# VERTICAL DISTRIBUTION OF COPPER CONTENT IN SOIL FROM ZLATNA AREA

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Abstract: Activity of non-ferrous metallurgical plant from Zlatna were released directly to atmosphere high levels of heavy metal, most of them were deposited on soil. The soil acts as a sink in which heavy metals are accumulated. The object of this study is to assess the distribution of copper along the different soil profile at specific distance from the pollution sources and under different land use. The vertical distribution of total copper was studied on 25 soil profiles. The main soils from investigated area are: Dystric Cambisols, Eutric Cambisols, Haplic Luvisols, Luvisols, Regosols, Fluvisols, and strongly eroded soils. The studied soils have been classified according to their main characteristics in agreement with WRB 98. The soil samples were taken from each soil horizons. The field studies were made on area of the influence of Ampellum Zlatna S.A, on 14 km upstream and 22 km downstream of contaminating source The total copper was measured with flame atomic absorption by a mixture of strong acids (hydrochloric,

sulphuric and perchloric acid-5:10:1 ratio). In the examined soils, generally, the copper soil profile distribution show a maximum value in the top soil and then decrease with depth. Between soils copper content and soil organic matter of studied soil was established a very significant correlation. The highest values of total copper were determined in the litter, followed by pasture and arable land. In soil used as forest, the cooper is highly accumulated in the forest litter and then decrease on soil profile. The highest contents of total copper in soils used as meadow are retained in the top few centimeters of the surface soil. In case of arable land use, the maximum values are recorded under plowed layer and then decrease on soil profile. The distribution of the copper on soil profile presented less variation with soil type, but rather with distance from pollution source and land use. The human impact of metal accumulation in top soil was confirmed by the fact that concentrations of copper decreased with depth.

Key words: Copper, vertical distribution, soil, Zlatna

#### INTRODUCTION

The Ampellum plant processed sulphide concentrates (~ 35-40% Cu) containing varying amounts of S and metals, including Au, Ag, Pb, Zn, Bi, Cd and Mo (WILLIAMSON et. al, 2003), here was produced between 30.000 and 10.000 tones Cu per year (MATOUSEK, 1994, quoted by WILLIAMS et. al, 2003). On the soil were annually deposited 168.785 tons of sediment particles containing heavy metals, including copper (RAUTA et al., 1998).

Contamination of soils with elements such as copper, lead and zinc appears to be largely irreversible (PURVES, 2003). Metallic pollutants are toxic even in very small amounts because of their non-biodegradability and cumulative nature (TEMBO et al., 2006).

Therefore, soil acts as a sink or filter in which heavy metals have accumulated rapidly but are depleting slowly. Unlike other environmental compartments (atmosphere, water), heavy metals in soil are characterized by long residence times (LOMBI et al., 1998).

The object of this study is to assess the vertical distribution of Cu in different soils and under different land use from Zlatna area.

#### MATERIAL AND METHODS

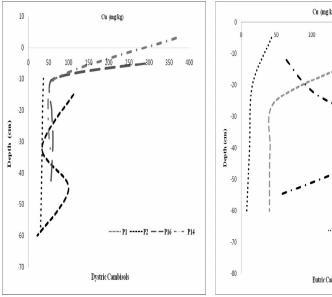
The vertical distribution of total copper was studied on 25 soil profiles. The main soils from investigated area are: Dystric Cambisols, Eutric Cambisols, Haplic Luvisols, Luvisols, Regosols, Fluvisols, strongly eroded soils. The studied soils have been classified according to their main characteristics in agreement with WRB 98. The soil samples were taken from each soil horizons. The field studies were made on area of the influence of Ampellum Zlatna S.A, on 14 km upstream and 22 km downstream of contaminating source.

The total copper was measured with flame atomic absorption by a mixture of strong acids (hydrochloric, sulphuric and perchloric acid-5:10:1 ratio).

## RESULTS AND DISCUSSIONS

The level and distribution of total and extractable Cu in the soil profile can be expected to vary with soil type and parent material from which the soils are derived. However, profile distribution of Cu can be altered by various pedological factors-physical, chemical and biological (ADRIANO, 2001).

