Master's Thesis Engineering Technology

2016-2017

Metal mobility assessment for the application of biochar amendments in acidic and neutral pH mine tailing soils under variable moisture conditions

Brittany Laing

Master of Chemical Engineering Technology

Introduction

- **The Cartagena-La Union mining district** has been an important mining area for over 2500 years. During the mining activity, mining wastes (i.e. mine tailings) were dumped in surrounding areas, still containing large amounts of heavy metals [1].

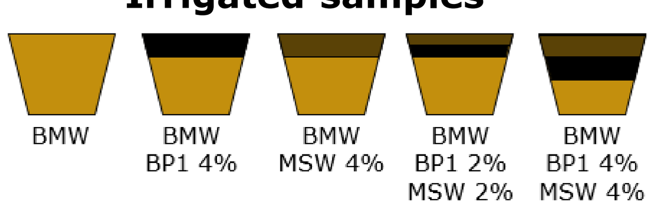
- Now, these **metal contaminants** are being transferred to surrounding areas, polluting the environment, due to several factors [1].
  - Wind erosion: Metal spread form mine tailing surface
  - Water run-off: Metals are carried out by rivers to wetlands
  - Leaching: Downward movement of metals to groundwater
- To manage the environmental risk of the contaminants, **metal mobility** needs to be assessed. By adding **organic amendments** (i.e. biochar and municipal solid waste (MSW)), metals can be immobilised, reducing their bioavailability [1] .
- Mine tailings are exposed to different moisture conditions (irrigation or flooding). Therefore, a pot experiment was set up one year ago with mine tailing soils amended with biochar, MSW or both, while simulation natural conditions with an irrigational or flooding water treatment. Consequently, the influence of soil incubation on metal mobility was investigated after one year under different humidity regimes [1].

Materials and methods

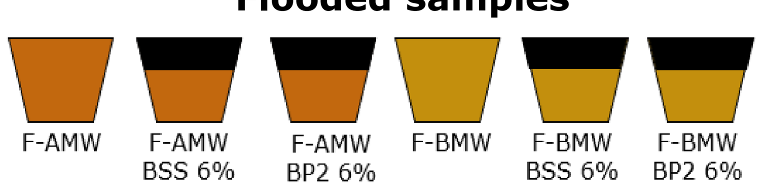
To determine the effect of soil humidity and organic amendments on metal mobility in acid mine wastes (AMW) and basic mining wastes (BMW), a re-evaluation has been done after one year of irrigation or flooding treatments on soil samples amended with biochar, MSW or both.

SOIL SAMPLES

Irrigated samples



Flooded samples



BP1 – Biochar from pruning type 1
BP2 – Biochar from pruning type 2
BSS – Biochar from sewage sludge

EXTRACTION METHODS

Metal (Cd, Cu, Mn, Pb and Zn) fractionation was assessed employing a single extraction (H_2O, $CaCl_2$, $NaNO_3$, EDTA, HCl) and a four-step sequential extraction procedure. Each extracting agent releases metals from a specific soil fraction, depending on the interaction with soil components, to represent their state of mobility.

Single extraction

Extracting agent	Released trace metals	Mobility
H_2O	Water soluble	High
$CaCl_2$	Exchangeable	High
$NaNO_3$	Exchangeable	High
HCl	Carbonate bound	Medium
EDTA	Carbonate and organically bound	Medium

Sequential extraction

Step	Extracting agent	Released trace metals	Mobility
1	CH_3COOH	Exchangeable and carbonate bound	High
2	$NH_2OH.HCl$ (pH 1.5, HNO_3)	Fe and Mn oxide bound	Medium
3	H_2O_2	Organically bound	Medium
4	$HClO_4$, HNO_3	Bound to the crystal matrix	Low

Results and discussion

EXTRACTION RESULTS (Zn)

Results from the single extractions (Figure 1) and sequential extraction (Figure 2) show the evolution in Zn mobility and fractionation. However, a general discussion is given for all metals.

