Copper geochemical behaviour in mine tailings phytostabilised using organic-waste amendments and grass cover

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Introduction

(Aided) phytostabilisation combines trace-element-excluding plants and soil amendments for the *in situ* inactivation of metal(oid)s in contaminated soils. Waste-based amendments can be useful for improving phytostabilisation, but long-term alteration can result into metal(loid) remobilization. Studies including long-term monitoring in the field are thus necessary. Here, the medium-term Cu stabilization mechanisms and geochemical transformations in mine soils under aided phytostabilisation were evaluated.

Materials and Methods

	PC	T1	T2
pH_{H2O}	6.9	7.8	7.8
Total element concentrations			
g kg^{-1}			
C	154.0	71.0	90.0
N	14.0	16.0	8.0
P	11.8	4.0	5.4
K	6.1	13.9	14.8
Al	31.1	34.3	41.5
Ca	30.1	34.5	48.8
Mg	7.2	10.5	10.2
Fe	28.2	37.3	23.0
mg kg^{-1}			
Cd	1.5	2.0	2.0
Co	13.4	10.0	12.4
Cr	63.2	46.7	51.7
Cu	409.0	190.0	146.0
Mn	903	2198	1975
Ni	48.8	39.8	42.0
Pb	88.5	50.5	43.7
Zn	569.0	226.0	199.0

Table 1. Soil amendment properties

Study site: abandoned Cu mine ore (Touro, NW Spain) . Geological substrate is amphibolite with metallic sulphides.

Experimental field plots (approx. 0.1 ha): amended and planted with *Agrostis capillaris* cv. Highland, spring 2011.

Soil amendments: Three organic waste-based amendments (C, T1, T2; Table 1), with different combinations of municipal wastes , bark chippings, biomass fly ash and Al or Fe nanoparticles

Soil sampling: 5 soil samples/sub-plot, 5x5 m, upper 20 cm. Time 0, 1, 2 and 3 years.

Soil analysis:

•Physicochemical characterization and fertility

•Two geochemical approaches :

➢Non-sequential selective extractions for Cu (and Al / Fe compounds): 1 M $NaNO_3$ (Cu_{Na}); 0.33 M $LaCl_3$ (Cu_L), Na pyrophosphate (Cu_p, Al_p, Fe_p); acid oxalate (Cu_o, Al_o, Fe_o), and sodium dithionite-citrate (Fe_d); $Cu_{Lp} = Cu_L - Cu_p$; $Cu_{op} = Cu_o - Cu_p$.

➢Sequential extractions: BCR protocol, operationally defined Cu fractions

Results and discussion

Mine tailings presented acid pH, low fertility and high concentrations of total Cu and showed a very high risk of Cu mobilization (Table 2). The three amendments in combination with herbaceous cover significantly reduced Cu mobility and bioavailability, with retention mechanisms depending on amendment characteristics. The three amendments increased organic C of the mine spoil. Additionally, PC amendment increased reactive Fe (mainly crystalline oxides, Fig 1), while T1 and, especially T2, increased reactive Al (mainly Al amorphous and organo-Al complexes, Fig. 2). The geochemical approach showed that > 30 % from Cu_T was extracted with amonium oxalate (Cu_o) in mine tailings and this fraction increased by up to >60% in the amended soils, while leaching was reduced. The retention of Cu was mainly produced in organo-metallic complexes and/or low crystallinity compounds, and this were maintained at least three years after treatment. Sequential Cu fractionation was consistent with these results. Nonetheless, a more long-term monitoring approach is also being carried out.

	Untreated soil	PC_{3years}	$T1_{3years}$	$T2_{3years}$
pH	3.1	6.5	6.9	7.5
%C	0.6	7.0	3.6	4.8
%N	0.1	0.5	0.3	3.4
CEC ($cmol_c$ kg^{-1})	11.9	17.4	21.6	26.6
Al	8.0	0.2	0.0	0.0
Ca	2.5	14.8	19.0	24.1
K	0.0	0.6	0.9	1.1
Mg	1.5	1.7	1.4	1.4
P olsen (mg/kg)	2.49	133	139	71.8
Cu (mg kg^{-1})				
Pseudo-total	684	481	363	358
$NaNO_3$ extract	94	0.5	0.3	0.2

Fig. 1. Soil characterisation (3-year plots, mean values, n = 3)

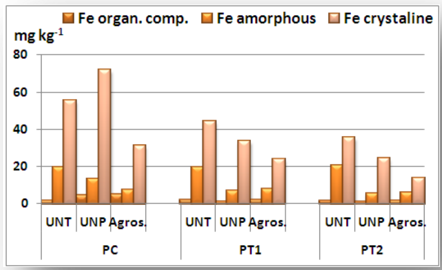

Fig. 2. Geochemical fractions of reactive Fe in soils (3-year plots). UNT, untreated mine spoil; UNP, unplanted amended; Agros, A. capillaris

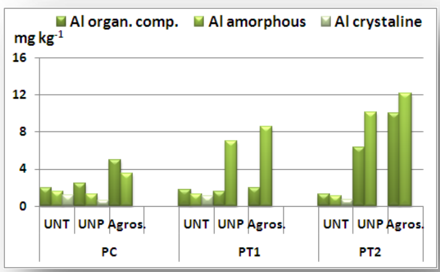

Fig. 3. Geochemical fractions of reactive Al in soils (3-year plots)

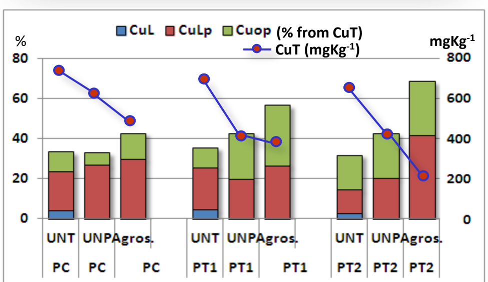

Fig. 4.Total and extractable Cu in soils (3-year plots)

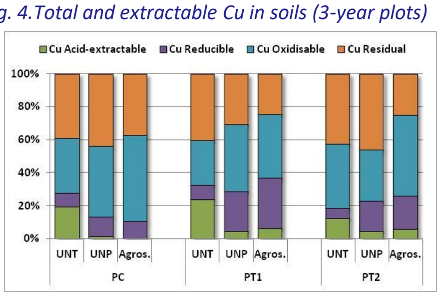

Fig. 5. Cu fractions operationally defined by BCR sequential protocol

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