ELSEVIER

Distribution of copper in the vicinity of a deactivated mining site at Carajás in the Amazon region of Brazil

Ricardo J. Cassella [a,*], Angela de L.R. Wagener [b], Ricardo E. Santelli [a],
Klaus Wagener [c], Lídia Y. Tavares [c]

[a] *Instituto de Química, Universidade Federal Fluminense, Outeiro de São João Batista s/n, Centro, Niterói/R 24020-150, Brazil*
[b] *Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro, Brazil*
[c] *Universidade Federal de Rio de Janeiro, Brazil*

Abstract

In this work the re-fixation of mobilized copper (Cu) that was released from a deactivated pilot Cu ore dressing plant in the tropical rain forest at Southeastern Amazon (Carajás) was studied. Samples of top soils, decay leaf litter deposited on soils, roots and leaves of standing biomass were taken for the determination of Cu concentration in order to evaluate the distribution of it between different environmental compartments. In the sampling points near to the now extinct plant, total Cu concentrations in the soil reached an average value of $2140 \, \mu g \, g^{-1}$ above the natural level of about $40 \, \mu g \, g^{-1}$, being that bioavailable Cu estimated by DTPA method varied from 1.9 to 20.7% of this total. From the data was possible to calculate that the soil compartment is able to hold around $10 \, kg \, Cu/m^2$ of ground. Roots of the standing biomass in that area hold around $17 \, g \, Cu/m^2$, while the Cu content in leaves showed to be largely independent of the Cu level in the soil. Copper in the leaves was estimated as around $1 \, g/m^2$ of ground area. In turn, the decay leaf litter deposited on soil can hold about $1.6 \, g \, Cu/m^2$. The terrestrial system surrounding the abandoned pilot plant demonstrated great buffer capacity to retain mobile Cu released by anthropogenic activities in the area.

Keywords: Cu; Mining; Terrestrial environment; Soils

1. Introduction

Nowadays, mining activity is one of the most prominent sources of metals releasing to the environment. During mining operations such as exploitation, ore processing and concentrating, wastewaters and mine tailings are generated, while great amounts of dust containing significant concentrations of metals are emitted. These activities lead to a great contamination of the surrounding environment resulting, in the most times, in considerable damage for human beings and ecosystems located near to the mining site [1].

Literature reports several cases of environmental pollution due to mining operations for exploitation and processing of different ores [2–13]. Some of these cases involve the releasing of copper (Cu) to the environment. Macklin et al. [2] reported

the releasing of Pb, Zn, Cu and Cd to tributaries of Tisa river, in Romania, due to the failure of two mine tailings between January and March of 2000. Because of transportation by the river system, high concentrations of metals achieved waters and sediments of rivers in Hungary and Ukraine.

Samecka-Cymerman and Kempers [3] studied the pollution of water, sediments and aquatic macrophytes of Legnica-Glogow district, in Poland, due to the operation of a Cu mining industry for 30 years (1953–1983). The results reported by authors showed that besides Cu, great amounts of other 11 metallic elements were released to the aquatic system near the factory, increasing the concentration of metals in aquatic plants even to levels higher than those considered as toxic.

