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Geochemical Characterization of Copper Tailings after Legume Revegetation

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ABSTRACT

Knowledge on the geochemistry of mine tailings is important in understanding the challenges in establishing vegetation cover on tailings dumps and mined out areas. In this study, the mineralogy and trace element composition of copper tailings were examined. Two legume species, *Calopogonium mucunoides* and *Centrosema molle*, were utilized to investigate the possible effects of these plants in the geochemical development of mine tailings into soil-like material. The initial mineralogical and chemical analysis of the tailings samples indicated poor conditions for plant growth—minimal levels of major nutrients and organic matter as well as elevated copper concentrations. Despite these conditions, the two legume species exhibited good growth rates. Both legumes have likewise significantly reduced heavy metal concentrations in the tailings, indicating the possibility of metal hyperaccumulation in the plant tissue. The mineral composition has been retained even after revegetation; nevertheless, breakdown of primary minerals and subsequent formation of clay minerals were detected. These results provide insights on the transformation of toxic materials into habitable substrates for sustained plant growth.

Keywords: Tailings characterization, mineralogy, heavy metals, revegetation

INTRODUCTION

Mine tailings have been identified as both a hazardous waste and an economically potential resource—a metal-rich material that can generate acid mine drainage and leachates but could also be an easily extractable low grade ore (Garcia-Meza and others 2004). As by-products of ore separation, tailings usually consist of fine-sand to silt-size particles of quartz, aluminosilicates, carbonates, oxides, and sulfides (Quispe and others 2013). This waste material naturally undergoes

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weathering due to exposure to air, water, ambient temperatures, and vegetation. Subsequently, the minerals present in mine tailings will determine the physical and geochemical stability of the material under different weathering conditions, and consequently, the nature and concentration of toxic, acid generating/neutralizing chemical species that may be released (Raudsepp 2011). For example, sulfidic minerals in tailings can weather within months or years and could lead to the formation of acid mine drainage (Robbed and Robison 1995). Tailings also frequently contain high concentrations of heavy metals, which contribute to plant growth deficiency in tailings dumps and mined out areas (Asensio and others 2013).

Revegetating these tailings dumps is usually considered to stabilize the substrate (Martinez-Ruiz and Fernandez-Santos 2005) therefore reducing the risk of polluting the surrounding environment. It can also improve soil quality with the increase in levels of organic matter and nutrients as well as in biological activity (Arienzo and others 2004). Consequently, selecting the appropriate plant species is another significant consideration to achieve successful revegetation. Indigenous plants are usually selected because these plants are often better able to grow and proliferate under the environmental extremes of the area, compared with other plants originating in other environments (Brown and Amacher 1997). Consideration should also be given to plants that have the ability to improve soil characteristics, such as leguminous species that can enhance organic matter and nutrient concentration (Parotta 1992, Domingo and David 2014). In addition, leguminous species exhibit rapid growth and high adaptation capacities in degraded lands (Maiti and Maiti 2014), making them viable candidates in rehabilitation programs.

The purpose of this paper is to present data on the mineralogy and trace element composition of copper tailings before and after a short-term revegetation using legumes. In addition, this study will also examine the potential effect of the selected plants in the geochemical tailings development. The results of this study would promote a better understanding on the challenges associated with revegetating mine tailings and the contribution of plants in its development.

METHODOLOGY

Site description and sampling

The sampling site is located in Philex Padcal Mine (Figure 1). It is situated 15 km southeast of Baguio City, Benguet Province, with an elevation of approximately 1500 m above sea level. The area experiences an average annual rainfall of 4500 mm, with maximum rainfall occurring on the months of May to October.

The primary mineral deposit in the area, called Sto. Tomas II deposit, is classified as a porphyry copper type. The mine started its underground block cave operations in 1958, and has since produced copper concentrates comprising copper, gold, and silver. It has three tailings storage facilities (TSFs), two of which have been decommissioned. Samples were collected at three random points on the upper 30 cm layer of TSF No. 3, and were homogenized prior to the pot experiment. Soil samples were also collected from a hill adjacent to the TSF.

