong to any unique chemical category. They are defined by combining all known aspects of their properties, including the process of their isolation. The most common definition is that HS are a general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight and refractory properties. [1] Soil HS constitute a physically and chemically

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heterogeneous mixture of macromolecular organic compounds of mixed aliphatic and aromatic nature. They are rich in chemically reactive functional groups, and formed by resynthesis and polymerization processes (humification) of a variety of contributing moieties originating during the microbial and chemical transformation of living organic matter in soil. [2]

Humic substances form major part of soil, water, and fossil carbon-containing mineral (peat, sapropel, brown coal). [3] Humic substances are formed through humification process as a result of decay and transformation of biomolecules and are formed from dead organisms as a result of action of microorganisms on organic matter. [1]

Distribution and level of HS in the environment is mainly determined by the formation during humification process. [4] It is a very complex biochemical process of plant and animal residue decomposition and mineralization of organic matter with additional microbial effects on it.

Humic substances are very stable against the microbial degradation, and the age of them can reach 15 000 yr [1; 5], also can bind with mineral components in soil and water. [6] HS contain functional groups capable of interacting with metal ions to form complexes with them. [7] Ability of HS to form stable complexes with soil or water inorganic and organic components play a key role in formation of the level of environmental pollution and the migration and transformation of pollutants. The protectory function of HS is the ability to link different types of pollutants. [8] HS can also act as a "geochemical barrier". [9] Main functional groups of HS capable of binding metal ions are carboxyl and amino hydroxyl groups. HS can significantly reduce the acute toxicity of metals and bioavailability of metals. [10] There are two types of metal ion binding mechanisms of HS: 1) covalent binding, where each attached atom donates one of associated electrons and 2) coordinated binding, where each metal atom accepts pair of electrons from non-metal. This process of binding among HS and metal ions usually is fast. [11] Humic-metal complex stability may be different for different metals. Metals such as Hg, Cd, Pb have higher stability, while the Ca, Na, Mg and Zn – lower. [12]

Excessive concentrations of heavy metals in soils result often from anthropogenic activities. [13] Remediation technologies can be divided into two categories: *in-situ* and *ex-situ* remediation methods as well as on site and off site technologies. [14] Humic acids (HA) can be considered as important remediation agent for the immobilization of heavy metals in soils. [15] The aim of this paper is to study possibilities to use humic substances as agents for remediation of environment contaminated with heavy metals and impacts of HS of metal speciation forms.

2. Materials and Methods

Mineral soil samples were collected during field works: sandy soil from the E horizon (IM *Haplic Podzols (LVh)*) and sandy loam with high organic content from Ap (*Haplic Luvisols (PZh)*) horizon. Sampling sites were chosen close to each other in Latvia, Vidzeme Highland - Taurene and Dzerbene.

Soil were crushed and weighted by 500 g of each sample. There were prepared metal Cu and Pb salt solutions in order to prepare heavy metal concentration of 1 g per kg of soil. Spiked soil was weighted by 10 g per sample. HS "Gāgu" were extracted from peat with such parameters: C 48.54%, H 5.54%; N 1.15%; S 0.84%; O 40.79%, ash content 3.99%, pH 2.5, humification level 29%, age 1150 yr. Conventional extraction technique of low temperature treatment was used, where humic acids are extracted and purified using procedures recommended by the International Humic Substances Society. [16] HS solution was added to each sample in such amounts: 0.0, 1.0; 5.0; 10.0; 20.0 (g l⁻¹). PLATFORM SHAKER UNIVERSAL PSU-20, BIOSAN was used for agitation. The prepared samples (20) were held for 4 months at 20°C temperature. Afterwards samples were dried in GALLENKAMP PLUS II OVEN.

In order to evaluate biological availability of metals, Andre Tessier has developed analytical method to determine availability of metals to living organisms (Table 1).