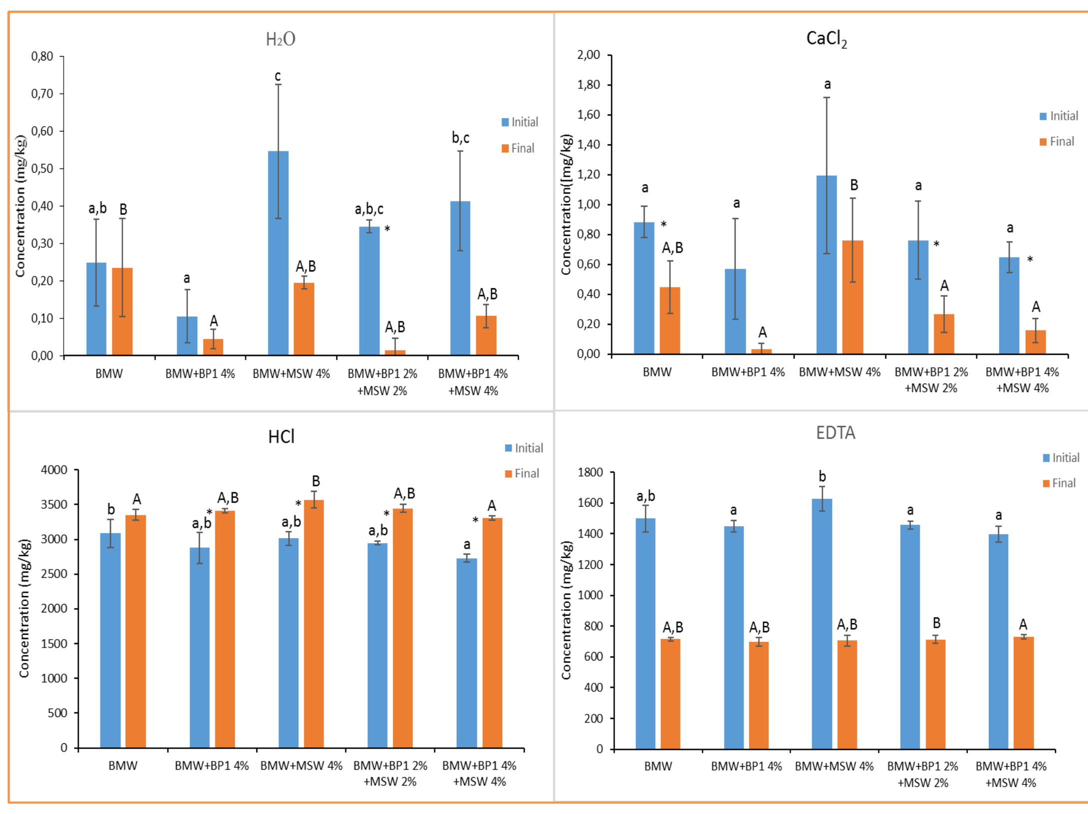


Figure 1: Concentration of Zn after extraction with H2O, CaCl2, NaNO3, HCl and EDTA . * refers to a significant difference between the initial and final stage ($p<0.05$); Lower case letters indicate a significant difference between initial treatments (ANOVA, Tukey, $p<0.05$); Capital letters indicate a significant difference between final treatments (ANOVA, Tukey, $p<0.05$); DL is detection limit (<0.025 mg kg-1).