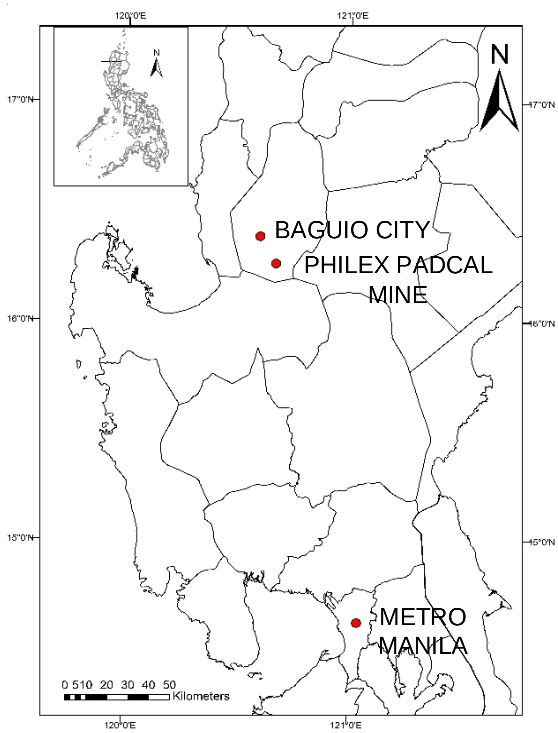

Figure 1. Location Map of Philex Padcal Mine, Benguet Province, Philippines.

Plant species

Leguminous species have been previously identified to naturally occur on the decommissioned tailings ponds of Philex Padcal Mine, particularly *Calopogonium mucunoides* Desv. (Rillorta and Lagunzad 2004). Seeds of this species, along with another legume, *Centrosema molle* Mart. ex Benth were obtained from the Bureau of Animal Industry, Department of Agriculture, Philippines. The seeds were germinated on garden soil for 10 d prior to the pot experiment.

Experimental design

The control group has two setups—the first consisted of 1 kg of pure mine tailings only to serve as baseline for the tailings parameters, while the other setup has 1 kg of soil and 10 legume seedlings. Meanwhile, the experimental setup is comprised of 1 kg of tailings and 10 legume seedlings. Different setups were prepared for each legume species and for different collection periods, all in triplicates. The pots were watered daily with approximately 200 mL of tap water and placed in a fenced 5 m x 5 m outdoor area in a randomized block design. Plant growth was monitored throughout the experiment. After four months, the plants were carefully removed before collecting the tailings material on each pot and dish. The samples were subjected to various analyses to examine the changes in the soil properties.

Geochemical Characterization

Mineralogy

Entire tailings materials were removed from the pots after the experiment. Samples were dried at room temperature to avoid possible phase transformation when heated inside an oven (Essene and Peacor 1995). Approximately 50 g of each sample was pulverized into fine powder with texture < 10 μm, using quartz mortar and pestle, to optimize the diffraction pattern from crystal lattice in the sample. Minerals present in the samples were scanned using an X-ray Diffractometer (Shimadzu Maxima XRD-7000) from the National Institute of Geological Sciences, University of the Philippines. The samples were further subjected to glycolation process to determine the type of clay present in the sample (i.e., non-expanding or expanding). Peak identification was performed by manual search using Materials Data, Inc. (MDI) Mineral and auto-search method with PDF-2, both of which are supplied by the International Centre for Diffraction Data.

Trace Metals

Each sample was filtered through a 63 μm sieve to obtain the clay fraction, and was oven dried at 60°C overnight. Digestion of samples was carried out in Teflon digestion tubes using concentrated HF and HNO_3, in a 2:1 volume ratio, with 1.5 mL mixed acid for every 0.01 g of the sample. River Sediment (GBW08301) Certified Reference Material was used, having the following certified values: As 56 μg g^{-1}, Ba 375 μg g^{-1}, Cd 2.45 μg g^{-1}, Co 16.5 μg g^{-1}, Cr 90 μg g^{-1}, Cu 53 μg g^{-1}, Mn 975 μg g^{-1}, Hg 0.22 μg g^{-1}, Pb 79 μg g^{-1}, Se 0.39 μg g^{-1}, Fe 3.94%, and indicative values for Be, Ni, V, Zn (Measurement Standards Laboratory of New Zealand 2009). The vessels were placed on a hot plate at 80°C overnight. Addition of HNO_3 was repeatedly done upon drying of the samples to ensure complete digestion. Digests were transferred into 15 mL centrifuge tubes before being filtered through a 0.45 ìm sieve onto 50 mL centrifuge tubes. Samples were diluted to 50 mL using ultrapure water, from which 5 mL aliquots were collected and used to scan for the following heavy metals: chromium, nickel, copper, zinc, arsenic, cadmium, and lead, using the Inductively Coupled Plasma – Mass Spectrophotometer (Agilent 7500CX) from the National Institute of Geological Sciences, University of the Philippines, Quezon City, Philippines.

