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# Ecotoxicological characteristic of a soil polluted by radioactive elements and heavy metals before and after its bioremediation

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ABSTRACT

Cinnamonic soils from southeastern Bulgaria are heavily polluted with radionuclides (uranium, radium) and toxic heavy metals (copper and lead) due to the aerial transportation of fine particles from flotation tailing dumps to the soil surface. As a result of this, the polluted soils are characterized by a slightly alkaline pH (7.82) and positive net neutralization potential (+136.8 kg $CaCO_3$/t). A fresh sample of cinnamonic soil was subjected to remediation under laboratory conditions in four lysimeters each containing 70 kg of soil. The preliminary study revealed that most of the pollutants were presented as carbonate, reducible and oxidizable fractions, i.e. pollutant ions were specifically adsorbed by carbonate and ferric iron minerals or were capsulated in sulfides. The applied soil treatment was connected with the leaching of the pollutants located mainly in the horizon A, their transportation through the soil profile as soluble forms, and their precipitation in the rich-in-clay subhorizon $B_3$. The efficiency of leaching depended on the activity of the indigenous microflora and on the chemical processes connected with the solubilization of pollutants and formation of stable complexes with some organic compounds and chloride and hydrocarbonate ions. These processes were considerably enhanced by adding hay to the horizon A and irrigating the soil with water solutions containing the above-mentioned ions and some nutrients. After 18 months of treatment, each of the soil profiles in the different lysimeters was divided into five sections reflecting the different soil layers. The soil in these sections was subjected to a detailed chemical analysis and the data obtained were compared with the relevant data obtained before the start of the experiment. The best leaching of pollutants from horizon A was measured in the variants where soil mulching was applied. For example, the best leaching of lead (54.5%) was found in the variant combining this technique and irrigation with solutions containing only nutrients. The best leaching of uranium (66.3%), radium (62.5%), and copper (15.1%) was measured in the variant in which the soil was subjected to mulching and irrigation with alkaline solutions containing hydrocarbonate ions. Despite the removal of higher amounts of these pollutants from the soil, the acute soil toxicity towards earthworms (*Lumbricus terrestris*) was higher in comparison to the toxicity of soil that had been treated in other variants. Furthermore, the highly alkaline soil pH (10.47) that was determined through the applied alkaline leaching resulted in an acute soil toxicity to oats (*Avena sativa*) and clover (*Trifolium repens*) that was even higher in comparison to the toxicity of the non-treated soil. These data revealed that the soil detoxification was depended not only on the decrease of the total concentration and on the bioavailable forms of the above-mentioned pollutants but also on the changes that had taken place in chemical and geotechnical properties of the treated soil.



## 1. Introduction

Remediation of soils polluted by radioactive elements and non-ferrous metals could be divided into two main groups with respect to a pollutant's behavior during the remediation process. The first group includes methods where the main goal is to stop/prevent pollutant migration into the environment. It could be achieved by means of their transformation into solid phases with higher stability due to addition of some sorbents (Castaldi et al., 2005; Chen et al., 2003), suitable change of soil acidity (Alva et al., 2000; Clemente et al., 2006) or redox conditions (Abdelous et al., 2000; Groudev et al., 2010) as well as establishment of suitable covers on the heavily contaminated sites (Komnitsas et al., 1999; Lu et al., 2013). The second group includes methods where the main goal is completely opposite to the previous group — to create and maintain conditions which enhance pollutant leaching from soil horizon and their downward migration by means of draining soil solutions (Kumar and Nagendran, 2009; Toth, 2005) or pollutant migration in upward direction by means of their uptake and accumulation into the plant biomass (Bhargava et al., 2012; Ebbs et al., 1998). Regardless of the chosen method, there are several key factors which preliminary evaluations determine the process efficiency at a

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later stage. First of all, solid phase pollutant characterization by means of suitable extraction tests (Pagnanelli et al., 2004; Tessier et al., 1979), the results of which throw light on the main mobile fractions as well as stimulation of which biogeochemical process will lead to their redistribution in a suitable direction. The second key factor is acid–base soil property which reflects on soil pH. Its value determines in large extent the size and charge, existing on the surface of soil grains (Dube et al., 2001) and if there is a need to manipulate it during application of the relevant remediation method (Harter and Naidu, 2001; Sakurai et al., 1989). The third factor concerns the chemistry of a pollutant itself — valence state(s), speciation and stability of its soluble forms, etc., which depend on the soil condition. Exact evaluation of all that information allows elaborating a suitable strategy for soil remediation. Regardless of the decreasing of the total concentration of a pollutant and/or its leaching in soil horizon, most methods for soil remediation are connected with changes of some basic parameters of the soil biotope. Assessing their effect towards soil biota is carried out by ecotoxicological tests which determine if there is a need for additional steps before the cleaned soil is used in agriculture.

The main aim of this study was to evaluate possibilities for in situ remediation of heavily polluted soils by means of leaching of soil contaminants from topsoil and their precipitation into the soil depth.

The approaches for soil remediation applied in this study to enhance the leaching of the soil contaminants from horizon A were transport of the released ions through the soil profile by means of soil solutions and contaminant precipitation in rich-in-clay soil horizon $B_3$. Four different variants of soil treatment were tested in this study by means of large scale lysimeters.

