Strategic reclamation of post-tin mining areas based on soil mineralogy, heavy metal and particle size constituent of refused materials

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Abstract

Characteristics of refused materials are prerequisite information required to determine the strategic reclamation of extreme land degradation in post-tin mining areas. The objective of the study was to evaluate mineralogical, chemical, and physical properties and heavy metals of spoil and tailing as the basis for reclamation measures. Seven representative soil profiles were made and sampled to a depth of 130 cm for various soil analyses. Results showed that tin mining has drastically altered the soil texture from sandy clay loam under native conditions to loamy sand and sand under post-tin mining. Mineralogical constituents of refused materials were mainly mineral resistant to chemical weathering, consisting of predominant quartz with small amounts of tourmaline, opaque, zircon and garnet. Total X-ray fluoresce elemental analysis showed extreme high SiO2 content (92-96%) associated mainly with quartz mineral, and extremely low oxides of Ca, Mg, P, K and S (< 0.2% altogether). This suggests all nutrients are severe problems for crops. Type of total heavy metals showed the Cr2O3 was high in sandy tailing (204 - 286 mg kg-1), while the SnO was low (0 -153 mg kg-1) and they were preserved in the structure of host minerals, thereby the health risk is negligible. Based on many serious constraints of soils, the strategic reclamation to recover soil productivity and ecological function was the building up soil organic matter, establishing "pot planting point" technique, complete fertilizer application, and selection of crops with an ability to fix N nutrient from the atmosphere, and adaptive to low soil nutrients.

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KEYWORDS: Post-tin mining, soil characteristics, heavy metals, tailing, spoil, strategic reclamation

1 INTRODUCTION

Mining left the legacy of environmental problems attributed by disposal of refused materials. Global land use for mining between 1976 and 2000 is cumulatively about 3,700,000 ha or about 0.2% of earth's land surface (Barney, 1980). Mines produce large amounts of refused-materials because the ore constituent of the total volume of the mined materials occurs only in a small fraction (Duhka and Adriano, 1997). For tin mining, the separation of tin ores, the heavy sand fraction (density > 4 g cm^{-3}), from the clay, silt and light sand fractions leads to the dumping of large amounts of spoils and tailings, and their cumulative amounts increase with time. The disposal of tailings is a major environmental issue that has become more serious with the increased exploration for metals and the exploitation of lower grade mineral deposits (Ozkan and Ipekoglu, 2002).

Southeast Asian countries (Indonesia, Malaysia, Thailand and Myanmar) produced 9.6 million tonnes of tin, equivalent to 54% of the world's tin production since 1800 (Schwartz et al., 1995). In 2017, Indonesia is the second larger world producer (50,000 metric tonnes) of tin after China (100,000 metric tonnes) with total world production of 290,000 metric tonnes (USGS, 2018). Further, tin world reserve is 4,800,000 metric tonnes in which China and Indonesian reserves are 1,100,000 and 800,000 metric tons, respectively (USGS, 2018). The major locations of tin producer in Indonesia are Bangka, Belitung and Singkep islands. Open pit mining of tin is destructive due to the complete removal of vegetation and topsoil. In addition, tin mining processes involving the dispersion and washing to separate heavy sand fraction of ores from refused materials could result huge piles of sandy tailing. The large idle bare land (abandoned tailings or waste piles) is massively occurred. The high economic return from tin mining activities are not reconciled with the existing environmental management.

In this study, tailing was referred to dumped materials left over after the process of separating the valuable heavy sand fraction ores from the uneconomic light sand fraction. Likewise, spoil was referred to an accumulation of displaced earthy material or other waste material removed during mining or excavation. Refused materials (e.g. spoils, tailings and slime) are mine's byproducts accumulated from the excavation, washing, concentration or treatment of ground ores to extract valuable ores. The Bangka island has been exploited for tin since 1711 (Ko, 1986), resulting a widespread of huge spoil and tailing disposal as the extreme threat to the environment. Hence, characterization of spoil and tailings in terms of chemical, physical, mineralogical properties and heavy metal contents should be done to obtain reliable information as a basis for reclamation measures.

Generally, mining is considered to be one of the most significant sources of heavy metal contamination (Acosta et al., 2011; Dudka and Adriano, 1997; Fryer et al., 2006). Ores and mineral extraction have inflicted serious environmental damage, especially in the heavy metal pollution (Acosta et al., 2011; Komnitsas and Modis, 2006; Zhou et al., 2007). Metals of major interest in bioavailability studies, as listed by the U.S. Environmental Protection Agency (EPA), are Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb (McKinney and Rogers, 1992). Heavy metals such as Pb, Zn, Cd, Hg and Cr generally refer to metals and metalloids having densities greater than 5 g cm^{-3} (Oves et al., 2012). Li et al., (2014) reviewed the soil heavy metal pollution from mines in China and concluded that the mean concentrations of As, Cd, Cr, Cu, Ni, Pb, Zn, and Hg in soils are higher (varying from 0.4 to 36.5 times greater, depended on a heavy metal type) than the Grade II environmental quality standard for soils in China. The geochemical flux explained the lithological origin of potential toxic elements (As, Cd, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Sc, Th, V) (Pinto et al., 2017)

Mineralogical composition plays a crucial role in understanding native nutrient sources for crops and heavy metals both short and long-term period of time. However, mineralogical composition of refused materials has been ignored in post-tin mining areas, and more attention is given to chemical properties and heavy metals.

