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The potential of a Technosol and tropical native trees for reclamation of copper-polluted soils

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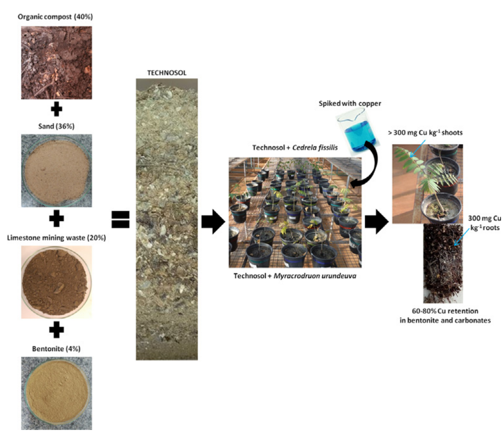
HIGHLIGHTS

- Bentonite in Technosols keeps high capacity to sorb Cu with compost.
- *Myracrodruon urundeuva* and *Cedrela fissilis* have a high availability to accumulate Cu.
- Technosol-trees system has a high potential to remediate Cu-polluted soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Technosols created to reclaim degraded soils is a promising solution that needs further research. The objectives of the study were: i) to create a Technosol with a very high capacity to immobilize copper from mining, ii) to assess the capacity of the Technosol to immobilize copper after planting two tropical native tree species, and iii) to analyse the capacity of the native trees for extracting copper from polluted soils. *Myracrodruon urundeuva* (aroeira) and *Cedrela fissilis* (pink cedar) were planted in pots with Technosol spiked with copper at concentrations of 125, 1525 and 3050 mg Cu kg^{-1}. Height and stem diameter were measured over 90 days. Biomass and Cu concentration in leaves, stem and roots were determined. Copper was analysed in soils by sequential extraction, as well as in leached water.

The Technosol showed a very high capacity to immobilize copper, since 60–80% of the added copper was strongly retained in the soil, mainly by bentonite and carbonates. The Technosol with trees showed the same capacity to immobilize copper as the control, since concentration in shoots was higher than 300 mg Cu kg^{-1} and concentration in roots was even higher. These results show that Technosol and both species are useful tools to immobilize copper in polluted soils. Further studies are necessary to determine

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the total capacity of these trees to immobilize and/or extract copper in the long term and under field conditions.

1. Introduction

Mine soils often show several limitations for plant growth, such as very low content of organic matter and nutrients, acidic reaction, salinity or toxicity by metals and/or metalloids (Akala and Lal, 2001; Asensio et al., 2013b; Chu et al., 2018; Otero et al., 2012; Perlatti et al., 2015a). The use of hyperaccumulator plant species has been proposed in reclamation programs to improve the quality of mine soils (Kang et al., 2018; Kasowska et al., 2018; Parra et al., 2016; Perlatti et al., 2015a). However, since metal-polluted mine soils usually have very low quality, it is necessary to improve it before plants. Therefore, the amelioration of polluted mine soils should be done by phytomanagement, i.e., by integrating phytoremediation with another reclamation technique (Robinson et al., 2009). Soils developed from materials made or exposed by human activity (i.e. waste, mine tailings), recently classified as Technosols (IUSS Working Group WRB, 2014), have been proven efficient in increasing the quality of mine soils and even providing a substrate where the original soil was lost (Asensio et al., 2014, 2013b; Párraga-Aguado et al., 2017; Rodríguez-Vila et al., 2016; Rodríguez et al., 2018). These man-made soils may not only add value to a wide range of waste types, but also play a key role in the reclamation of degraded areas, where they can restore several soil functions (Asensio et al., 2014; Hafeez et al., 2012; Séré et al., 2010). Moreover, Technosols used as soil amendment in degraded soils can enhance plant and microorganisms growth (Asensio et al., 2013a; Mingorance et al., 2017; Montiel-Rozas et al., 2018; Wang et al., 2017).

