THE USE OF SOIL WITH HIGH CONTENT OF HUMIC SUBSTANCES FOR THE REMEDIATION OF SOIL POLLUTED WITH COPPER

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Abstract
Within the environmental study in the area of future accumulation lake (54 millions cubic meters and 230 ha) Rovni near Valjevo (Serbia and Montenegro) it was concluded that 10 cm of the upper layer of the forest soil should be removed in order to prevent the emission of organic carbon. This portion of soil (53 ha) had low copper content (20 mg/Kg) and high content of organic carbon (up to 4.7 %). High content of humic substances made this soil interesting for studies of the possible protective effect. The wheat is very sensitive for the presence of copper in the soil and therefore it was used in all experiments. The protective effect of the upper soil layer from inundation area was found for copper content up to 1000 mg/Kg. Dilution of the soil with quartz sand (and consequent lowering of the concentration of humic substances) decreased considerably the protective effect. For the mixture of soil with the quartz sand (2:1), the phytotoxicity was found for the copper content of abaout 500 mg/Kg. The results of these and similar experiments indicated that the upper soil layer from inundation area of a future lake Rovni could be used for the remediation of soil polluted with copper.

Introduction
Within the preparation of inundation area of a future accumulation lake it is often necessary to remove huge amount of the soil rich in humic substances. That was the case with the accumulation lake (54 millions cubic meters) Rovni near Valjevo (Serbia and Montenegro). Within the environmental study it was concluded that 10 cm of the upper layer of the forest soil should be removed to prevent the emission of organic carbon. In order to reduce the cost of this operation and to improve the economy of the accumulation lake Rovni the possibilities for the use of this waste forest soil for remediation of another soil polluted with high concentrations of copper were studied. The afinity of fulvic acids for binding od copper ion was described in the literature (1,2,3). However, the afinity of fulvic acids to complex copper can vary due to the complex structure of fulvic acids and their different origin. Therefore, we had to study on the specific soil sample the protective effect of humic substances on the phytotoxicity of copper.

Methods
Humic substances were extracted from the soil with sodium hydroxide solution. After centrifugation one part of the solution was acidified to pH 6.4, evaporated and dried to the constant mass. The content of organic carbon in the dry residue was determined by elemental microanalysis and it was used for the calculation of the content of humic carbon in the soil.
The main portion of the solution was acidified to pH 1-2 in order to precipitate the humic acids. The remaining solution of fulvic acids was used for:
a) interactions of fulvic acids with copper (II) ions; fluorometric in vitro measurements (4)

b) experiments in which the influence of copper(II)sulphate on the wheat in the soil with or without quartz sand.
Experiments were performed with in the glasses filed with soil with different content of copper(II)-sulphate and humic substances. Young wheat plants were placed in so prepared soil samples and the measurements were taken after eight days. Fluorescent emission was measured at Specol 10 at 465 nm with excitation at 365 nm. Similar measurements were made with the solutions with the same ratio of copper and fulvic acids. All measuremets of the influence of copper(II)-ions on wheat in the soil were repeated six times.

Results and discussion
It was found that the soil sample contained 8.251 g C/kg. Such highly humified soil should contain high concentrations of humic and fulvic acids and therefore their protective effect on the toxicity of heavy metals on plants could be expected. The influence of high concentrations of copper(II) ions on the length of young wheat plants were presented in Table 1 and Figure 1.

Table 1: Dependence of plant length after 8 days with the content of added copper in soil

Sample	[Cu] (mg/Kg)	Plant length (cm)	Root length (cm)	Shaft length (cm)
1	0	33.44 ± 11.42	7.44 ± 2.04	22.11 ± 12.51
2	100	34.36 ± 5.66	7.57 ± 1.65	26.23 ± 5.67
3	250	35.98 ± 6.93	8.55 ± 1.65	27.43 ± 6.54
4	400	28.54 ± 9.32	7.94 ± 1.30	21.41 ± 8.77
5	500	19.82 ± 7.22	5.84 ± 2.18	14.08± 7.61
6	750	14.48 ± 3.32	5.82 ± 1.95	8.66 ± 1.75