Ramirez et al. [4] investigated the contamination of a sandy beach in Chile due to Cu mining activities. Several metals were found as contaminants and their maximum concentrations were verified in the area near the discharge point. Copper concentrations ranged from 746 to $22,739 \, \mu g \, g^{-1}$ and levels lower than background were only observed in the control site. Also in Chile,
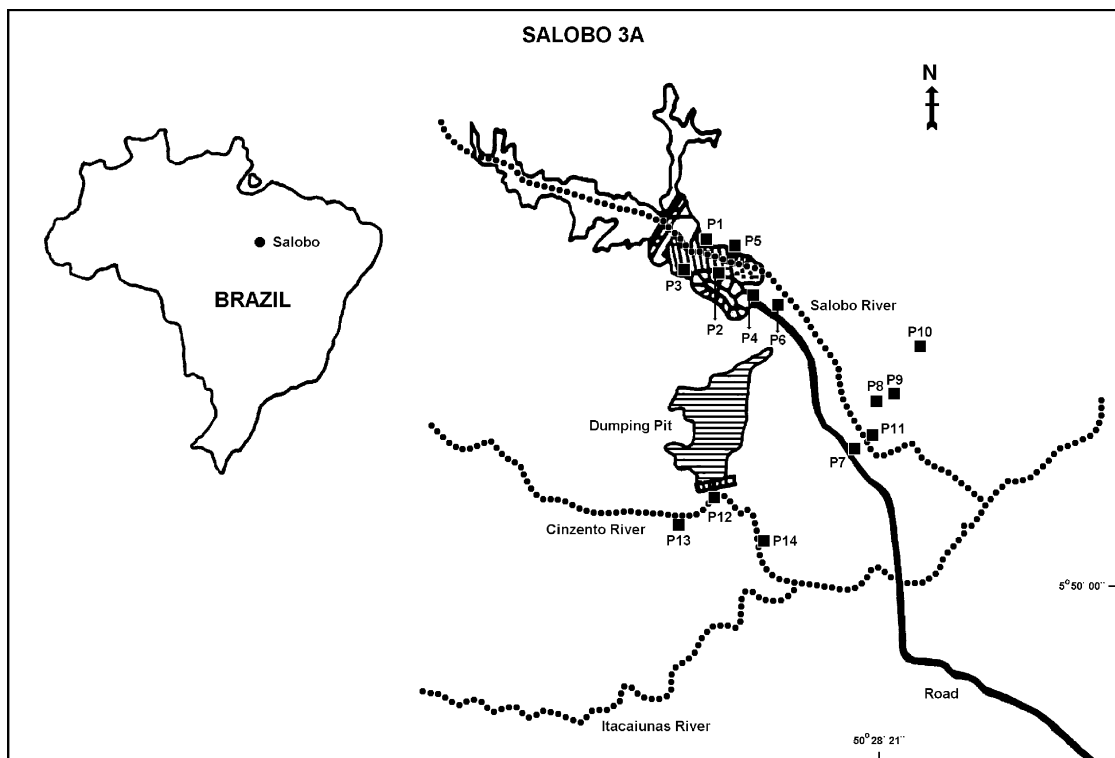
Fig. 1. Salobo 3A region with the sampling stations utilized in this work.

environmental pollution was observed because of exploitation of a Cu–Au–Hg mine. Although in this location (Coquimbo, Punitaqui and Andacollo) Hg seems to be most important contaminant, the levels of Cu in the stream sediments of the region of Andacollo achieved concentrations as high as 2200 μg g^{-1} [5].

Here in Brazil, the exploitation of Cu has already caused soil pollution in the poor Northeastern region of the country. An inhibition of growth of native plants of the region was reported and attributed to high concentrations of Cu found in the soils [6].

The Carajás area in the Southeastern part of the Amazon region holds big Cu ore deposits which shall be explored in the near future. The area is now a natural reservation region. From 1986 to 1988, a pilot scale plant was operated there processing around 80 tonnes/day of ore, including flotation, to study conditions for Cu production and the environmental effects of large scale mining in the area.

The goal of this work was to investigate the amounts of Cu mobilized during operation of the pilot plant and its retention in the terrestrial environment that surrounds the pilot plant, which is a typical tropical rain forest. Samples of soils, roots, leaves and decay leaf litter deposited upon soil were taken and analyzed in respect to their Cu content. The sampling stations were chosen in order to show Cu distribution in the highly polluted area around the former pilot plant activity, its periphery and in areas sufficiently far away to be undisturbed.

2. Characteristics of the studied area

The Serra de Carajás is a chain of mountains located at the Southeastern part of the Amazon region. In the region, the main

interest for Cu mining is focused on an area called Jazida do Salobo, which holds an estimated amount of 1200 million metric tonnes of Cu in an area of about 250 km^2. The climate is tropical with pronounced seasons: November to May bring about 90% of the total annual precipitation (average precipitation is 2116 mm/year), while June to October are dry months. Average temperatures are between 19 and 35 °C.

The vegetation of the region is formed by a large variety of trees, among which *Lacre* (of the family of *Gutiferas*) is clearly predominant. The area is drained by a dense river system (Cinzento and Salobo) which leads the waters finally to the river Itacaiunas. The limits of the studied area are 5°46′42″ and 5°48′12″S and 50°31′24″ and 50°33′41″W, called the mining area Salobo 3A (Fig. 1).

Copper ores found in the area show a close relationship between their iron content and that of other metals present such as Mo, Au and Ag. The principal ores are magnetite, bornite, chalcosite and chalcopyrite. Lesser amounts of hematite, safflorite and cobaltite are also present [14].