## 2. Materials and methods

### 2.1. Soil characteristic and remediation

The soil sample used in the experiment belonged to the cinnamonic soil type. The soil profile was consisted of: horizon A (0–30 cm), horizon B (31–70 cm), horizon C (71–90 cm), and a clay horizon (91–110 cm). The soil pH was determined at 1:2.5 ratio with distilled water. Humus content, cation exchange capacity (CEC) and carbonate content were determined by means of suitable methods (Pansu and Gautheyrou, 2006). The net neutralization potential was determined by a static acid–base accounting test (Sobek et al., 1978). Elemental analysis of the digested soil sample was determined by atomic absorption spectrometry (AAS) and induced plasma spectrometry (ICP). The specific activity of Ra-226 was measured by means of a gamma-spectrometer (ORTEC-USA). The mobile forms of heavy metals and uranium were determined by means of a sequential extraction method (Tessier et al., 1979) and a bioavailability test (Lindsay and Norvell, 1978).

The soil permeability was determined by means of a double ring infiltrometer method (U.S.EPA, 1991).

The soil sample was treated in zero suction type lysimeters. Each lysimeter was charged with 70 kg of soil keeping the natural soil structure. A sand layer was located beneath the soil profile which enhanced the soil solutions to drain easily.

The soil in Lysimeter 1 was irrigated with solutions containing 0.10 g/l $NH_4Cl$ and 0.02 g/l $K_2HPO_4$. The soil in Lysimeter 2 was irrigated with the above-mentioned solution plus 0.05 N $NaHCO_3$.

Plant biomass (as a finely cut hay) was added to and mixed with the soil horizon A in Lysimeter 3 and Lysimeter 4 to a final content of 4%. The hay consisted of 36% cellulose, 24% hemicellulose, 18% lignin and 6.1% ash. The soils in Lysimeter 3 and Lysimeter 4 were irrigated with the same solutions as those used in Lysimeter 1 and Lysimeter 2, respectively. The irrigation rate was 50 l/t soil per week per lysimeter. Each week the pregnant effluents from the lysimeters were replaced with fresh solutions with the relevant initial composition. The leaching was carried out at temperatures varying in the range of about 15–23 °C for a period of 18 months.

A nutrient solution containing equimolar concentration of acetic and lactic acids (total organic carbon of 200–220 mg/l), preliminary neutralized to pH 6.1–6.3, was injected weekly at a depth of 75 cm during the soil treatment.

### 2.2. Chemical analyses

The heavy metal transport through the soil profile was monitored regularly by means of sampling of the drainage soil solutions. The collected solutions were characterized by measurement of pH, Eh, alkalinity, and dissolved organic carbon (APHA, 1995). The concentrations of heavy metals and uranium were determined after the preliminary digestion of dissolved organic compounds by means of 705 UV Digester (Metrohm). The heavy metals were analyzed by means of ICP spectrophotometry. Uranium concentration was measured photometrically using the Arsenazo III reagent (Savvin, 1961).

### 2.3. Ecotoxicity analyses

The ecotoxicity analyses were carried out with the non-treated soil sample of the horizon A as well as samples of the topsoil which have been remediated at relevant conditions.

The soil toxicity towards oats (*Avena sativa*) and clover (*Trifolium repens*) was determined in accordance to a range-finding test (OECD, 1984) with a purpose to establish dose–response relationship for the plant species towards the tested soil sample. The test concentrations of the soil sample were in the range of 10–100% (weight) and the rest milieu for plant growth was composted biomass. Each pot was sown with ten seeds of one of the two plant species. Three replicates were used for each test concentration as well as for controls of each species. In the control the seeds were sown in composted biomass (pH ($H_2O$) 5.9–6.1). The test was carried out in a greenhouse at temperatures 16–22 °C, and precise control on the duration of photoperiod (16 h) and the soil humidity (maintained by means of distilled water). The test's duration was 30 days.

The soil toxicity towards earthworm (*Lumbricus terrestris*) was carried out with a synchronized population which was cultivated preliminary for 1 year at laboratory conditions in brown forest soil. The toxicity of the soil sample was determined by range-finding and definitive tests (U.S.EPA, 1996) which were carried out in plastic boxes with a volume of 1.0 l. The test concentrations of the soil sample were in the range of 10–100% (weight) and the rest milieu was brown forest soil. Three replicates were used for each test concentration with ten worms with similar lengths added to each. Ten worms were added to the control too which consisted of brown forest soil only. The duration of the test was 30 days. The worms' survival and marks of their activity were determined at the end of the toxicity test.

The data from all replicates of each test concentration of the relevant soil sample to the relevant species were statistically assessed by means of determination of the average values and standard deviation. The main ecotoxicity parameters—No Observed Effect Concentration (NOEC), Lowest Observed Effect Concentration (LOEC), $LC_{50}$ and $LC_{100}$ were determined by processing experimental data by means of Shapiro–Wilk's test and the Probit method (U.S.EPA, 1994).

### 2.4. Study site

Some soils from the Southeast Bulgaria are heavily polluted with radioactive elements as well as non-ferrous metals. In that area, one of the facilities for mining and processing of copper ores in Bulgaria — Burgas Copper Mine is situated. The flotation tailings generated during the ore's processing had been deposited on a flotation dump for decades. That dump was a point source for the soil pollution with those contaminants due to the aerial transportation of mineral particles and their deposition on the soil surface. So, a soil plot with a surface area of almost a decare was excluded from agricultural activity due to the concentration of the