The distribution of total Copper in soil profile is studied in different soils from the researched area. The most spread soils in this area are Dystric Cambisols. In figure 1 is shown the vertical distribution of total copper in different sites belongs to Dystric Cambisol soil type. The vertical distribution of copper is uniformly distributed ranging between 37 and 30 mg/kg in case site 1 located 14.4 km upstream on the north-west direction, used as meadow. In case of Dystric Cambisols located in forest area copper has a maximum values on the litter as in the site 14 (367 mg/kg) and then the value decrease to 56 mg/kg at the depth of 40 cm. In soil profile located around pollution source with lands devoided of vegetation the maximum values were reached in the first few cm of soil and then there is a little variation on soil profile. In heavily polluted area, copper content became similar to a depth of 10 cm.



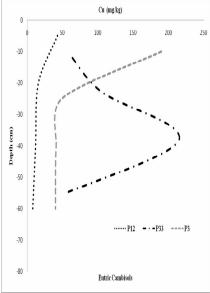


Figure 1. Concentration of copper along some Dystric Cambisols and Eutric Cambisols profiles

An exception is site 2 in which a second maximum was determined at a depth of 32-45 cm. KABALA C., SZERSZEN, 2002, examined the profile distributions of Cu in twenty-five soil profile of forested Dystric Cambisols developed from granite and gneiss in SW Poland and Cu was found to accumulate in topsoil and decrease with depth, but showed secondary increase of the concentration in bedrock. Also they consider that organic matter and oxides were important factors of Cu distribution.

In soil profile belong to Eutric Cambisols the soil profile distribution of copper presented a maximum (190 mg / kg-profile P3) in the top soil and at a depth of 20 cm the total Cu content was uniformly distributed on soil profile, except for site 33 used as arable, that presented the maximum value (215 mg / kg) at 23-38 cm depth (fig. 1).

Total copper content in the soil profile decreases on soil profile in steppe and the forest-steppe soils, while in forest soils copper is concentrated mainly in the B horizon (DAVIDESCU et al., 1988). Also, THORTHON (1979), quoted by ADRIANO, 2001, stated that Cu is redistributed in the profile as a result of podzolization with decrease in A2 and accumulation in the B horizon.

According to BĂJESCU AND CHIRIAC, 1984, on case of luvisols there are a second maximum of the Cu content in the Bt horizon due to the increase of clay content. In the profile of studied soils was found an increase of Cu content in the B horizon, but the second maximum was achieved only in site 26. This profile was located at 8 km away from the pollution sources and the copper content in A horizon was low so it could put out a second maximum (fig. 2). In case of luvisols used as arable land the highest values were recorded below plowed layer (fig. 2).

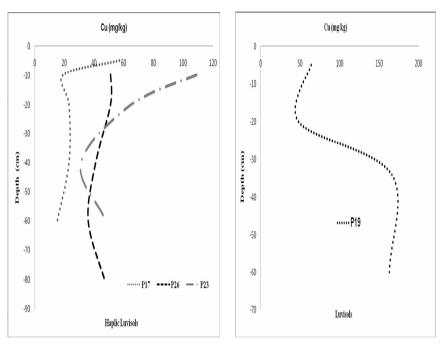


Figure 2. Concentration of copper along some Haplic Luvisols and Luvisols profiles

In case of Regosols, distribution of copper decreased on soil profile and the content in

top soil was different according to distance to pollution source. The contents were similar at the depth of 40 cm (fig. 3).

Copper content distribution in Fluvisols profile had the maximum level in A horizon, which had values between 500~mg/kg and 84~mg/kg, depending on the distance from the pollution source, but at the depth of 40~cm total Cu content had similar values.

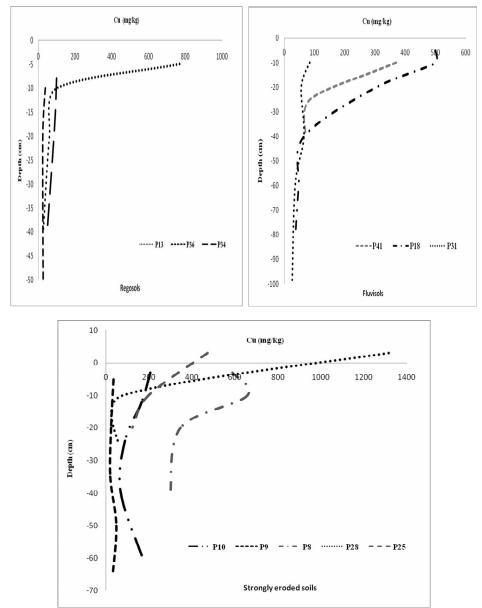


Figure 3. Concentration of copper along some Regosols, Fluvisols and Strongly eroded soils