RESULTS AND DISCUSSION

Tailings characterization

Analysis of the general characteristics of the tailings samples indicate neutral to slightly basic pH and poor soil nutrients (Table 1). Total nitrogen in the sample was minimal at 0.01%. Phosphorus was not detected initially in the samples, i.e., less than 0.1 mg kg^{-1}, whereas the potassium content of the sample was 78.0 mg kg^{-1}. The organic matter content of the tailings material was likewise very low at 0.2%. Meanwhile, the initial concentration of the heavy metals examined in the tailings were below the Effects Range Median sediment quality guidelines set by the National Oceanic and Atmospheric Administration and the Australian and New Zealand Environment and Conservation Council, with the exception of copper (Domingo and David 2014). These heavy metals are considered to be the most common trace elements of mine tailings (Allan 1995). With these conditions, the tailings present unsuitable conditions for plant development, lacking the essential nutrients while containing heavy metal concentrations that could hinder biological processes in the substrate (Liu and others 2012).

Plant growth

One of the primary considerations in rehabilitating degraded areas such as tailings dumps and mined out lands is the proper selection of plant species. Indigenous plants, or plants that naturally grow in the area, are recommended because they are already adapted to the environmental conditions and because they minimize the risk of introduced species being invasive to the native ones.

In the experiment, a discrepancy in the plant heights was observed between the soil and tailings setups for *C. molle* (Figure 2). On the other hand, no significant

Table 1. General physico-chemical characteristics of pure mine tailings used the experiment

Tailings control (t = 0 months)	
pH	7.63±0.13
Total Nitrogen %	0.01±0.00
Phosphorus (mg kg^{-1})	Not detected
Potassium (mg kg^{-1})	78.0±0.0
Organic Matter %	0.19±0.03
Chromium (ppm)	166.1±17.5
Nickel (ppm)	23.0±2.4
Copper (ppm)	3355±608
Zinc (ppm)	269±27
Arsenic (ppm)	2.87±0.40
Cadmium (ppm)	0.69±0.04
Lead (ppm)	15.5±0.6

Values indicate Mean ± SE; n = 3.

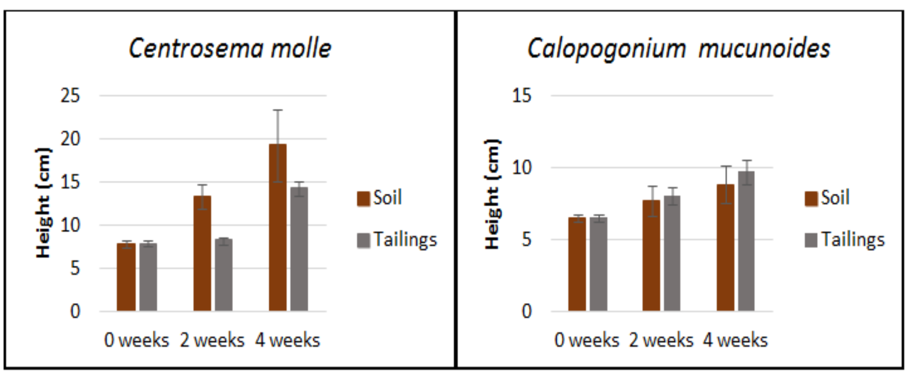

Figure 2. Plant heights in the soil and tailings setups; values indicate Mean ± SE.

difference exists among the *C. mucunoides* setups. This could be explained by the fact that *C. mucunoides* is naturally occurring in the tailings ponds (Rillorta and Lagunzad 2004). Hence, the plant has already adapted to the poor tailings status and will likely exhibit better growth compared with an introduced species such as *C. molle*. This also emphasizes the advantage of using native or indigenous plants in rehabilitation schemes.