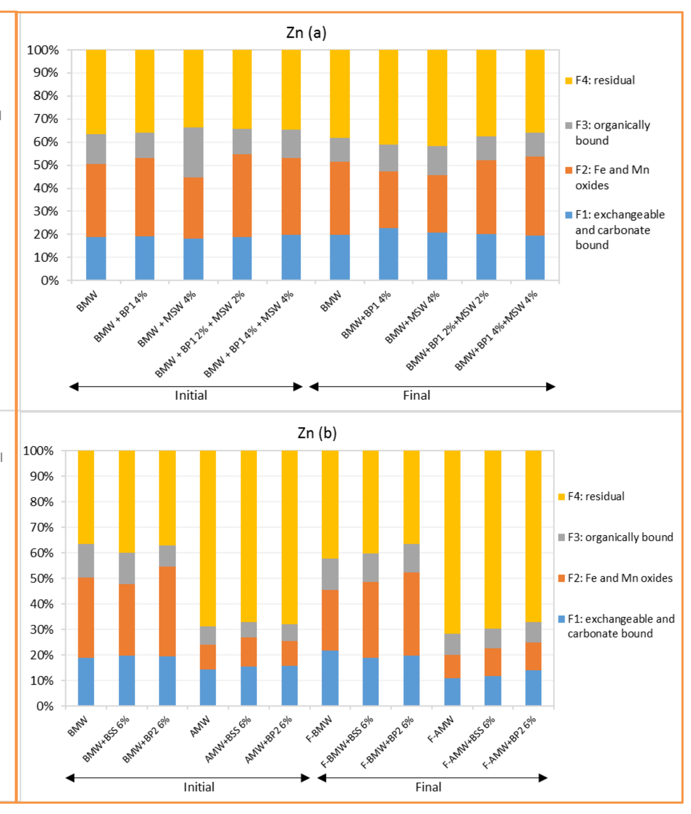


Figure 2: Distribution of Zn in the sequentially extracted mine tailing soil samples at the beginning (Initial) and after one year of incubation (Final). The irrigational treatment (a) consisted of basic mine wastes. The flooding treatment (b) consisted of both basic and acidic mining wastes

- The most mobile metals, extracted with **H_2O, $CaCl_2$ and $NaNO_3$** (Figure 1) were below 0.5 mg kg^{-1}, causing almost no release into the environment.
- **HCl and EDTA extracted** high concentrations due to changes in pH and decomposition of the organic matter under oxidising conditions [2] (Figure 1) .
- Metal fractionation in **the basic amended mine tailings** (Figure 2 a and b) showed a high correspondence of Zn, Cu and Pb with the residual fraction and labile Fe and Mn oxide fraction, characterising them, paradoxically, by a short-term mobility and long-term persistence. Mn was mostly bound to the iron and manganese oxides, regardless of the humidity treatment. Finally, Cd was principally bound to the most mobile fractions due to its high solubility [12].
- In **acidic amended mine tailings** (Figure 2 b), Zn, Cu and Pb were residually bound, with Cu and Zn showing even higher persistence than the neutral soils. Mn also became more residually bound due to a higher association with the crystalline matrix. Cd did not behave different than in the neutral mine tailings.
- The sequential extraction showed that **MSW** immobilised all metals, except Mn, in basic mine tailings after irrigation.

Conclusion

- **BMW+MSW 4%** was generally most beneficial treatment to immobilise metals in basic mine tailings under oxidising conditions, i.e. irrigation
- **The biochar amendments** were unsuccessful for metal immobilisation under changing redox conditions, i.e. periodically flooding.

RECOMMENDATIONS

Further research can be done to investigate if MSW would also be affective under changing redox conditions. In addition, the single and sequential extractions did not always show similar changes in the most mobile fractions. Therefore, a more elaborate extraction would be required to analyse changes in metal mobility, i.e. seven-steps sequential extraction and to confirm immobilisation by MSW.

[1] I. M. Parraga-Aguado, *The importance of edaphic niches and spontaneous vegetation for the phytomanagement of mine tailings under semiarid climate,* Cartagena: Universidad politechnica de Cartagena, 2015.
[2] C. Rao, A. Sahuquillo and J. Lopez Sanchez, "A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soils and Related Materials," *Water Air Soil Pollution*, pp. 291-333, 2008.
[3] H. M. Conesa, B. H. Robinson, R. Schulin and B. Nowack, "Metal extractability in acidic and neutral mine tailings from the Cartagena-La Union Mining District (SE Spain)," *Applied Geochemistry*, vol. 23, p. 1232–1240, 2008

Supervisors / Cosupervisors:

Dr. ir. Kristel Sniegowski
Dr. ing. Héctor Miguel Conesa Alcaraz
Dr. ing. Isabel María Párraga Aguado

Environmental Soil Science, Chemistry and Agricultural Technology
ETSIA-UPCT

ETSIA Cartagena

Universidad Politécnica de Cartagena

UHASSELT

KU LEUVEN