The soils of Salobo 3A show, in general, the following structure: 10–30 cm organic detritus and humus, roots and sometimes a fraction of quartz sand (O horizon). Below this organic surface layer, down to 60 m, there is a clayish soil without structure of lighter or darker brownish color (A horizon), which represents an altered surface rock containing copper in high concentrations (0.3–1.2%) bound to goethite, limonite, mica and clays that overlays the main reservoir of copper sulfides. The soil mineralogy is dominated by quartz, kaolinite, plagioclases, amphiboles, biotite, montmorinollites, chlorites and K-feldspar [15]. Water table is, except aside rivers, 2–4 m below surface.

As mentioned before, a pilot plant for testing process parameters and the degree of leakage of Cu into the environment was operated during 1986–1988 with a capacity of processing of around 80 tonnes of ore per day. The process included the following steps: ore extraction from nearby sites, grinding the material to particle sizes of less than 37 μm, flotation with additives such as methyl-isobutyl carbinol and/or polyglycolic alcohols, sodium silicate, sodium thiophosphate diisobutyl or sodium dithiophosphate diisoamyl. This work was only focused on the terrestrial environment pollution by Cu.

3. Experimental

3.1. Sampling

Sampling points were chosen to demonstrate the variation of the Cu concentration in the terrestrial environment with increasing distance from pollution sources. Their locations and number were elected due to the facilities, in terms of physical structure, already present in each site as well as because their distances from pollution sources. As potential pollution sources were considered the site of the pilot plant and the dumping pit of the discharged material after flotation which, due to its fine particle size, seems to offer best conditions for mobilization of any metal content. The sampling was performed at the end of dry season, on November of 1994.

Samples of soil, decay leaf litter deposited upon soil (which was principally leaves in various stages of decomposition), roots and leaves from standing biomass (*Lacre*, from the family of *Gutiferas*) were collected at each point. The leaf index (m^2 of leaf area per horizontal m^2 of soil) [16] at the sampling site was estimated and the type of trees nearest to the sampling point was determined from which the leaf samples were taken.

Sampling sites P1, P2, P3, P4, P5 and P6 were considered close to the extinct pilot plant; P7, P8, P9, P10, and P11 are at about 3 km distance from the site of the pilot plant. Samples at P12 site were taken at the foot of the damping pit that holds the material dumped from the flotation. The area of sampling points P13 and P14 can be considered, due to their topography, as unaffected by the pilot plant activity. They are separated from the *Salobo* river valley by a chain of mountains.

3.2. Materials and methods

3.2.1. Materials and reagents

All glass and plastic flasks used along the experimental work were decontaminated according to Patterson and Settle [17]. They were soaked sequentially in 5% neutral Detertec (detergent containing EDTA, Vetec, Rio de Janeiro Brazil) for 24 h, 50% (v/v) HNO$_3$ solution for 24 h and then 10% (v/v) HNO$_3$ solution also for 24 h. Between and after each step, the materials were rinsed with purified water obtained in a Milli-Q Water System (Millipore, Saint Quentin Yvelines, France). All reagents and acids were of analytical grade and used without further purification.

For Cu measurements, a Perkin-Elmer 3100 flame atomic absorption spectrometer was employed. The spectrometer was equipped with a hollow cathode lamp for Cu, operating with a current of 30 mA. A slit width of 0.7 nm and a wavelength of 324.8 nm were adjusted and the atomization was carried out with a lean blue air-acetylene flame. A detection limit, in solution, of 55 ng ml^{-1} was calculated for the FAAS method. This detection limit showed to be enough to determine Cu concentrations in all samples analyzed during work.

For pH measurements an Analyzer 300 (São Paulo, Brazil) potentiometer was employed together with a combined glass electrode from the same manufacturer.

3.2.2. Collection

Superficial soils (upper 20 cm) were collected by using a plastic scoop. They were conditioned in plastic bags that were sealed just after air removing. The material was carefully maintained at 4 °C until analysis in the laboratory.

Leaves were taken as high as reachable. They were handled by using sterilized plastic gloves. They were also conditioned in sealed plastic bags without air and maintained at 4 °C until analysis in the laboratory. The same was performed for the collection of decay leaf litter on soil.

Roots were also collected with a plastic scoop and suffered the same conditioning procedure used for soils and leaves.

3.2.3. Pretreatment of samples [18]

After transportation from the field to the laboratory, the soils were kept out of refrigerator until achieve room temperature. Then the aggregated particles of the soil samples were carefully broken with the aid of a wood roll in order to release individual particles of the soil. Afterwards, the disaggregated soils were dried in a stove at 50–55 °C. The dry soil was then sieved with a plastic device with 1 mm pore diameter (nine mesh). The dried and sieved soil samples were utilized in the analysis described in Sections 3.2.4, 3.2.5, 3.2.8 and 3.2.9.

