

Assessment of Metal(loid)s phytoavailability in mining soils

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Overview

The field experiment was performed in Borralha mine (northern Portugal) and consisted on six 9 m² plots sown with sunflower: **three control plots and three inoculated with an arbuscular mycorrhizal fungi (AMF) and a plant growth-promoting rhizobacteria (PGPR).** Soils were analyzed (TIME 0) before plants harvesting. Four months later rhizosphere soils (TIME 1) were collected to determine metal content. Total metal content (As, Cd, Cu, Pb and Zn), sequential chemical extraction and bioavailability in each soil (TIME 0 and TIME 1) were assessed. Enrichment factors, Potential ecological hazard index and Ecological risk were calculated. Results were compared and % extractions in mobile phases decreased from TIME 0 to TIME 1; nevertheless metal mobility and bioavailability of metals, mainly Cd, a toxic and carcinogenic metal, was considered high.

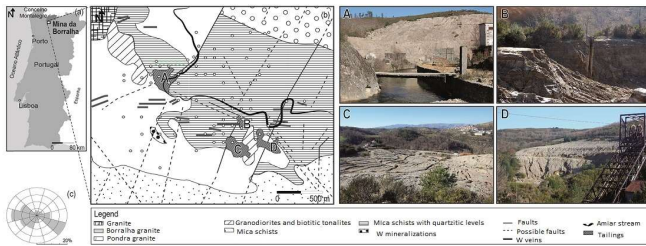
Introduction

Mining operations are one of the major soil disruptors. The release of hazardous compounds, such heavy metals and metalloids (HM), pose serious risks to human health and contribute to the decline of soil's quality. The use of phytotechnologies (application of plants and microorganisms) in mine areas has the potential of reducing the amount or the toxicity of deleterious HM, promoting ecological restoration. Moreover, they can provide relevant economic revenues by using these brownfields to produce bioenergy crops.

This work is harbored by PhytoSUDOE project that aims the management of degrading environments and their restoration through the application phytotechnologies. A transnational network of contaminated sites distributed through Portugal, Spain and France was established to demonstrate the sustainability of phytomanagement options for degraded sites. In this context, the main goal of this work is to assess the environmentally available concentrations of metal(loid)s and their distribution in soil fractions before and after implementing phytotechnologies by means of bioenergy crops (e.g. sunflower - *Helianthus annuus* and *Populus sp.*) assisted by AMF and PGPR that have a high potential for success in adapting to soils of this nature.

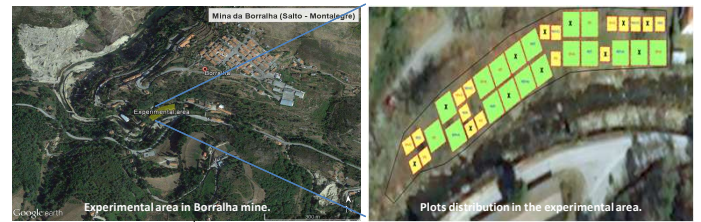
METHODS

Geological/mining framework - main sources of contamination



- ✓ Borralha mine (1179 ha): Explored between 1902-1986;
- ✓ Granitic rocks of different lithological types intrusive in the metasedimentary formations of the Silurian host, both in eruptive rocks and metasedimentary formations, the tungsten mineralization;
- ✓ Quartz, wolframite, scheelite and sulfides as chalcopyrite, pyrite, sphalerite, molybdenite and bismuthinite characterize the mineralogical assemblage
- ✓ 52 concessions [28 (W), 12 (W, Sn), 10 (Sn) and 2 (W, Cu, Ag, Mo)]. Economic exploitation: wolframite, scheelite, chalcopyrite;
- ✓ Sources of contamination: (i) tailings with huge volumes (~ 1.5x10⁶ m³); (ii) mud and slush, rejected from the ore process treatment discharged into a pond (~ 0.2x10⁶ m³) and (iii) sulfides directly deposited into the ground (~ 3475 m³)

EXPERIMENTAL DESIGN



Experimental surface area	~ 700 m ²
Design of experimental area	4 experimental blocks (36 plots) Each block is divided into four of: <ul style="list-style-type: none"> • 5 x 5 m for Poplar (no cropping pattern and intercropping with alfalfa; inoculated and non-inoculated with MF and PGPR) • 3x3 m for Sunflower (wintercropping and intercropping with clover, inoculated and non-inoculated with Micorrhizal fungi and PGPR); • 3 plots within each block without cultivation.
Experimental plot size	Each plot: 25 m ² (x 18) for Poplar 9 m ² (x 18) for Sunflower (plots without cultivation)