Phytoremediation is defined as the use of plants to remove, contain, or render harmless potential contaminants such as metals, metalloids, trace elements, organic and radioactive compounds in soil or water (Sharma and Pandey, 2014). It is a cheaper and more ecological technique than physical or chemical treatments (Wang et al., 2017). The phytoremediation techniques more widely observed in metal-polluted soils are phytostabilization and phytoextraction (Koptsik, 2014; Mahar et al., 2016). Phytoextraction is the uptake of contaminants from soil or water by plant roots and their translocation to and accumulation in aboveground biomass (Nanda Kumar et al., 1995). Phytostabilization is the use of certain plants for stabilization of contaminants in contaminated soils (Chaney et al., 1997). Previous studies have identified a number of species suitable for phytoremediation of metal-polluted soils, but most of them are herbaceous and shrub species (Koptsik, 2014), whose final biomass is lower than that of trees. Therefore, it is important to identify fast-growing, high-biomass tree species capable of extracting or phytostabilizing metals in polluted soils. Although phytoremediation with trees has received increasing attention in recent years (Courchesne et al., 2017; Liu et al., 2013; Pajević et al., 2016), there is little information on tropical tree species with potential for the phytoremediation of metal-polluted soils (Caires et al., 2011; Gomes et al., 2011; Da Silva et al., 2011). Moreover, very few studies have combined the use of Technosol and phytoremediation (Forján et al., 2018; Novo et al., 2013a, 2013b; Rodríguez-Vila et al., 2016), and none of them were conducted under tropical conditions. For that reason, the main goals of the present study were: i) to evaluate the capacity of a constructed Technosol to immobilize high amounts of copper, ii) to assess the capacity of the same Technosol planted with two Brazilian native tree species to immobilize copper, and iii) to analyse the capacity of the native trees for extracting copper from the polluted soils. It was hypothesised that: i) the Technosol provides a geochemical barrier against copper mobilization by retaining most metal in the less labile soil fractions and ii) the combined use of the Technosol and tree species immobilizes more copper than the use of each one of these techniques separately.

2. Materials and methods

2.1. Greenhouse experiment

Two native tree species from Brazil were selected for the greenhouse experiment: *Myracrodruon urundeuva* Allemão (aroeira, MU) and *Cedrela fissilis* Vell. (pink cedar, CF). *M. urundeuva* is widely distributed in South America, mainly in the Atlantic Forest, Cerrado (tropical savanna) and Caatinga (tropical semiarid) biomes (Luz and Pirani, 2018). *M. urundeuva* was selected for the present study because it is a fast-growing species with a wide geographic distribution and a potential metal phytoextractor (Asensio et al., 2018; Gomes et al., 2013). To our knowledge, there are no previous studies testing the tolerance of *M. urundeuva* to high concentrations of copper in soils. Nevertheless, there are evidences that this species is zinc-tolerant (Gomes et al., 2013).

C. fissilis is also widely distributed in South America, naturally occurring in the Cerrado, Atlantic Forest and Amazon biomes (Flores, 2018). It is also a fast-growing species with and a potential metal phytoextractor (Caires et al., 2011; Marques et al., 2000). This species was reported to naturally grow in copper-polluted sites (Perlatti et al., 2015a).

The greenhouse experiment was set up by planting seedlings of the two selected species in plastic pots with 1.35 kg of a soil, tentatively classified as Hyperartefactic Technosol according to the IUSS Working Group WRB (2014). The Technosol was made of organic compost (40%), sand (36%), limestone mining waste (20%) and bentonite (4%). The general characteristics of the Technosol, sand, limestone and bentonite are presented in Table 1. The mineralogical composition of the clay fraction of bentonite and limestone are in Table 2. The elemental characterization of clays was done by X-ray fluorescence (XRF) using a Philips PW 2400 spectrometer.

The organic compost was prepared from tree pruning, crop residues, waste from food industries and manure, and it was selected for the Technosol because organic matter has a high capacity to retain copper (Alloway, 1995; Covelo et al., 2008).

The limestone mining waste came from a limestone mine in the region of Rio Claro (SP, Brazil), and it was selected because carbonates can reduce the mobility of copper in soils, mainly by precipitation as both metal carbonate and metal hydroxide (Selim and Sparks, 2001).

Bentonite is a rock formed by highly reactive and plastic clays composed mainly of montmorillonite. The bentonite used was a residue from a limestone mine at Pernambuco state (Brazil), and it was rich in Fe^{3+} and interlayer cations like Na^{+}, K^{+} and Ca^{2+}. Bentonite was selected for the Technosol due to its high cation exchange capacity (CEC), which would increase the sorption capacity for Cu^{2+} (Sartor et al., 2015).

Finally, sand was added to the Technosol in order to favour its

Table 1
General characteristics of the Technosol (Tech), as well as the organic compost (OC), sand, limestone (LM) and bentonite (B) used to construct the soil.