Table 1. Determination of biological availability of metals to living organisms. [17]

Metal forms	Extraction procedure
Free exchange forms	1 M MgCl ₂ (pH 7, 2 h, 25° C)
Bound with carbonates forms	1 M CH ₃ COONa (pH 5, 12 h, 25° C)
Bound with Fe/Mn oxides forms	0.1 M NH ₂ OH+0.01 M HNO ₃ (pH 2, 12 h, 25° C)
Bound with organic sulphides forms	30% H ₂ O ₂ +0.01 M HNO ₃ (pH 2, 3 h, 80° C)
Stable forms	HNO ₃ (2 h, 100° C)

This approach helps to study the possible use of HS for contaminated soil recultivation. Atomic absorption spectroscopy (AAS) using Perkin Elmer instrument at the laboratory of the University of Latvia was used as a spectroanalytical procedure for the quantitative determination of chemical elements to determine concentration of Cu and Pb in samples.

3. Results

Spiked sandy loam soils from the Ap horizon have shown that increasing amount of HS additives allow to diminish the amount of copper and lead ions that are biologically available and increase the content of stable metal complexes (Fig. 1 and 2). Characterizing the interaction of HS with heavy metals, it is essential to assess the factors which determine the process of binding. Influential factors include soil texture and mineral composition – the process is dependant on the type of soil, as well as ability of soil-forming minerals to interact with both metals and HS. Amount of free exchange copper and lead cations is generally decreasing, the trend go upwards if the amount of HS amended is increased up to 20 g l⁻¹ (Fig. 3). Increasing concentration of HS increase with organic matter and sulphides associated and stable forms in soil. Significant increase of HS amount in sandy soil decreases easily available free exchange forms (Fig. 4). Metals in the Ap horizon during the time of 4 months has been bound in more stable complexes than at the beginning before the HS amendment – stable fraction has increased for both Cu and Pb. By adding HS is increasing the stability of metal complexes even further (Fig 1 and 2).

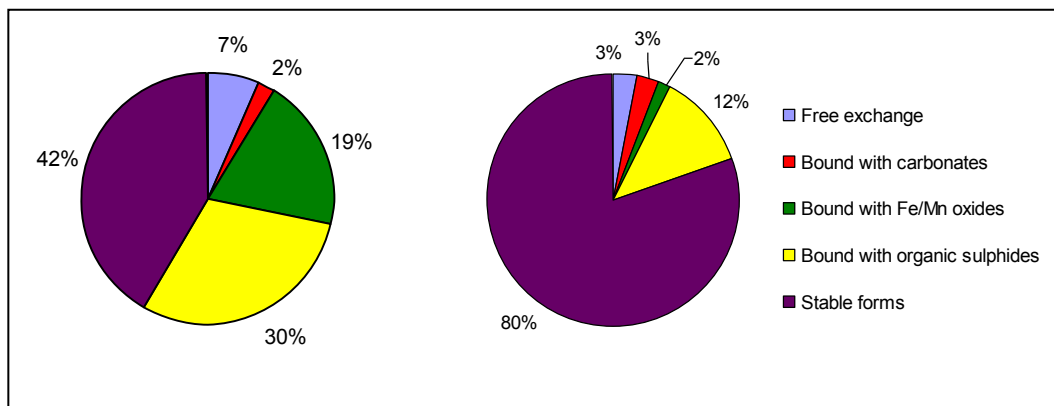


Fig. 1. (a) Forms of copper in sandy loam soil (Ap horizon) with no amendments of HS; (b) Forms of copper sandy loam soil (Ap horizon) with HS solution amendment of 20 g l⁻¹.