Figure 1 : Dependence of plant length with the content of Cu (II) ions

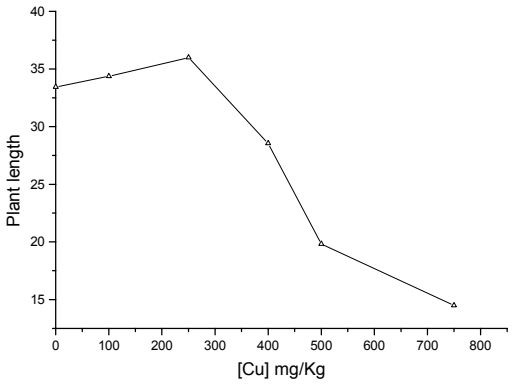
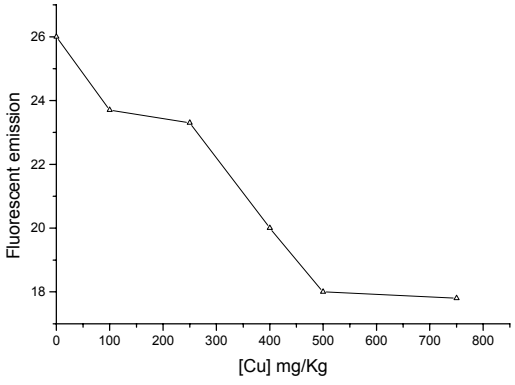
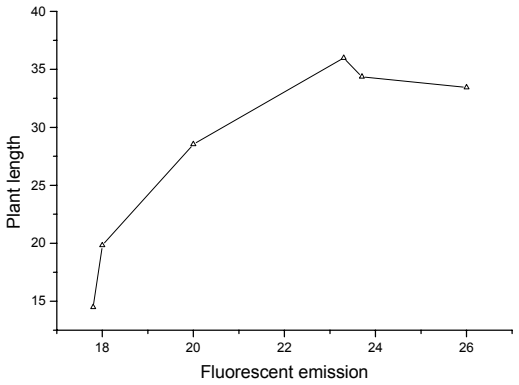


Figure 2 : Dependence of fluorescent emission (465 nm) with the content of Cu (II) ions



The addition of small amounts of copper was stimulative for plants (Figure 1). Further increase of copper to 400 mg/Kg resulted in the lose of protective effect of soil. Similar shape of the curve in Figure 1 with the corresponding shape in Figure 2 (dependence of the fluorescent emission with the content of copper ions) indicated that the main protective effect of the soil could be attributed to fulvic acids. Dependence of plant length with fluorescent emission (Figure 3) corroborated this finding.

Figure 3 : Dependence of plant length with the fluorescent emission



In another series of experiments diluting of soil with quartz sand (2 :1) decreased the content of humic substances and it was found that the protective effect towards poisoning with copper (II) ions was diminished (Table 2). In the sandy soil the smaller length of plants were noted also in the control samples (without addition of copper ions). However, the toxic effect of copper (II) ions was greater. Comparative results of the toxicity of copper (II) ions concentration of 0 and 400 mg/Kg were shown in Table 2.

Table 2. Comparative results of the toxicity of Cu (II) ions

Sample	[Cu] mg/Kg	Plant length (cm)
Soil	0	28.3 ± 1.1
Soil	400	17.9 ± 5.1
Soil and quartz sand	0	23.0 ±1.5
Soil and quartz sand	400	8.6 ± 2.6

Conclusions

The protective effect of humic substances in the forest land from the inundation area of the future accumulation lake Rovni near Valjevo (Serbia and Montenegro) was studied under laboratory conditions. The length of wheat plants obtained in several series of experiments was measured in order to investigate the influence of humic substances on the toxicity of copper (II) ions in the range of concentrations 0-750 mg/Kg. The purpose for this study was to explore the possibility for use of the forest soil rich in humic substances for the remediation of soils containing phytotoxic concentrations of copper.

On the basis of the results obtained it could be concluded:

1. Forest land contained high content of humic substances (8.251 g C/Kg).

2. Humic components of soil exhibited strong protective effect due to the binding of copper up to the concentrations of 400 mg/Kg.

3. Diminishing of the concentration humic substances in soil (by dilution of soil with quartz sand) the toxicity of copper was increased 2.67 times.

4. Comparison of the measurement of fluorescent emission of the solution with the same ratio of fulvic acids to copper (like in the experiments with wheat) it was found that the protection of wheat could be attributed mostly to fulvic acids (due to their ability to complex copper ions). Therefore the effect of humic acids was minor.

5. Very good correlation was found between the fluorescent emission at 465 nm (EXC = 365 nm) and the average length of plants that were subjected to copper ions. The correlation coefficient (r) was +0.95 and P>99%.

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