	Characteristics										
	pH		OM	P	K^+	Ca^{2+}	Mg^{2+}	Na^+	H + Al	Al^{3+}	CEC_t
	H_2O	KCl	g kg^{-1}	mg kg^{-1}	$mmol_{(+)}kg^{-1}$						
Tech	8.0	6.8	30	268	6.9	112	150	47.5	3	<0.1	319
OC	–	6.3	388	3580	125	380	205	–	–	–	800
Sand	6.8	5	5	4.5	0.2	5	2	0.8	9	1	17
LM	6.5	5.7	24	179	2.4	149	250	4.2	10	<0.1	415
B	10.4	8.4	6	43.7	3.7	59	31	565	1	<0.1	660

Note: OM = organic matter, P = phosphorus by Mehlich 1, CEC_t = total cation exchange capacity.

Table 2
Mineralogical analysis analyses of the clay fraction of bentonite and limestone.

%	Bentonite[a]	Limestone
SiO_2	57.500	50.479
TiO_2	0.992	0.375
Al_2O_3	18.780	10.846
Fe_2O_3	8.010	3.242
MgO	2.610	8.001
CaO	1.190	1.037
Na_2O	2.120	u.l.
K_2O	0.380	u.l.
SO_2	u.l.	2.330

[a] Data collected by Sartor et al. (2015). u.l.: undetectable level.

aeration and drainage, especially due to the high swelling of bentonite.

The components of the Technosol were dried and sieved to < 2 mm, and then manually mixed in a plastic sailcloth by using a shovel. Twelve non-planted pots were kept as a control treatment. Seedlings were supplied by SOS Mata Atlântica seedling nursery (Itu, Brazil). The pots were black, circular, 18 cm diameter and 15 cm high. After planting, seedlings were fertilized with 80 mg N kg^{-1}, 80 mg K kg^{-1}, 150 mg P kg^{-1} and 0.5 mg B kg^{-1} in the form of ammonium nitrite, potassium chloride and phosphate mono-ammonium, respectively. Nutrients were added to the pots in three different applications in order to avoid their loss by leaching. Planted and non-planted Technosols were unpolluted (Cu concentration = 0) and polluted at concentrations of 125, 1525 and 3050 mg Cu kg^{-1} by irrigating with $CuSO_4$ solutions over three months. The total volume of irrigation was estimated to reach 960 mm, which is the average annual rainfall in a former copper mine (see Perlatti et al., 2015a), taking into account the size of each pot (18 cm diameter and 15 cm high). Therefore, each pot was irrigated with 100 mL 45 times. All treatments were done in triplicate. Pots were distributed in randomized blocks and kept at 80% field capacity over three months. The total amount of run-off water during the greenhouse experiment was collected periodically from each pot in plastic recipients coupled to the pots in order to determine pH and copper concentration in leachates by atomic absorption spectrometry, AAS (AANALYST 400, PerkinElmer).

2.2. Soil analyses

After harvesting, soils were removed from each pot and air-dried. Copper concentration in all Technosols was extracted using a sequential extraction procedure as described by Perlatti et al. (2014). The following extractions were performed sequentially, and the different extracted fractions were operationally defined as:

- F1 (exchangeable fraction, Ex-Cu): extracted with 8 mL of 1 M $MgCl_2$ at pH 7.0 for 1 h at room temperature.
- F2 (carbonate bound, Carb-Cu): extracted with 30 mL of 1 M NaOAc at pH 5.0 for 5 h at room temperature.
- F3 (associated with organic matter, OM-Cu): extracted with 10 mL of 6% NaOCl at pH 8.0 for 6 h at 25 °C. This step was repeated three times.
- F4 (associated with amorphous iron oxides, AOx-Cu): extracted with 30 mL of 0.2 M oxalic acid + 0.2 M ammonium oxalate at pH 3 for 2 h in the dark.
- F5 (associated with crystalline iron oxides, COx-Cu): extracted with 0.25 M sodium citrate + 0.11 M sodium bicarbonate + sodium dithionite (3 g) for 30 min at 75 °C.
- F6 (precipitated with sulphides, S-Cu): extracted with 4 M HNO_3 in a water bath for 16 h at 80 °C, with occasional shaking. This fraction was extracted because the limestone waste had sulphides.
- F7 (residual, Res-Cu): extracted with *aqua regia* in a microwave oven. The extracts were transferred to plastic recipients and the volume was made up to 50 mL with ultrapure water.
- F8 (no reactive fraction F8, NR-Cu). The amount of Cu that was not extracted by the chemical sequential extraction, taken up by plants or lost by leaching was assumed to remain in the residual soil phases (Fig. 1). This fraction was obtained as the difference between the total Cu content in the soil at the beginning of the experiment and the total amount of Cu extracted at the end, which is the sum of Cu extracted from F1 to F7, in leachates and in plants.

