Detoxifying Ability of Coal Humic Acids and Their Hydroquinone Enriched Derivatives in relation to Copper under Field Conditions

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1. INTRODUCTION

Humic substances (HS) have been the subject of numerous scientific studies due to their mitigating effects on contaminants toxicity to biota. The detoxifying properties of HS are generally attributed to their capability for binding ecotoxicants of different classes including heavy metals. The binding of heavy metals to HS causes formation of less bioavailable complexes followed by lowering their toxicity and bioaccumulation. Therefore, development of approaches which are aimed to intensify binding ability of HS in relation to ecotoxicants are of ultimate importance. Oxygen containing functional groups of HS are supposed to be responsible for HS binding properties in relation to heavy metals. Thus, enrichment of HS with above mentioned moieties might provide increase in chelating properties of humics followed by increase in detoxifying ability of HS. The goal of this study was to estimate detoxifying ability of coal derived HA and their hydroquinone enriched derivatives in relation to copper.

2. MATERIAL AND METHODS

For this study humic acids isolated from leonardite was used (CHP). To synthesize hydroquinone enriched derivatives, polycondensation of CHP with hydroquinone has been carried out using HS : hydroquinone ratio as 1 g : 250 mg. Two initials concentration of CHP such as 5 and 12% were used and two corresponding derivatives assigned as CHP-HBQ250-5% and CHP-HBQ250-12% were obtained. The total and carboxylic acidity of the preparations was determined using standard barita and calcium acetate techniques, respectively. The obtained results demonstrated higher contents of both carboxylic and phenol acidic groups in the synthesized derivatives as compared to the initial humic material. That finding indicated successfulness of the performed modification.

Detoxifying activity of the humic preparations was estimated by two-years field experiments conducted under sod-podzolic soil conditions. Plants of wheat *Triticum aestivum* L. were used as a target object, and fresh weight of 10 plants was used as a response. To create contamination with copper, copper solution was applied in the first year of the study in the form of $CuSO_4 \times 5H_2O$ up to dosage of 3 t of $CuSO_4 \times 5H_2O$ per hectare. Humic preparations was introduced at the application rate of 100 kg/ha in the first year of the experiment as well. To determine mobile copper content in soil, samples were collected after plant harvesting and subjected to extraction with acetate-ammonium buffer (pH 4.7) at the soil : solution ration 1: 10 followed by AAS detection in propane-air flame.

3. RESULTS AND DISCUSSIONS

The obtained results demonstrated significant decrease in copper toxicity in the presence of humics (Fig. 1), and detoxifying ability of CHP-HBQ250-12% was the most pronounced that corresponded well to the highest contents of acidic groups in that preparation.