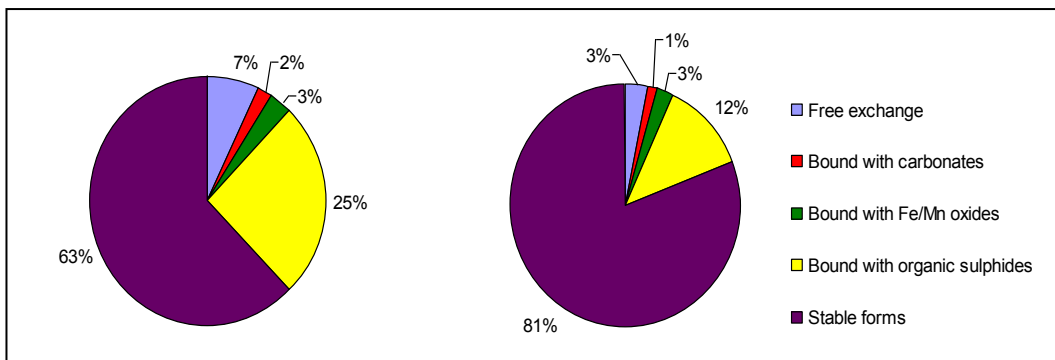


Fig. 2. (a) Forms of lead in sandy loam soil (Ap horizon) with no amendments of HS; (b) Forms of lead in sandy loam soil (Ap horizon) with HS solution amendment of 20 g l⁻¹.

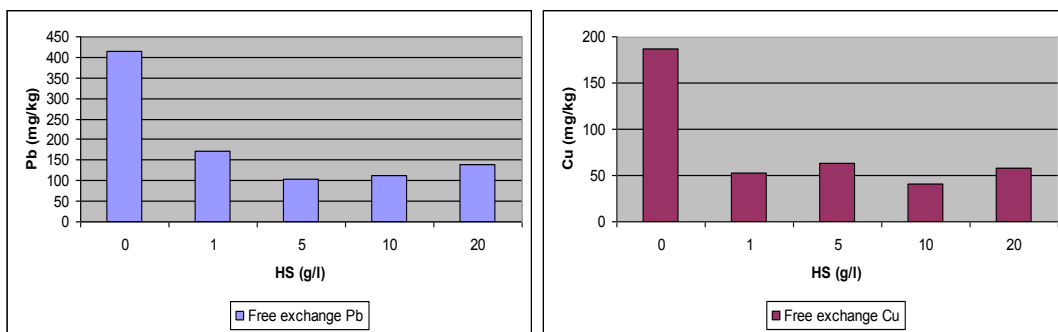


Fig. 3. (a) Free exchange lead (Pb) in sandy soil (E horizon) with various HS solution amendment 0-20(g l⁻¹); (b) Free exchange copper (Cu) in sandy soil (E horizon) with various HS solution amendment 0-20(g l⁻¹)

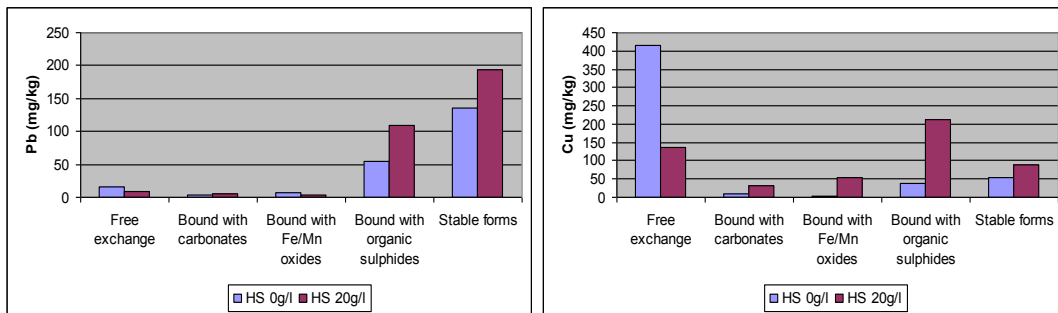


Fig. 4. (a) Lead (Pb) in sandy soil (E horizon) with various HS solution amendment 0-20 (g l⁻¹); (b) Copper (Cu) in sandy soil (E horizon) with various HS solution amendment 0-20 (g l⁻¹)

Adding HS for both types of soil improves the forming of stable metal complexes where both lead and copper are less available for plants.

4. Conclusions

Remediation by using HS has shown good result for diminishing the content of biologically available copper and lead. Contaminated sandy loam and sandy soils from Ap and E soil horizons exposed to HS additives transform metals to biologically unavailable stable forms and diminish amount of free exchange cations.

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