Between each extraction step, the residual soil was washed with 20 mL of ultrapure water, manually shaken and centrifuged at

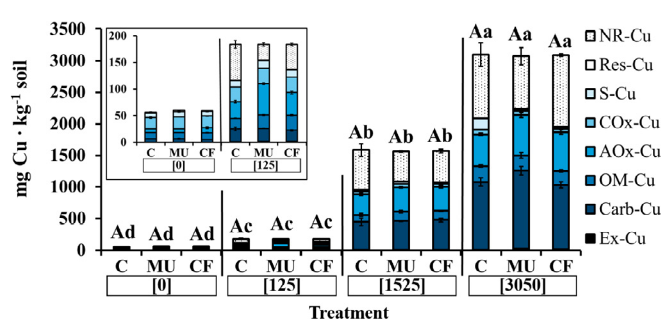

Fig. 1. Copper partitioning (mean and SD values, n = 3) in the soil without plant (control, C), planted with *Myracrodruon urundeuva* (MU) or *Cedrela fissilis* (CF). Soils were unpolluted and polluted to rise 125, 1525 or 3050 mg kg^{-1} Cu. Soil fractions are Ex-Cu (exchangeable), Carb-Cu (carbonate bound), OM-Cu (associated with organic matter), AOx-Cu (associated with amorphous iron oxides), COx-Cu (associated with crystalline iron oxides), S-Cu (associated with sulfides), Res-Cu (residual) and NR-Cu (nonreactive). Capital letters indicate significant differences ($p < 0.05$) in the total concentration of copper (sum of all fractions) between C, MU and CF in each concentration of pollution. Lowercase letters indicate significant differences in the total concentration of copper between the different concentration of pollution for C, MU and CF.

3000 rpm for 15 min. The supernatant was discarded to prevent interference from the previous reagent in the subsequent extraction. All the extracts were centrifuged at 3000 rpm for 15 min and filtered prior to being analysed by AAS (AANALYST 400, PerkinElmer) to determine copper concentration. All samples were analysed in triplicate.

2.3. Plant analyses

Height and stem diameter were measured 0, 30, 60 and 90 days after planting. Plants were harvested and split into leaves, stem and roots. In the laboratory, plant samples were washed with tap water and rinsed three times with distilled water. Plant samples were then oven-dried at 60 °C for 72 h and weighted to determine dry-weight biomass. Dry plant samples were digested with nitric-perchloric acid in order to extract copper from plant tissues, following the method of Zasoski and Burau (1977). One gram of ground plant sample was digested with 2 mL HNO_3 overnight. Samples were then heated at 80 °C for 1 h. After cooling, 1.5 mL 72% perchloric acid ($HClO_4$) was added to each tube and left to digest at 180-200 °C for 3 h. Samples were cooled to 60 °C and then filled with distilled water to a final volume of 25 mL. Copper concentration in the supernatant was determined by AAS (AANALYST 400, PerkinElmer).

2.4. Statistical analyses

The data obtained were statistically treated with the SPSS software version 15.0 for Windows. Analysis of variance (ANOVA) and test of homogeneity of variance were carried out. In case of homogeneity, a post-hoc least significant difference (LSD) test was carried out. If there was no homogeneity, Dunnett's T3 test was performed. Pearson's correlation analyses were also performed between some studied variables and the treatments.

3. Results

3.1. Copper in Technosol and leachates

The Technosol immobilized almost all of the copper added by irrigating with $CuSO_4$ solutions (99.9%) (Fig. 1). Moreover, 60–80% of Cu was strongly retained in the Technosols, mainly in the OM-Cu and NR-Cu fractions.

After three months, there were no significant differences in total Cu concentrations between soils with *Myracrodruon urundeuva* Allemão (aroeira, MU) or *Cedrela fissilis* Vell. (pink cedar, CF) and control soil (Fig. 1). Nonetheless, the presence of trees changed copper distribution in the different soil fractions. In soils polluted at a concentration of 125 mg Cu kg^{-1} ([125]), both MU and CF had higher Cu concentrations in the Ex-Cu, OM-Cu and AOx-Cu fractions than the control. In soils with [1525], MU had significantly higher Cu concentrations than CF and C in the residual fraction ($p < 0.05$) (32, 24 and 22 mg kg^{-1}, respectively), while in soils polluted at [3050], both species had significantly higher concentrations in Ex-Cu than the control ($p < 0.05$) (30, 22 and 9 mg kg^{-1}, respectively).