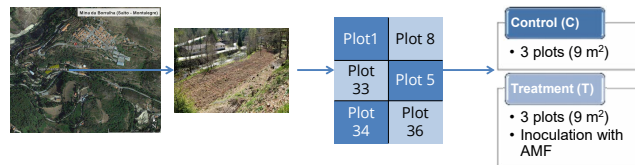
TIME 0

RESULTS

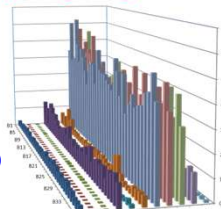
TIME 1 - Sunflower

- ✓ **Soil physico-chemical parameters:** 52% sand, 42.4% silt, 2.1% clay; pH 5.0; 10.5% OM; 4.2% CO₂, 0.36% N; 5.3% C and 113 μS/cm EC.
- ✓ **Total TE:** Mean contents (mg/kg) As=44.3; Cd=3; Cu=825.2; Pb=92.3 and Zn=138.6. According to the proposed Portuguese Guidelines [As=22; Cd=0.6; Cu=35; Pb=34 and Zn=85 mg/kg] (Ferreira, 2004). Cu exceed 24 X and Cd 15 X the proposed guideline values.
- ✓ **Sequential chemical extraction:** most pollutant fraction consists of metals bounded to sulfides and released under oxidizing conditions in AMD production, nevertheless, **Cu and Cd were extracted with acetic acid suggesting linkage to the easily mobilized phases.**

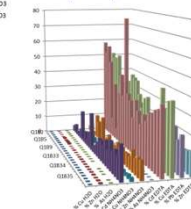
Sampling (6 months after seed) - 3 control plots no treatment and 3 plots with treatment



- ✓ **Bioavailability of TE:** All soluble concentrations, in single extraction with H₂O were **above toxic levels** (As=0.04, Cd=0.03, Cu=0.7, Pb=1 and Zn=0.5 mg/kg Ewers, 1991) revealing metal mobility. Cd (H₂O) 3.7X, Cd (NH₄NO₃) 8.3X, Cd (EDTA) 40X and Cu (H₂O) 1.3X, Cu (NH₄NO₃) 15.7X, Cu (EDTA) 407X. **Mobility and bioavailability of metal(loids) declines as Cd > Zn > Cu > As > Pb.**



- ✓ **Bioavailability of TE:** 1) Extraction H₂O: Cu and Zn below toxic level; **As above toxic level; no extraction for Cd and Pb** 2) Extraction NH₄NO₃: **As below toxic level; Cd, Cu and Zn above toxic levels; no extraction for Pb.** Extraction EDTA: all soluble concentrations above toxic levels (except As – no data). **Mobility and bioavailability of metal(loids) declines as Cd > As > Cu > Zn > Pb.**



Mean values	% Cu			% Zn			% As			% Cd		
	H ₂ O	H ₂ O	H ₂ O	NH ₄ NO ₃	NH ₄ NO ₃	NH ₄ NO ₃	EDTA	EDTA	EDTA	EDTA	EDTA	EDTA
Plot 1	0,17	0,04	0,17	3,04	0,27	2,42	0,13	53,68	50,00	28,26	27,07	
Plot 5	0,28	0,74	0,08	8,24	3,34	13,37	0,08	20,82	34,37	24,13	14,91	
Plot 8	0,17	0,12	0,06	9,56	1,57	4,92	0,07	46,00	41,24	19,50	8,43	
Plot 34	0,16	0,26	0,03	9,09	1,20	6,41	0,04	27,92	32,17	20,83	9,30	
Plot 33	0,16	0,33	0,07	12,86	1,70	7,47	0,08	25,76	26,28	17,19	8,42	
Plot 36	0,21	0,46	0,05	14,65	1,99	10,70	0,09	34,65	39,49	20,42	14,03	

Extractions with H₂O and NH₄NO₃ decreases from TIME 0 to TIME 1, which means that extraction of free ions in a physicochemical mobile phase and cation exchangeable fraction decreased after the first phytoremediation step. **Metals bioavailability of metals decreased.**

Cd available fraction increases with ammonium nitrate in bio-inoculated plots. NH₄NO₃ dissolve cation exchangeable fraction a mobile and easily available phase . Cd is toxic, carcinogenic and non biodegradable

Acknowledgements

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