The samples of leaves and roots were dried in a stove at 105 °C. They were then triturated in an agate mortar before analysis. Triturated samples of roots and leaves were employed in the analysis described in Section 3.2.10. Decay leaf litter samples did not suffer any pretreatment. Only the solid particles present on their surfaces were removed with a soft brush before their analysis, which is described in Sections 3.2.6 and 3.2.7.

3.2.4. Determination of the pH of the soil samples

The determination of soil pH was performed according to the procedure recommended by Sumner [19]. In this procedure, 10 g of treated soil sample (according to Section 3.2.3) was mixed with 25 ml of 0.010 mol l^{-1} CaCl$_2$ solution. After vigorous stirring during 5 min, the suspension was left to stand during 30 min to promote deposition of the particles. Then, the pH of the supernatant was measured by immersing the previously standardized electrode into the solution.

3.2.5. Determination of available copper in the soil

This procedure was carried out according to the recommendations of Lindsay and Norvell [20]. For the evaluation of available Cu present in the soils, 5 g of the treated soil (according to Section 3.2.3) sample were placed in a 125 ml erlenmeyer flask

and then 20 ml of the extraction solution (1.9 g DTPA, 1.5 g $CaCl_2·2H_2O$, 15 g triethanolamine; in 1 l of pure water) were added. After 2 h of shaking, the suspension was filtered and Cu in the filtrate was determined by FAAS, after suitable dilution when necessary.

3.2.6. Determination of copper fixed on the surface of decay leaf litter

In order to determine the amount of copper deposited on the surface of decay leaf litter, an adapted form of the extraction method used for available Cu determination in soils (Section 3.2.5) was employed. In the procedure, 0.45 g of the dead organic material (not dried and triturated) was mixed with 20 ml of the extraction solution. The mixture was shaken for 2 h and, after filtration, the concentration of Cu in the extract was determined by FAAS.

3.2.7. Determination of total copper in the decay leaf litter [18]

The determination of total copper in the decay leaf litter was done by total dissolution of the material that passed in the treatment described in Section 3.2.6. For this purpose, around 0.25–0.30 g of the decay leaf litter were mixed with 15 ml of concentrated HNO_3 and left to stand during 48 h. After this, the mixture was heated until the solution gets clear. Then, 2 ml of concentrated $HClO_4$ were added and the solution was heated again until near to dryness. The residue was then dissolved in 25 ml of 1 mol l^{-1} HNO_3. Before the determination of Cu by FAAS, the solution was filtrated to remove eventually present silica. Total Cu in the decay leaf litter was derived by the sum of the Cu concentration obtained in this experiment with that obtained in the experiment described in Section 3.2.6.

3.2.8. Determination of percentage of organic matter in the soil [18]

For the determination of organic carbon in the soils around of 0.5 g of dry soil free of decay leaf litter were mixed with 10 ml of a 0.10 mol l^{-1} $K_2Cr_2O_7$ solution and 10 ml of concentrated H_2SO_4. The resultant suspension was heated mildly for 10 min and, after cooling down to room temperature, 80 ml of pure water, 1 ml of 85% phosphoric acid and five drops of a 0.5% diphenylamine solution were added. The final mixture obtained was titrated with a standardized 0.2 mol l^{-1} Fe(II) solution until color change from green to blue. The amount of organic matter in the soil was calculated as:

Organic matter (%) = organic carbon (%) × 1.724

3.2.9. Determination of total copper in the soil [18]

Dry soil material was ground in an agate mortar. Then, around 0.2 g of the soil was weighted in a plastic beaker and 5 ml of concentrated HNO_3 were added. After mixture standing overnight, the acid was vaporized by a careful heating. Then, 2 ml of 70% $HClO_4$ and 8 ml of 48% HF were added, followed by heating until white smoke of $HClO_4$ appeared. After this, 1 ml of 70% $HClO_4$ and 7 ml of 48% HF were added again and heated again near to dryness. The obtained residue was then dissolved in 50 ml of 1 mol l^{-1} HNO_3 solution and, after filtration, Cu was determined in the obtained solution by FAAS.