The partitioning of copper in the Technosol was not significantly different between the control and planted soils (percentages not shown). However, there were significant differences in Cu percentage in each soil fraction between the different Cu-pollution treatments. In unpolluted soils, most of the copper was associated with crystalline iron oxides (37–39%). After pollution at a concentration of 125 mg kg^{-1}, most of the Cu was in NR-Cu in the control (36%), but in planted soils Cu was mostly in AOx (23–32%), followed by NR-Cu (16–25%). When polluted at a concentration of1525 mg kg^{-1}, most Cu was again in NR in the control (40%), while planted soils had the highest proportions in Carb-Cu (29–30%) and NR-Cu (30–32%). In polluted soils with the highest concentration [3050], most of the Cu was found in Carb-Cu in MU (40%), while in

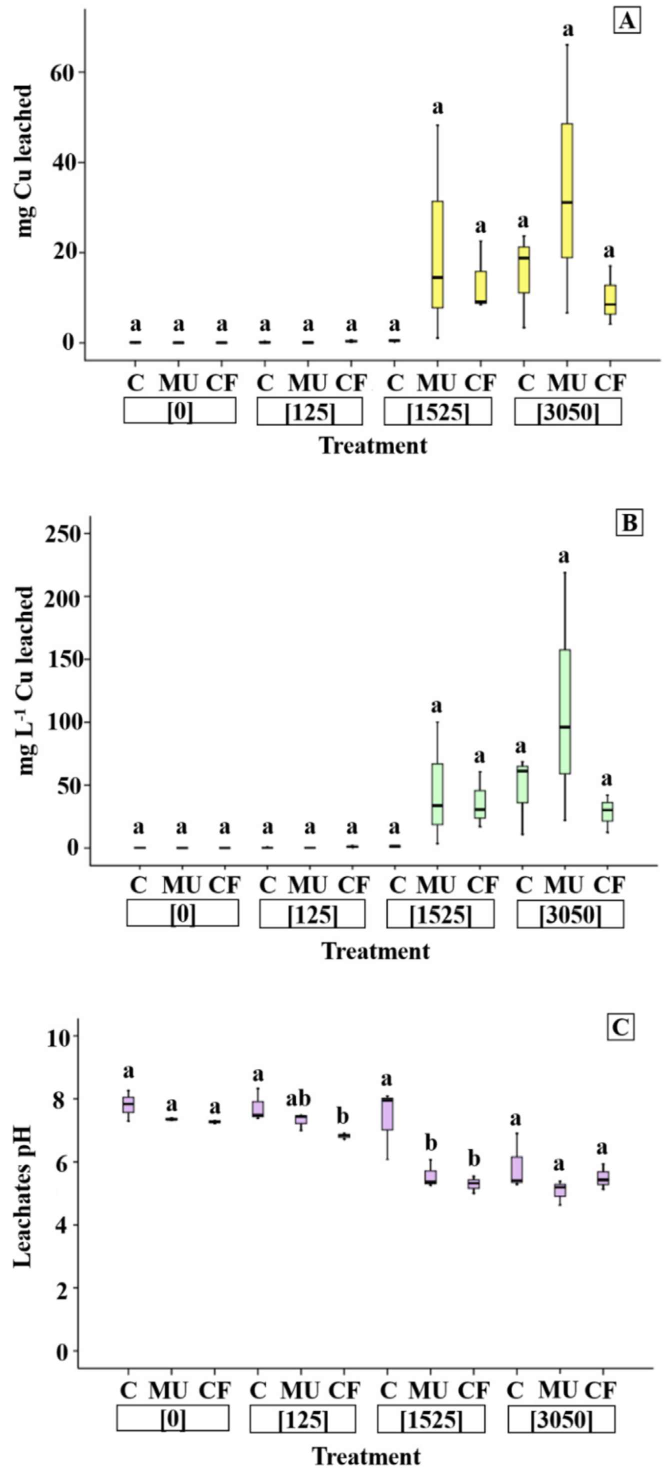

Fig. 2. **A)** Total content of copper leached, **B)** concentration of copper in leachates and, **C)** pH in leachates from soil without plant (control, C), planted with *Myracrodruon urundeuva* (MU) or *Cedrela fissilis* (CF), when they were unpolluted and polluted to rise 0, 125, 1525 or 3050 mg kg^{-1} Cu. The solid line is the median, the box represents the upper and lower quartiles, and whiskers are the 10th and 90th percentiles. Letters indicate significant differences ($p < 0.05$) between C, MU and CF in each concentration of copper pollution.

the control and CF most Cu was in the Carb (33–34%) and NR (33–37%) fractions.