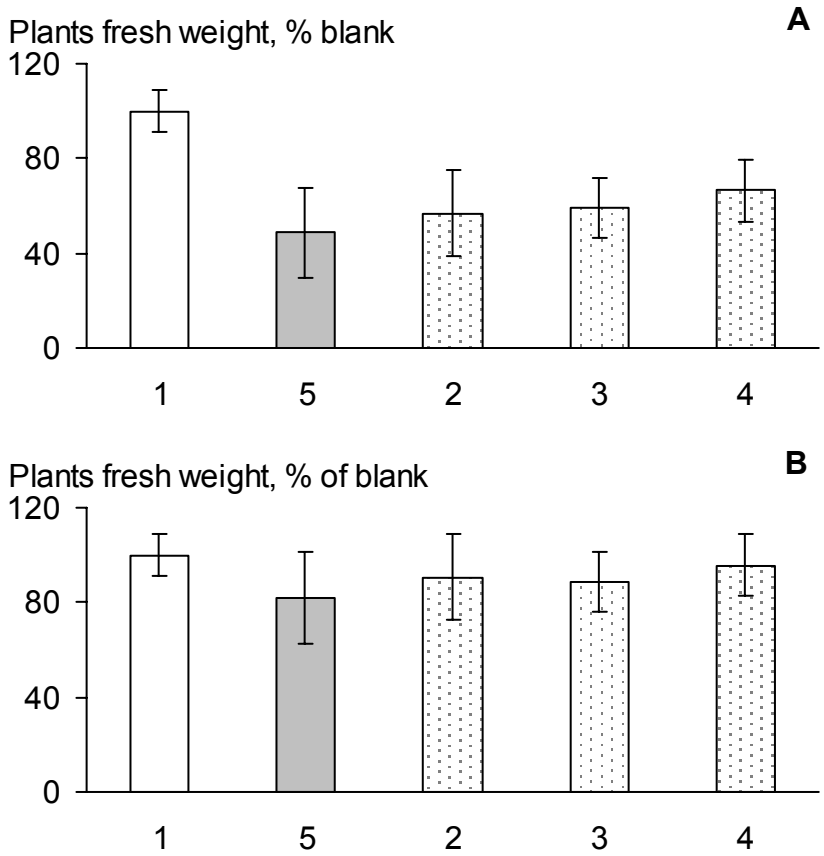

Fig. 1. Detoxifying ability of humic derivatives under study towards copper in the first (A) and second (B) year of treatment.

1 – blank; 2– CHP, 3 – CHP-HBQ250-5%, 4 – CHP-HBQ250-12%, 5 – $CuSO_4 \times 5H_2O$.

In the first year of treatment humics introduction into the copper-contaminated soil resulted in remarkable increase in plant biomass. However, even in case of CHP-HBQ250-12%, fresh weight of wheat plants did not exceed (67±13)%, i.e. was lower blank values. The latter meant that higher humic detoxicant : copper ration then 100 : 7 should be used for soil remediation.

In the second year of the study copper toxicity was less pronounced probably due to copper migration from the soil. Similarly to the first year, humic introduction resulted in significant decrease in copper toxicity to plants (Fig. 1B). When CHP-HBQ250-12% was applied to the copper contaminated soil, biomass of wheat did not differ statistically from that value for the blank variant. Therefore, prolonged detoxifying activity of humic preparations in relation to copper has been demonstrated.

According their detoxifying ability, the tested humic preparations can be put in the following descending order: CHP-HBQ250-12% > CHP-HBQ250-5% > CHP. Based on the conducted experiments, CHP-HBQ250-12% could be recommended as the most promising detoxifying agents towards heavy metals.

Contents of mobile copper in soil presented in Table 1.

Table 1. Content of mobile copper in sod-podzolic soil contaminated with copper and treated with humic detoxicants

Variant	Mobile copper content, mg/kg of soil	
	First year of treatment	Second year of treatment
Blank	10±4	8±3
Copper	600±5	75±10
Copper + CHP	580±5	79±10
Copper + HBQ250-5%	590±5	76±15
Copper + HBQ250-12%	406±10	73±11

Obtained results demonstrated that soil used could be characterized with content of mobile copper common for sod-podzolic soils. When copper was introduced into the soil, it concentration increased to 600 mg/kg. On the contrary to variants without added blue vitriol, treated of copper-contaminated soil with all the studied humics resulted in considerable decrease in content of mobile copper. Among the humics studied, the highest lowering in toxicant content in soil was observed for variant with HBQ250-12% which was

shown to possess the highest detoxifying ability. That finding indicated that introduction of both parent humic material and humic-based detoxicants led to lowering of copper available for plants.

In the second year of the study mobile copper contents lowered considerably as compared to the year of treatment. Similar tendency of decrease in contents of mobile copper was observed for the variants with humics introduction. Taking into consideration, however, the fact that humics decreased contents of mobile copper in the year of treatment, it must be concluded that residual contents of copper in soil related to endogenous soil organic matter rather than introduced HS. So, humics introduction into copper-contaminated soil did not influence significantly on copper mobility in soil.

4. CONCLUSIONS

Our results demonstrated clearly that detoxifying ability of HS in relation to heavy metals could be increased by means of polycondensation with hydroquinone. The obtained detoxicant possessed prolonged activity for least two years after treatment and did not influence significantly on copper mobility in soil profile.

ACKNOWLEDGEMENTS

This work was supported by ISTC (#KR-964).