Trace metals

One-way Analysis of Variance (ANOVA) was utilized to determine whether the heavy metals had been substantially reduced in legume-planted tailings after the experiment. Results of the ANOVA indicate significant differences in the concentrations of copper, arsenic, and cadmium ($P < 0.05$) (Domingo and David, 2014). In particular, the *C. molle* setup had undergone 14% As, 15% Cd, and 10% Cu reduction; while an even greater decrease in the heavy metals was observed in the *C. mucunoides* setup, having 52% As, 38% Cd, and 78% Cu removed from the tailings (Figure 3). The results suggest that the selected plants could hyperaccumulate the metals in their tissues, particularly *C. mucunoides*. The reduction of these heavy metals will promote the proliferation of nitrogen-fixing bacteria, nitrogen mineralization, and decomposition of organic matter (Liu and others 2012), and thus could help in the soil development of mine tailings.

Mineralogy

The results of the X-Ray Diffraction (XRD) Analysis for the tailings indicate that the material is composed of quartz, plagioclase-feldspars (albite, anorthite), amphiboles (actinolite), muscovite, and clay minerals (Figure 4a). After the experiment, the legume-planted tailings exhibited similar mineralogical composition, with anorthoclase and tremolite detected in addition to the previous minerals (Figures 4b and 4c). The detected minerals are consistent with the dioritic/andesitic parent rock in the Philex area, and belong to the most abundant gangue silicate and oxide minerals in porphyry copper deposits, as well as biotite, magnetite, anhydrite, and epidote (Berger and others 2008). Furthermore, these minerals are also included in the most common alteration minerals in silicate-rich rocks, which may indicate that a percentage of these minerals are products of weathering of the original material. Other minerals associated with the detected minerals, e.g., sulfides and magnetite, are most likely present in the tailings but in amounts below the detection limit of the XRD apparatus. Moreover, the peaks of the more crystalline minerals (i.e., quartz, plagioclase) in the sample could have masked the peaks of the other minerals. Still, evidence of smectite clay minerals was observed in the samples that have been planted with legumes, indicating hastened breakdown of primary minerals due to the plants. A longer experimental period is recommended to observe significant effects in the mineralogy of mine tailings. Experimental work on the clay type and accurate quantification of the clay content would further help in understanding the contribution of these plants in the improvement of tailings mineralogy.