3.2.10. Total copper in leaves and roots [18]

Sample masses employed in the determination of copper varied between 0.75 and 1.40 g in the case of leaves and 0.10–3.2 g for roots, according to the expected concentration of copper in each sample. Samples were ignited at 450 °C in a muffle furnace for one night. Then, 13 ml of concentrated HNO_3 were added to the solid residue and the suspension was transferred

Table 1

Results found after three independent analysis of soils, roots, leaves and decay leaf litter collected at Salobo 3A, Carajás, in the Amazon region of Brazil (nd = not determined)

Sample	Total Cu in soils (μg g^{-1})[a]	Available Cu in soil (μg g^{-1})[a,b]	pH	Organic matter content of soil (%)[a]	Total Cu in decay leaf litter (μg g^{-1})[c]	Cu on the surface of decay leaf litter (μg g^{-1})[c]	Cu in roots (μg g^{-1})[a]	Cu in leaves (μg g^{-1})[a]
P1	1200	168 (14%)	5.79	0.43	nd	nd	810	57
P2	1300	185 (14.2%)	5.55	2.84	166	63	1000	32
P3	2600	242 (9.3%)	5.59	nd	99	57	1590	41
P4	7600	1110 (14.6%)	5.31	3.81	nd	nd	nd	nd
P5	960	31.7 (3.3%)	4.17	1.41	71.9	9.9	785	34.5
P6	1600	30.4 (1.9%)	4.84	1.26	87	48	830	31
P7	340	16.3 (4.8%)	4.38	2.12	79.5	19	180	24
P8	100	4.7 (4.7%)	3.91	1.24	43	5.1	48	24
P9	48	1.6 (3.3 %)	4.55	1.48	15.8	3.5	nd	nd
P10	400	15.6 (3.9%)	5.05	4.07	18.7	4.9	nd	42
P11	36	1.0 (2.8%)	5.38	3.91	14.7	3.7	nd	nd
P12	480	11.5 (2.4%)	4.99	3.86	68.9	9.3	nd	42
P13	31	4.5 (14.5%)	3.59	2.00	17.7	5.8	nd	nd
P14	42	8.7 (20.7%)	4.46	2.52	20.5	5.3	110	20

[a] Results expressed in a dry weight basis.

[b] Between parenthesis is the percentage of available Cu in relation to total Cu in the soil.

[c] Results expressed in a wet weight basis.

to a beaker. After standing overnight, the following heat treatment was applied to the mixture (with the beaker closed with a glass lid): 15 min at $100\,^{\circ}C + 15$ min at $150\,^{\circ}C + 15$ min at $200\,^{\circ}C$. After cooling down, 13 ml of 70% $HClO_4$ were added to destroy completely the rests of organic material and the system was heated again to $200\,^{\circ}C$ until solution gets clear. Then the lid was removed and the solution was heated near to dryness. The remained solid was dissolved with 50 ml of $1\,mol\,l^{-1}$ HNO_3 solution and Cu was determined by FAAS in the final solution.

4. Results and discussion

4.1. Copper in the soils

The region of Carajás is known to have mineral soils with low content of organic matter. This statement was confirmed by the analytical results obtained for the soil samples (Table 1), with the content of organic matter ranging from 0.43 to 4.07% (excluding the amount of dead organic upon soil). These values could indicate that the complexing capacity of the soils of the *Salobo* region is low. Additionally, the measured pH for such soils varied between 3.79 and 6.03 with an average value of 5.13 ± 0.67, characterizing them as strongly acid soils, which favors the releasing of Cu in the ionic form to the soil solution, increasing its mobility in this compartment. In face of these conditions, it would be expected that the transport of Cu through terrestrial environment could be enhanced, leading to high concentrations of total Cu in the river system that surrounds the region under study. However, this is not really true as related by Damous et al. [15] that found concentrations of only around $20\,\mu g\,l^{-1}$ of Cu(II) in the river waters in the vicinity of the pilot plant. These data suggest that there is a buffer mechanism for Cu releasing in the terrestrial environment of the region.

In order to identify the pilot plant as the potential source of copper pollution, the total content of this metal was determined in the soil samples. The obtained results allowed to divide the sampling sites into a heavily polluted area (stations P1, P2, P3, P4, P5 and P6), which presented an average Cu concentration in the soil of $2180\,\mu g\,g^{-1}$; a partly polluted area (stations P7, P8, P9, P10, P11 and P12) with an average Cu concentration in the soils of $234\,\mu g\,g^{-1}$ and a region which was evidently unaffected by the activity of the pilot plant (stations P13 and P14) with an average Cu concentration of $36.5\,\mu g\,g^{-1}$. Copper levels in these areas differ from each other by roughly a factor of 10 and are clearly related to the distance from pilot plant, indicating that those levels above the natural background are man-made.