Neither copper concentration (mg L^{-1}) nor total copper contents in leachates (total mg leached) were significantly changed by planting trees, despite the fact that mean values were very different due to the high standard deviations (Fig. 2). However, both the concentration and total content of Cu increased in leachates with increasing Cu pollution. In general, Cu concentration was high in leachates in highly polluted soils ([1525] and [3050]), with mean values ranging from 28 to 112 mg L^{-1}. The pH in leachates significantly decreased when planting trees at [125] and [1525], but there were no differences between the control and planted soils at [3050].

3.2. Plant growth

Total plant biomass did not significantly differ between species at any pollution concentration (Fig. 3). However, there were differences between species in terms of the biomass of each plant tissue. In the control soil ([0]), CF had higher stem biomass than MU, while MU had higher root biomass. In [125], CF showed higher biomass in the aerial parts (leaves and stem), while MU showed higher root biomass. In polluted soils ([1525] and [3050]), CF had higher leaf biomass than MU and there were no differences in root biomass. *M. urundeuva* plants showed no significant differences in biomass between Cu concentrations. On the other hand, *C. fissilis* decreased its leaf and stem biomass in the [3050] treatment, but increased its root biomass with respect to [125].

The height of both species did not significantly change due to copper pollution after three months of experiment (Table 3). Stem diameter increased in MU [3050] when compared to [0], while it decreased in CF plants (Table 3).

3.3. Copper in plants

Both species extracted similar total amounts of copper from Technosols (Fig. 4). However, there were differences between species when comparing total Cu content in each plant tissue. In the control soil and in soil polluted at [125], MU roots extracted more Cu than CF roots. Contrarily, CF shots extracted more copper than MU shoots in all treatments. Despite these differences, both species accumulated the highest amounts of copper in roots in most cases (51–97%). As expected, the higher the degree of pollution, the higher the amount of copper in each plant organ (leaves, stem or roots) (Fig. 4).

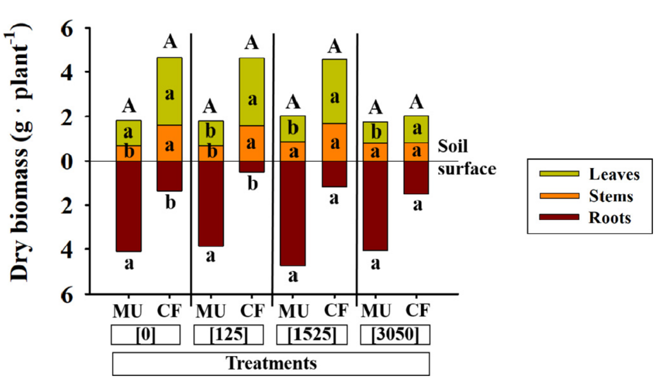

Fig. 3. Dry biomass (mean values, n = 3) in the soil unpolluted and polluted to rise 0, 125, 1525 or 3050 mg kg^{-1} Cu. Soils were planted with *Myracrodruon urundeuva* (MU) or *Cedrela fissilis* (CF). Lowercase letters indicate significant differences (p < 0.05) of biomass in each plant organ (roots, stems or leaves) between plant species for each Cu concentration. Capital letters indicates differences in the total biomass (roots + stems + leaves).

Table 3
Height (cm) and stem diameter (mm) in *Myracrodruon urundeuva* (MU) or *Cedrela fissilis* (CF) in the four different copper treatments at the beginning of the experiment (T0), 30, 60 and 90 days after planting (T1, T2 and T3, respectively).