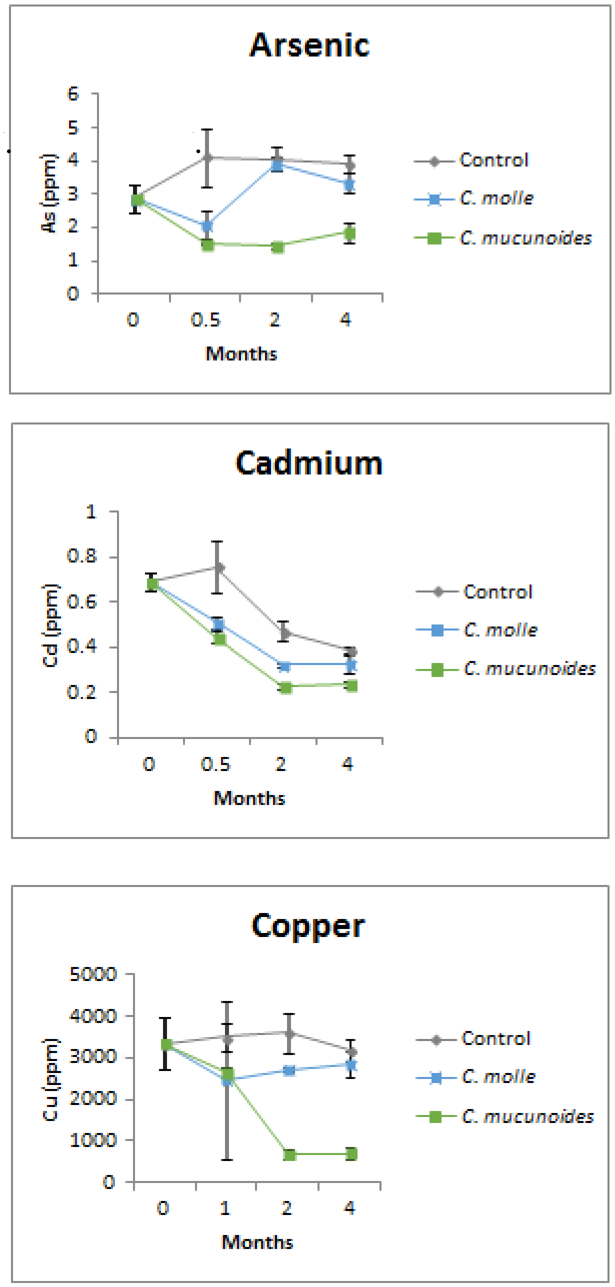

Figure 3. Reduction of As, Cd, and Cu concentrations in mine tailings before and after the experiment. Values indicate Mean ± SE; n = 3; in parts per million.

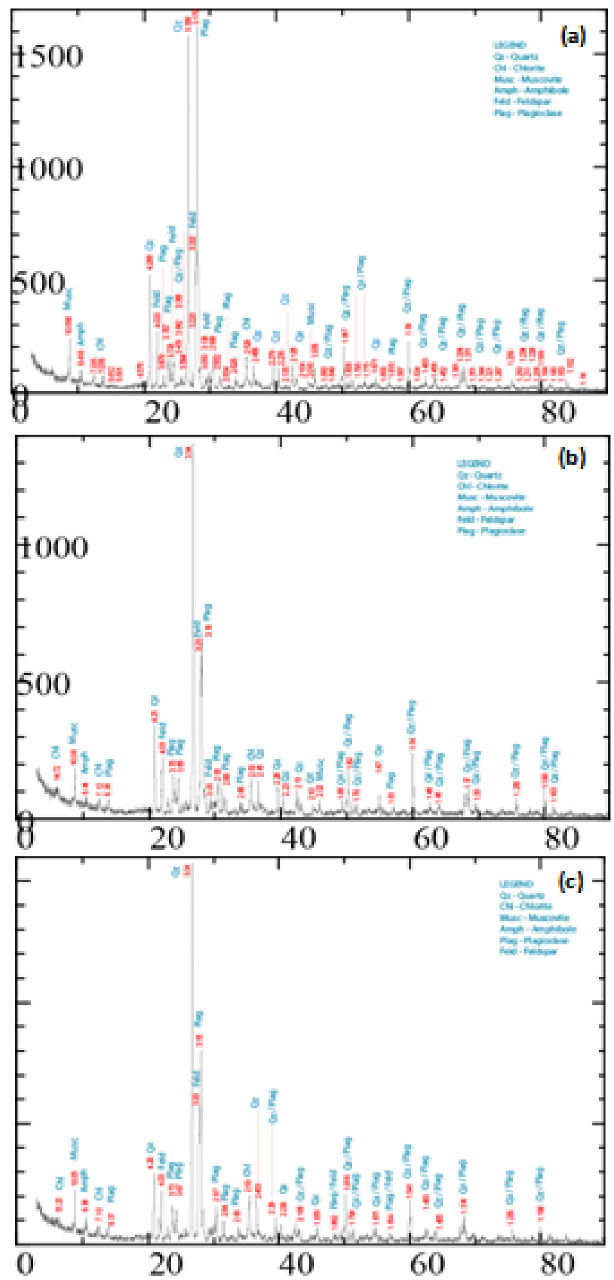

Figure 4. Mineralogical composition of (a) copper-gold tailings; (b) *C. molle*-planted tailings; (c) *C. mucunoides*-planted tailings.

CONCLUSIONS AND RECOMMENDATIONS

The mineralogical and chemical analysis of the mine tailings showed minimal levels of major plant nutrients and organic matter, and high copper concentrations. Between the two plants used in the study, the legume species *C. mucunoides* has exhibited better growth in tailings than *C. molle*. The presence of these legumes significantly reduced heavy metal concentrations in the tailings, indicating the possibility of metal hyperaccumulation. Lastly, evidence of clay mineral formation indicates the hastened breakdown of the material into more soil-like substrates that are dominated by clays and organic matter.

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