



Application of humic compounds for remediation of soils contaminated with heavy metals: the benefits and risks

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Applicability of humic compound (HC) "Extra" (potassium humate produced from coal) was studied to remediate soils contaminated with copper in model experiments.

Field experiments were carried out in 10-litter plastic containers. The upper layer was prepared as a mixture of loam (pH=5.3), sand (pH=7.4) and peat(pH=5.5). It was underlain consequently by loam and gravel. To study water migration we installed lysimeters. The experiment was conducted in 3 variants: 1) control, 2) control+Cu, 3) control+Cu+HC. Copper was applied in the form of dry powder ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) over the upper layer of the soil column in a concentration of copper equaling to 1000 mg/kg. Total concentration of copper was determined by ICP AAS, its free ions was measured with the help of ion-selective electrode. Humic compound was sprayed on the surface in liquid form. The vessels stayed outdoors from July to October 2014 with additional watering in dry periods.

Analysis of lysimetric waters obtained from this model field experiment revealed significant impact of pH. Application of the humic compound produces almost 5 times higher content of soluble organic substances than in the variant without it, and in the first portions of lysimetric waters the difference is 20-fold. Generation of extra organic content in soluble form was accompanied by the 2-6 times increase of the water soluble copper yield. However the content of the free copper ions in lysimetric waters in case of addition of the potassium humate was negligible, because almost all copper was bounded with water-soluble organic substances.

The copper content in water extract from the top layer of soil in the variant with HC was about 1 mg/l, that was 2 times higher than without HC. The content of water-soluble organic carbon in HC variant was 100 mg/L, and without HC was 10 times lower (10 mg/l). The water extract from soils enriched in HC was passed through a column filled with weakly basic anion exchange resin DEAE (Cl-form), the eluate was found to contain only 3-9% of copper. The content of free Cu^{2+} ions in the sample extract was negligible.

The samples used for field experiments were tested in laboratory to estimate their sorption capacity for Cu. For this purpose, 300 g of substrate (loam and mixed organic substrate) with addition of water (control) and humic preparation (same dose as in the field experiment) were kept in the laboratory for 1 week. Soil samples were then dried and brought into equilibrium with the solution of copper sulfate at concentration of 50 mg/l. The concentration of copper in the solution in equilibrium with HC was 2.5-4 times higher than in the control variant; absorption of copper by solid phase decreased by 5-6%. Results of the laboratory study were in good agreement with the results of the field experiment. Addition of HC increased the content of soluble organic matter and copper complexation by an order of magnitude and thus reduced the

activity of copper ions in the liquid phase that was treated as a possible remediation effect of the humic compound for plants and biota. However the increased total metal content mainly in a migration-capable form (negatively charged complexes with organic matter) may increase the risk of contaminating ground waters with heavy metals. Therefore, application of the artificial humic compounds for remediation of soils contaminated with heavy metals requires monitoring and further development of means to prevent their migration.