Time	Copper added (mg kg^{-1})	Plant species			
		Height (cm)		Diameter (mm)	
		MU	CF	MU	CF
T0	0	18.9a	18.3a	4.3a	9.1a
	125	18.6a	15.8a	3.7a	7.6a
	1525	20.6a	14.3a	4.2a	8.9a
	3050	20.0a	16.6a	5.1a	7.9a
T1	0	18.5a	19.3a	4.0 ab	8.4a
	125	17.6a	18.3a	3.5b	8.6a
	1525	21.3a	14.3a	4.3a	8.7a
	3050	19.3a	16.6a	5.3a	8.3a
T2	0	18.0a	21.3a	4.3a	8.8a
	125	21.3a	24.0a	4.2a	9.8a
	1525	20.3a	18.0a	5.2a	9.5a
	3050	18.6a	16.6a	6.4a	6.8a
T3	0	18.0a	22.6a	4.8b	10.3a
	125	24.0a	22.0a	4.9 ab	9.6 ab
	1525	19.0a	20.6a	5.9 ab	9.6 ab
	3050	20.3a	20.1a	6.4a	8.1b

Mean values (n = 3). Values followed by different letters in each column for each time (T) differ significantly with p < 0.05.

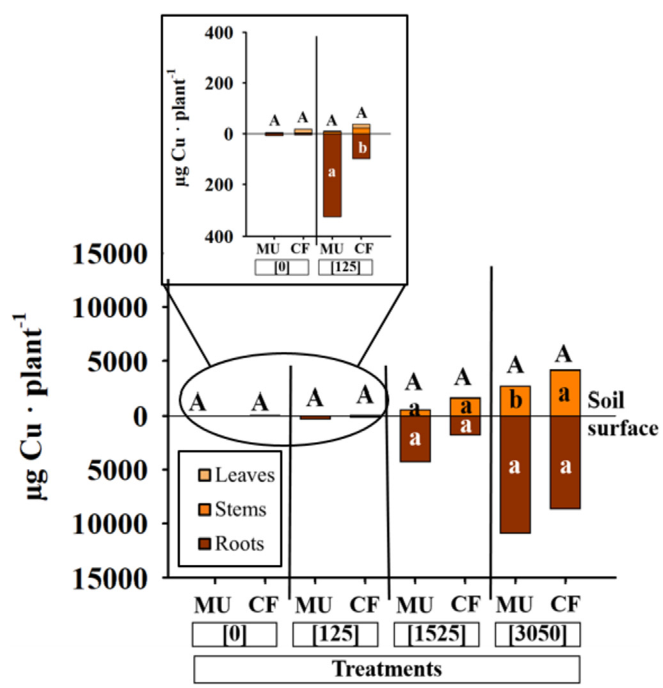

Fig. 4. Copper contents in plants (mean values, n = 3) in the soil without addition of copper [0], polluted to 125, 1525 and 3050 mg kg^{-1} Cu. Soils were planted with *Myracrodruon urundeuva* (MU) or *Cedrela fissilis* (CF). Lowercase letters indicate significant differences (p < 0.05) of Cu content in each plant organ (roots, stems or leaves) between plant species for each Cu concentration. Capital letters indicates differences in the total Cu content (roots + stems + leaves).

The highest Cu concentration in shoots and roots was reached when polluted to 3050 mg kg^{-1} for both plant species, with most of the Cu in roots (Table 4). In the control soils and in soils polluted at [1525], there were no differences between species for Cu concentration in each plant organ. However, CF showed higher concentrations in leaves and roots than MU in [125] and [3050] treatments.

Table 4
Copper concentration (mg kg^{-1}) in *Myracrodruon urundeuva* (MU) and *Cedrela fissilis* (CF) roots, stem and leaves in the different treatments.

Copper added (mg kg^{-1})	Plant organ	Plant species	
		MU	CF
0	leaves	2.6a	4.9a
	stem	2.3a	1.3a
	roots	2.0a	4.0a
125	leaves	2.8b	4.6a
	stem	9.3a	14.0a
	roots	82.6b	196a
1525	leaves	18.9a	10.7a
	stem	636a	954a
	roots	986a	1546a
3050	leaves	12.4b	52.2a
	stem	3241a	5008a
	Roots	2600b	5800a

Mean values (n = 3). Values followed by different letters in each row differ significantly with p < 0.05.

4. Discussion

4.1. Technosol capacity for copper immobilization

The Technosol showed a high capacity to immobilize copper. Even with the addition of high amounts of Cu in soluble form (3050 mg kg^{-1}, treatment [3050]), the Technosol control (without plants) was capable of immobilizing 99% of the total Cu added, with most Cu associated to the NR fraction (Fig. 1). This non-reactive fraction, from which Cu was neither extracted by chemical extractions, or by plants nor leached, was assumed to correspond to a strong sorption in recalcitrant silicates, probably in association with bentonite. In fact, previous studies showed that bentonite has a high sorption capacity for metals (Ling et al., 2007; Merrikhpour and Jalali, 2013), but other phyllosilicates such as montmorillonite also have a high sorption capacity to sorb metals into the inter-layer space of pillared clays (Sartor et al., 2015).