The extractable Cu from soils by DTPA (supposed as available copper for plants) varied between 1.9 and 20.7%, with an average value of 9.2%. Although the determined percentage of available Cu was low, it was possible to identify that the amount of Cu released for plants is high, because of the high total content of Cu in the soils, especially in the vicinity of the pilot plant. There was no observed correlation of these values with the organic matter content of the soil, which was also low.

How Cu level in the soil nearest to the pilot plant presented an average value of around $2140\,\mu g\,g^{-1}$ above the presumable natural level of around $40\,\mu g\,g^{-1}$, it was assumed that the amount
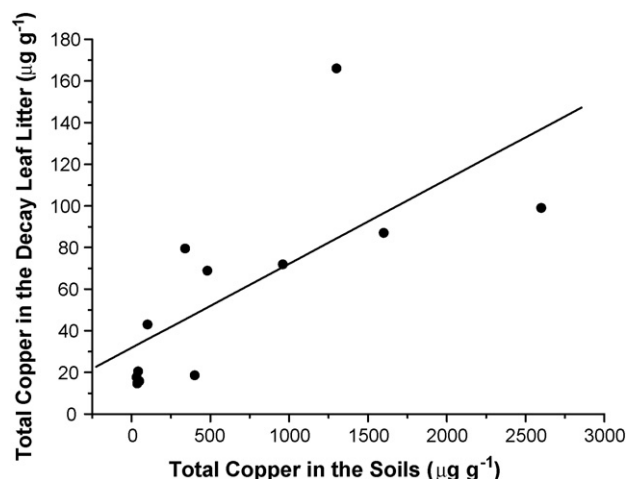

Fig. 2. Relation between total Cu in the soils and Cu on the surface of decay leaf litter. Correlation coefficient equal to 0.709.

of metal released for the environment during Cu ore processing was huge. Taking this number into account and considering that remarkable amounts of released metal did not reach the aquatic system, the total capacity of this absorber compartment was estimated to be around $10\,kg\,Cu/m^2$, if it is taken an effective depth of the order of 1–2 m.

4.2. Copper in the decay leaf litter

The total Cu content in decay leaf litter reflected again the different levels of pollution and leads to the same classification of the sampling areas exposed in Section 4.1. The average values are $106 \pm 42\,\mu g\,g^{-1}$ (heavily polluted areas), $40 \pm 28\,\mu g\,g^{-1}$ (partly polluted) and $19 \pm 2\,\mu g\,g^{-1}$ (natural background). A significant correlation of 0.709 was found between total Cu in the soils and the total Cu in the decay leaf litter (Fig. 2). The same could be observed between total Cu in the soils and Cu on the surface of decay leaf litter (Fig. 3) with a correlation coefficient of 0.871, indicating that some of Cu present (natural and/or dispensed) in the soil is in fact proportionally transferred to the
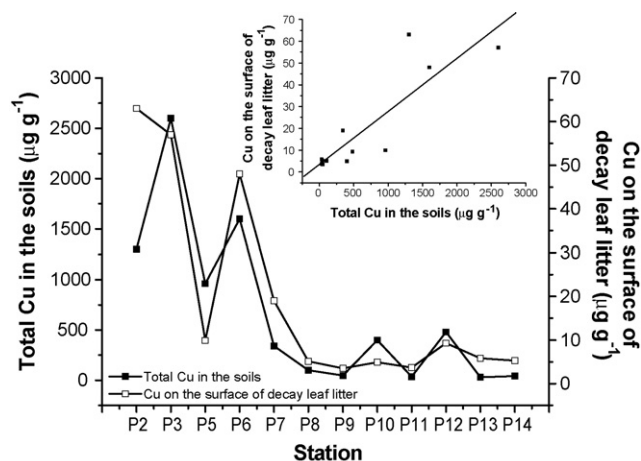

Fig. 3. Relation between total Cu in the soils and Cu on the surface of decay leaf litter. Correlation coefficient equal to 0.871.
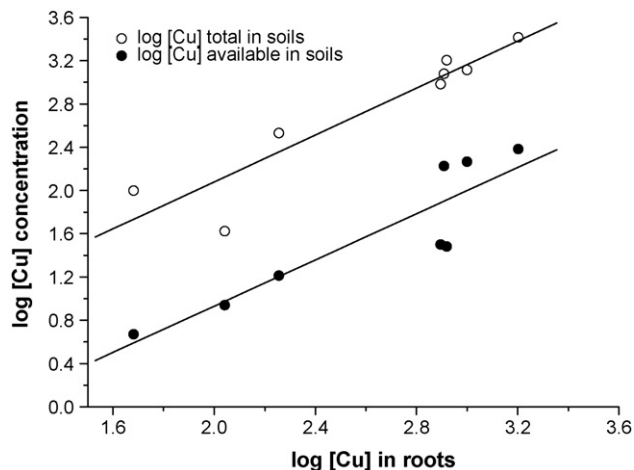
Fig. 4. Relation between log total Cu in roots with log available Cu in soils (●) and log total Cu in the soils (○). Correlations coefficients are 0.931 and 0.971, respectively.

