Geochemical aspects of heavy metal fractionation in eucalyptus soils

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Helder de Oliveira
Center for Nuclear Energy in Agriculture (CENA/USP)
E-mail: helder@cena.usp.br

Diego Vendramini
Center for Nuclear Energy in Agriculture (CENA/USP)
E-mail: dvendram@cena.usp.br

Jefferson Mortatti
Center for Nuclear Energy in Agriculture (CENA/USP)
E-mail: jmortatt@cena.usp.br

ABSTRACT

Aspects of heavy metals fractionation (Cu, Cr and Co) in main eucalyptus cultivated soils were investigated after total extraction by alkaline fusion and selective sequential extractions. The study aimed to identify the major geochemical fractions and phases involved in metal complexation. Possible pollution classes were investigated through index of geo-accumulation (Igeo), considering the local natural background level. Among the main soils, Typic Hapludox showed the highest concentrations of these metals. However, there was no contamination according to the calculated Igeo. The selective sequential extractions showed that, for most analyzed soil, there was a predominance of these metals in the residual phase (> 80%), compared to the bioavailable fraction, and in this case, an association with the geochemical phase of Fe oxides. Cultural treatments, performed in this region during the eucalyptus cultivation, did not have residual effects in terms of heavy metals in soils.

Keywords: Heavy metals, Micro-watershed, Sequential extractions, Index of geo-accumulation.

1 INTRODUCTION

The heavy metals introduced into the earth system can come from various sources such as industrial waste and domestic sewage, mining activities, atmospheric depositions, agricultural practices, etc. In the soil they can be distributed in different compartments or fractions and their mobility and bioavailability will depend on their total concentrations, and the form in which they are associated with the solid phase, according to Tessier et al. (1979). Selective sequential extraction allows inferring about the potential for remobilization of heavy metals between labile fractions, mainly to distinguish between the natural and anthropogenic origin of soils and river sediments (Ure et al., 1993). The degree of pollution or toxicity of heavy metals in soils and sediments can be assessed in terms of the concentrations of these metals in the natural geochemical background (*background*), usually obtained in deep soils, without contamination, as proposed by Müller (1979), using the geoaccumulation index. The present work aimed to investigate the partition of heavy metals Cu, Cr and Co in the main fractions and geochemical phases in soils cultivated with eucalyptus, identifying the possible classes of pollution.

2 AREA OF STUDY

The studied area is located in São Paulo between the parallels 23o16'30" and 23o17'30" S and the meridians 48o25´30" and 48o26´30" W at an average altitude of 624 m and area of 1.6 km2, being composed of six plots planted with *Eucalyptus grandis* Hill Ex Maiden of varying ages and occupying 68.7% of the total area. The rocks of origin of the soils belong to the São Bento Group, Pirambóia formation. The main soil classes found were: Dystrophic Red Latosol, clayey phase (LVd); Ortic Quartzarenic Neosols (RQo) and Dystrophic Tb Haplic Cambisols (CXbd). In the study area, agricultural inputs were used for more than ten years of successive annual applications for planting fertilization and cover fertilization in the cultivation of eucalyptus trees.

3 MATERIAL AND METHODS

Soil sampling was carried out in triplicate with the aid of a Dutch auger in stainless steel, at depths of 0-10, 10-20 and > 50 cm. The composite samples were air-dried, homogenized and sieved for the fraction of 63 µm. The method of total extraction of heavy metals used was that of alkaline fusion (Samuel et al., 1985). Heavy metals were analyzed by ICP OES, including white metals and international reference material Soil-7 (IAEA) in triplicate.

The procedure of selective sequential extraction of heavy metals was performed according to the method proposed by Leleyter & Probst (1999), and allowed to identify the association of each heavy metal with the labile fractions, S1 (soluble in water), S2 (exchangeable), S3 (carbonate), S4 (oxides Mn), S5 (oxides Fe) and S6 (organic matter) by means of successive extractions of the phases. The residual fraction was calculated from the difference between the total content of the sample and the sum of the leachable fractions (S1 to S6) and considered as labile or bioavailable fraction.

To characterize the natural geochemical background, Cu, Cr and Co concentration values were used in the soil samples CXbd, LVAd, LVd and RQo at depths > 50 cm. In comparative terms, the average concentrations of the Earth's crust of these heavy metals were used, according to Taylor & Mc Lennan (1985), with concentrations of 25, 35 and 10 µg g^{-1}, for Cu, Cr and Co, respectively.

4 RESULTS AND DISCUSSION

The results of the mean concentrations (± standard deviation) in µg g^{-1} of Cu, Cr and Co were 17.6±9.1; 27.1±4.2 and 9,2±4,1 for soil samples CXbd, LVAd and RQo, ndepths of 0-10, 10-20 and > 50 cm, respectively. For LVd, the mean concentrations were 206.9±0.9; 89.4±1.1 and 184.1±3.9 respectively, for the depths studied.

Lows were observed *Igeo* for all soils (0-10 cm) concerning Cu, Cr and Co, when the local natural geochemical background was considered, showing no occurrence of pollution. However, when the chemical composition of the Earth's crust was considered, moderate to strong pollution classes were verified for the LVd soil and especially for Co and Cu. At depths of 10-20 cm they presented results similar to those observed for the shallower soils and when the local natural geochemical background was used, there were no possible toxicities of these metals. Likewise, elevated *Igeo* were observed when the weighting parameter of the Earth's crust was used, identifying possible pollution problems for Co and Cu.

From the results obtained from the selective sequential extraction of Cu, Cr and Co, it can be verified (LVAd and LVd) that Cu and Co were preferentially in the residual fraction (80 %) at the depth of 0-10 cm with bioavailability lower than 20 %. For Cu there was a predominance of the geochemical phase associated with Fe oxides for the LVAd soil and an equilibrium between the geochemical phases of Fe oxides and organic matter for the LVd soil. Cr was relatively more bioavailable for LVAd soil (50 %) being mainly associated with the phases of Fe, exchangeable oxides and organic matter, and LVd soil presented about 30 % of bioavailability with association with Fe oxides.

To the ground CXbd, Cu and Co presented preferentially in the residual fraction (84%) with bioavailability lower than 16 and 20 %, respectively, with predominance of the geochemical phase associated with Fe oxides, only being observed a relative influence of organic matter for Co at depth (> 50 cm).

The Cr presented a high percentage of bioavailability (> 40 %) being preferentially associated with Fe oxides, and also present in the exchangeable phases and organic matter, evidencing the relative ease of interaction and availability. For the RQo soil, Cu and Cr were preferentially in the residual fraction, with respective averages of 83.4 and 66.8 %. The bioavailability observed was mainly related to Fe oxides. Co showed high bioavailability in this soil, especially on the surface, being associated with Fe oxides and organic matter, showing to be only soluble in strong acids.

5 CONCLUSION

The LVd soil presented concentrations of Cu, Co and Cr above the CETESB quality reference values and the average concentrations of the Earth's crust, however, the calculations of the *Igeo*, did not present any evidence of contamination. The use of selective sequential extraction of Cu, Co and Cr allowed to verify for all soils, a predominance of the residual fraction in comparison with the bioavailable fraction, even in the case of LVd, with preferential association to the phase linked to Fe oxides. Thus, it was not possible to verify that the use of agricultural inputs over 10 years in the cultivation of eucalyptus brought contamination of Cu, Co and Cr in the studied area.

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