On the other hand, 33–40% Cu was bound to carbonates and, thus, weakly immobilized; this Cu could be solubilised more easily. Moreover, copper concentration in leachates (Fig. 2) from non-planted soils with the highest level of pollution (C [3050]) largely exceeded the intervention value for groundwater (2 mg L^{-1}) established by Brazilian legislation (CONAMA, 2009). Threshold/trigger values for copper in groundwater established by other countries such as Canada, USA or Germany are even lower than those for Brazil. These results indicate that, despite the high capacity of the Technosol to immobilize copper, this soil is not sufficient to maintain copper concentration in leachates below safety values for extremely high concentrations of Cu (>1525 mg kg^{-1} Cu in the soluble form). Nevertheless, the reported concentrations of available copper in polluted soils under field conditions is usually between 1.4 and 1010 mg kg^{-1} (Arenas-Lago et al., 2014; Asensio et al., 2013c; Lombi et al., 1999; Perlatti et al., 2015b; Pietrzak and McPhail, 2004; Touceda-González et al., 2017). Therefore, the studied Technosol could be efficient in immobilizing large amounts, especially those usually reported in Cu-polluted soils.

4.2. Technosol-plant system for copper immobilization

The total concentration of Cu immobilized in vegetated Technosols did not significantly differ from the control, because the amount of copper accumulated in roots was low (Figs. 1 and 4).

The concentration of copper in exchangeable form (Ex-Cu), which could be considered as the readily bioavailable form, increased in the polluted Technosols when vegetated with MU or CF. This result could be related to the copper released by sulphides, since its percentage in the S-Cu fraction decreased in planted soils, or to soil acidification by root exudates (Fig. 2c), which may promote solubilisation or release of copper associated with different soil fractions (Hinsinger et al., 2003). However, Cu concentrations in leachates did not increase in planted Technosol. In fact, a significant negative correlation between the "plant/no plant" factor (1/0) and pH of leachates ($r = -0.40$, $P < 0.05$) was found.

M. urundeuva and *C. fissilis* showed a high potential to phytoremediate copper-polluted soils. The biomass of both species did not decrease even at high concentrations of Cu [3050], which indicates that these species would probably reach a much higher biomass in a longer-term experiment and therefore take up more copper from contaminated soils.

Previous studies (Carvalho, 1994) showed that, under field conditions, *M. urundeuva* reached 5.50 m^3 wood ha^{-1} $year^{-1}$ and *C. fissilis* 3.25 m^3 wood ha^{-1} $year^{-1}$. Based on these values, wood density (Carvalho, 1994), and copper concentration in stems obtained in the present study (g kg^{-1}), the amount of Cu that could be extracted per year with the studied trees under field conditions can be estimated. *M. urundeuva* would extract up to ~17,000 kg of Cu per hectare per year in the stems alone, while *C. fissilis* would extract up to ~9000 kg Cu per year. Estimations for leaves or roots were not possible due to the lack of bibliographic data on leaf and radicular biomass of these trees under field conditions. Both species showed very high concentrations of copper in shoots and roots (Table 4). In fact, they can be considered as potential hyperaccumulators for copper, because they reached values of over 300 mg kg^{-1} Cu in shoots, and they survived and grew (van der Ent et al., 2013). Additionally, the concentration and amount of copper in roots was higher than in shoots; therefore, *M. urundeuva* and *C. fissilis* have potential to act as phytostabilizers and as phytoextractors.

5. Conclusions

The Technosol made of organic compost, sand, limestone mining waste and bentonite, showed a very high capacity to immobilize copper. The components with the highest capacity of sorption for copper were bentonite and carbonates. The Technosol planted with the native Brazilian trees *Myracrodruon urundeuva* (aroeira) or *Cedrela fissilis* (pink cedar) showed similar capacities to immobilize copper. Both tree species have potential to act as phytoextractors and phytostabilizers of copper in polluted soils, since they accumulated more than 300 mg kg^{-1} of this metal in shoots, even higher concentrations in roots, and they survived and grew. Therefore, the use of Technosols with bentonite and *M. urundeuva* or *C. fissilis* could be an efficient reclaiming system for copper-polluted soils, both to immobilize and to extract the metal. Further studies are necessary to assess the total capacity of the Technosol-trees system, as well as of bentonite, to immobilize and/or extract copper in the long term and under field conditions.

Declarations of interest

None.

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