decay leaf litter. It is possible that this occur during flooding, with Cu(II) ions being released from soil (acidic and with low complexing capacity) to the solution and then complexed by organic matter in different stages of decomposition present on the surface of the decay leaf litter.

As the same way for soils, it was possible to estimate the total Cu content stored in the decay leaf litter of the region from Cu concentrations determined in this work. Taking into consideration that there is around 2–2.5% of decay leaf litter on the soil, a total amount of 12–15 kg of decay leaf litter per m^2 can be attained for the soil of the region. Employing the pollution level in the heavily polluted area (106 μg g^{-1}), an estimated mass of 1.3–1.6 g Cu/m^2 is fixed in this compartment. This value is really low when compared with that estimated for the soil, which is able to store around 10 kg Cu/m^2. However, due to the significant correlation between total Cu concentration in the soil and total Cu in the decay leaf litter, we can assume that the decay leaf litter can be considered as a suitable monitor for evaluation of Cu level in the terrestrial environment of *Salobo* region.

4.3. Copper in the standing biomass

The concentrations of Cu in the roots of the standing biomass corroborate the hypothesis raised before that the amount of Cu released to the terrestrial environment of *Salobo* was high. Analyzing the data obtained for samples collected in areas considered almost unaffected and totally unaffected by pilot plant operations (P7, P8 and P14) it is possible to assume that the natural level for the region is around or below to 100 μg g^{-1}. However, in samples collected in areas near to the plant (heavily polluted areas), Cu levels raised substantially reaching concentrations always greater than 785 μg g^{-1} with an average value of 1003 μg g^{-1}. As expected, remarkable correlation coefficients were observed between log of the concentration of Cu in roots versus log of the available Cu in the soil (0.931) and versus log of the total Cu in the soil (0.971) (Fig. 4).

Mature biomass in tropical rain forest has about 9 kg of root system per m^2 [16]. This gives, again calculated for the heavily

polluted area, 17 g Cu/m^2 in this compartment. In terms of leaves of the standing biomass, the data obtained for Cu concentrations showed that there is no noticeable correlation between leaf Cu content and the Cu concentration in the soils. This indicates that the level of Cu in the aerial parts of the plants is limited to a maximum value and it is independent of Cu concentrations in the soil. Such limits were 57 μg g^{-1} in the heavily polluted areas (mean value of 39.1 μg g^{-1}) and 42 μg g^{-1} in the partly polluted areas (mean value of 30 μg g^{-1}). The natural level seems to be around 20 μg g^{-1}.

Leaf indexes for the area were estimated to range between 5 and 10 m^2/m^2. This value is in good agreement with literature data which gives a range from 6 to 16 [16]. Taking such data into account, it was possible to evaluate that this compartment retains about 1 g Cu/m^2 of area, but its content is rather independent of the copper level in the soil.

5. Conclusions

Data obtained in this study showed that there is no doubt that the dressing of copper ores released mobilized metal to the environment. The terrestrial environment seems to represent a buffer system for mobile Cu, and the absorbing compartments are soil, decay leaf litter and standing biomass (especially its root system). The amount of Cu fixed in these compartments increases with a rising level of mobile Cu in the soil. However, it was not possible to measure what is the actual capacity of this system to retain mobilized Cu if a large scale production starts up and what will be the effect of the high Cu concentrations on the standing biomass of the region.

As mentioned before, the environment in that tropical rain forest represents an effective buffer system for man-made mobilized copper. The soil presented greatest capacity to hold Cu, which could be estimate as being the order of 10 kg Cu/m^2 of area. The root system of the standing biomass fixes about 17 g Cu/m^2 under a pollution level, which existed in the immediate environment of the pilot plant, while decay leaf litter and the leaves of the standing biomass play a minor role. The results obtained in this study support the hope that the high binding capacity of the soil and the relatively small percentage of available Cu for plants can prevent that the pollution becomes toxic for the standing biomass.