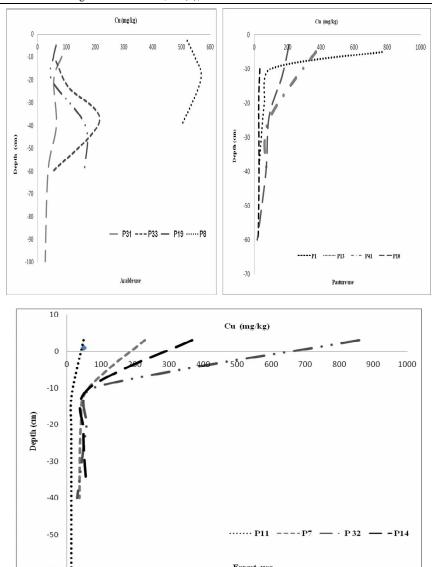


Figure 4. Concentration of cooper along some soil profiles under different land use (arable, pasture and forest use)

The vertical distribution of cooper in case of Strongly erodated phases show a maximum of 1315 mg/kg in the litter (P 28), which decreased to 59 mg/kg at a depth of 25 cm. In another soil profile (P8), the content of total copper decreased with depth but remained at levels above 300 mg / kg at 40 cm depth, this being due to both the use as arable land, and represented the parent rock deposits derived from basic sedimentary rocks.

In the examined soil, generally, the copper soil profile distribution show a maximum

value in the top soil and then decrease with depth. According to SPIEGEL, 2002, the human impact of metal accumulation in top soil was confirmed by the fact that heavy metals concentrations decreased with depth.

Also Adriano, 2001, Honda, 2010, stated the cooper is one of the least mobile heavy metals in soil and the common characteristic of copper distribution in soil profile is its accumulation in the top horizons (Kabata & Kabata, 2001). Mihailescu et al., 1988, found that the distribution and accumulation of heavy metals in surface horizons are determined in particular the quality of organic matter (mainly humic acids) as a geochemical barrier in the path of heavy metal leachate and dispersion.

The relationship between soil total copper content and organic matter content found in soil samples was very significant, but not clear relationship can be assessed with soil clay content.

Vegetation can exert some influence on the distribution profile of Cu (ADRIANO, 2001) and also the land use and land management (REIHER et al., 2004).

In figure 4 is presented the distribution of cooper content in soil profile according to land use. In soil used as forest, the cooper is highly accumulated in the forest litter and then decrease on soil profile.

The similar results were obtained by KELLER AND VEDY, 1994, who studied the distribution of Cu in soil profile under forest use.

The highest contents of total copper in soils used as meadow are retained in the top few centimeters of the surface soil. The highest values (768 mg/kg) were determined in the depth of 0-5 cm (P13) which decreased drastically to 56 mg at the depth of 40 cm. The values of total copper from strongly polluted area are lower compare with value reported by Rauta et al. 1988, where in soil samples from strongly polluted site under pasture use the total copper had values of 1060 mg/kg at the depth of 0-5 cm and 35 mg/kg at the depth of 5-20 cm.

In case of arable land use, the maximum values are recorded under plowed layer and then decrease on soil profile. Assessment of the contamination of cultivated soils by Cu around smelters in the north of France showed that contamination by Cu is confined to the top 30 cm and depended on the distance from the plant (STERCKEMAN et al., 2002).

In agricultural soils, heavy metal contents are lower compared with forest soils, but generally maintain a greater depth due to tillage and lack of barrier formed by litter (RĂUȚĂ et al., 1998).

Due to severe erosion, lack of vegetation, values of soil copper content were lower than copper released by Ampellum S.A.

## CONCLUSIONS

In the examined soils, generally, the copper soil profile distribution show a maximum value in the top soil and then decrease with depth. The human impact of metal accumulation in top soil was confirmed by the fact that Cu concentrations decreased with depth.

The distribution of copper in the soil profile presented less variation with soil type, but rather with land use and distance from pollution source.

The highest values of total copper were determined in the litter, followed by pasture and arable land.

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