References

[1] B.E. Davies, Heavy metal contamination from base metal mining and smelting: implications for man and his environment, in: I. Thornton (Ed.), Applied Environmental Geochemistry, Academic Press Inc., London, 1987.
[2] M.G. Macklin, P.A. Brewer, D. Balteanu, T.J. Coulthard, B. Driga, A.J. Howard, S. Zaharia, The long term fate and environmental significance of contaminant metals released by the January and March 2000 mining

tailings dam failures in Maramures, County, upper Tisa Basin, Romania, Appl. Geochem. 18 (2003) 241–257.

[3] A. Samecka-Cymerman, A.J. Kempers, Toxic metals in aquatic plants surviving in surface water polluted by copper mining industry, Ecotoxicol. Environ. Safety 59 (2004) 64–69.

[4] M. Ramirez, S. Massolo, R. Frache, J.A. Correa, Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile, Mar. Pollut. Bull. 50 (2005) 62–72.

[5] P. Higueras, R. Oyarzun, J. Oyarzun, H. Maturana, J. Lillo, D. Morata, Environmental assessment of copper–gold–mercury mining in the Andacollo and Punitaqui districts, northern Chile, Appl. Geochem. 19 (2004) 1855–1864.

[6] C.E.L. Lins, U.M.T. Cavalcante, E.V.S.B. Sampaio, A.S. Messias, L.C. Maia, Growth of mycorrhized seedlings of *Leucaena leucocephala* (Lam.) de Wit. in a copper contaminated soil, Appl. Soil Ecol. 31 (2006) 181–185.

[7] I. Riba, J. Blasco, N. Jimenez-Tenorio, T.A. Del Valls, Heavy metal bioavailability and effects. I: Bioaccumulation caused by mining activities in the Gulf of Cadiz (SW, Spain), Chemosphere 58 (2005) 659–669.

[8] H.A. Liu, P.B. Liao, Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China), Sci. Total Environ. 339 (2005) 153–166.

[9] I. Riba, J. Blasco, N. Jimenez-Tenorio, M.L.G. de Canales, T.A. Del Valls, Heavy metal bioavailability and effects. II: Histopathology–bioaccumulation relationships caused by mining activities in the Gulf of Cadiz (SW, Spain), Chemosphere 58 (2005) 671–682.

[10] B. Liao, Z. Guo, A. Probst, J.-L. Probst, Soil heavy metal contamination and acid deposition: experimental approach on two forest soils in Hunan, Southern China, Geoderma 127 (2005) 91–103.

[11] J. Ansorena, N. Marino, I. Legorburu, Agricultural use of metal polluted soil near an old lead–zinc mine in Oiartzun (Basque Country, Spain), Environ. Technol. 16 (1995) 213–222.

[12] B.A.D. Hetrick, W.T. Wilson, D.A.H. Figge, The influence of micorrizhal symbiosis and fertilizer amendments on establishment of vegetation in heavy metal mine spoil, Environ. Pollut. 86 (1994) 171–179.

[13] J. Sanchez, M.C. Vaquero, I. Legorburu, Metal pollution from old lead–zinc mine works: biota and sediment from Oiartzun valley, Environ. Technol. 15 (1994) 1069–1076.

[14] A. Vianna, N. Farias, R. Saueressig, Jazida de cobre Salobo 3A, Ciências da Terra 5 (1982) 13–18.

[15] N.R. Damous, A.L.R. Wagener, S.R. Patchineelam, K. Wagener, Baseline studies on water and sediments in the copper mining region of Salobo-3A, Carajás, Amazon, Brazil, J. Braz. Chem. Soc. 13 (2002) 140–150.

[16] R.H. Whittaker, R. Marks, Primary Productivity of the Biosphere, Springer-Verlag, Heidelberg, 1975.

[17] C.C. Patterson, D.M. Settle, The Reduction of Magnitude Errors in Lead Analysis of Biological Materials and Natural Waters by Evaluating and Controlling the Extent and Sources of Industrial Lead Contamination During Sample Collection and Analysis, National Bureau of Standards Special Publication, Pasadena, USA, 1978.

[18] S.E. Allen, Chemical Analysis of Ecological Materials, 2nd ed., Blackwell Scientific Publications, London, UK, 1989.

[19] M.E. Sumner, Measurements of soil pH: problems and solutions, Commun. Soil Sci. Plant Anal. 25 (1994) 859–879.

[20] W.L. Lindsay, W.A. Norvell, Development of a DTPA soil test for zinc, iron, manganese and copper, Soil Sci. Soc. Am. J. 42 (1978) 421–428.