Hence, we investigated mineral composition of refused materials deriving from different parent materials in post-tin mining areas and relating the minerals to soil chemistry, nutrients and heavy metals. The objective of the study was to evaluate mineralogical constituents, particle sizes, chemical and physical properties and heavy metal contents of refused materials in post-tin mining areas as the strategic basis for reclamation of soil productivity and ecological function.

2 MATERIALS AND METHODS

Study site and field samplings

The study areas locate in Bangka Island, Kepulauan Bangka Belitung province, Indonesia between X 626183 -Y 9757090 and X 632834 -Y 9752946 UTM grid, Zone 48 M with the elevation of 27 to 60 m above sea level. The areas were selected based on their lithological type that represents most of the post-tin mining areas in Kepulauan Bangka Belitung province. Lithologically, Bangka Island occurred on granite and sandstone parent rocks. The granitoid plutons of the Indonesian Tin Islands was Triassic age (193-251 Ma) (Aleva,1985; Ko, 1986). It was expected that the similarity in lithology of the areas would produce a similar property of tailings and spoils. The process of tin mining and deposition of refused material were mainly gravitational separation without any chemical treatment. The companies having tin mining land concession extracted the tin-host ores by dry-excavating of soils and the underlain deposit layers, mostly down 5 to 50 m. The companies used conventional bulldozers, loaders and haulers for the excavation of deposit ores. The separation of non-tin layer sediment such as white clay was directly dumped as a spoil, during the excavation. Hydraulic mining by spraying the ore deposits associated soils to form a slurry and pumped to the wet separation (concentrator) facility. The slurry was then passed through sequences of cyclones and separator in which clays, silts, and some very fine sands (collectively referred to as slimes) were separated gravitationally from the sand fractions. The heavy mineral sand of ores (particle density > 4.0 g/cm^3) was further separated from the light sand fraction by cyclones water. The refused fractions consisting of light sand were dumped as tailings.

The characteristics of spoils (mostly a mixture of native soil, light sand and white clay) and sandy tailing piles of post-tin mining were assessed and evaluated as a basis for reclamation measures. Tailings and spoils deriving from sandstone and have been mined from 2000 to 2015 were represented by two sandy tailing profiles (TBB1 and TBB2), and a spoil profile (TBB3). The topsoil of TBB3 profile consisted of initial native soil with some tailing (0-30 cm), while the underlying layers consisted of a mixture of white clay and sandy tailing. For tailings resulting from granite materials and mining from 1960 to 1998 were represented by TBB6 and TBB7 profiles. The native soil profiles adjacent to post-tin mining areas were included for each type of parent materials (TBB4 for sandstone, and TBB5 for granite materials) as a comparison to spoils and tailings. We excavated a soil profile with the dimensions of $100 \times 200 \times 120–130$ cm (width $\times$ length $\times$ depth) for morphological property observation and soil sampling. We collected a composite soil sample for each soil layer from all sides of the profile; the sample was thoroughly mixed prior to subsampling ˜1 kg for mineralogy, chemical and heavy metal analyses.

2.2 Laboratory analyses

The potential of soil nutrient sources in spoils and tailings was assessed by analyzing the primary mineralogical compositions of 50-250 µm sized sand fraction. Mineral types were identified using a polarizing microscope (Carl Zeiss Microscopy, Germany). The number of each mineral type was counted from 300 grains by line count traverses.

X-ray diffraction (XRD) analysis for tin ores and white clay sediment was carried out using a Rigaku (SmartLab, Japan). Tin ores and white clay were analyzed to determine host-mineral of Sn and that white clay for type of clay minerals. The refused white clay layer during tin mining could be potential to be used as ameliorant for sandy tailing. The tin ores were collected from re-mined tailing by local miners nearby the study site. The tin ores were dried and finely ground as powder to pass through a 50 µm sieve and kept for XRD analysis. For white clay sediment, it was collected from the spoil profile, dried and finely ground as powder to pass through a 50 µm sieve. The powder specimen was mounted on glass slides and run on X-ray diffractometer, using Cu-alpha radiation target, operated at 40 kV and 25 mA. The powder specimens were scanned from 3 to 45º 2ϑ at 1°/min. XRD data were collected and stored by IBM compatible PC.

The scanning electron microscope (SEM) analysis was performed for finely ground tin ores (< 50 μm) using an EVO MA10 (Carl Zeiss Microscopy, Cambridge, England) to observe their morphological features and resistance to weathering processes. The specimens were oven dried prior to gluing into an aluminum stub and then coated with carbon and gold/palladium in a vacuum evaporator. The specimens were viewed at 11.0 and 15.0 kV, using a secondary electron detector. The chemical surface compositions of specimens were analyzed using energy dispersive X-ray (EDX).

The particle sizes of soil were determined by the pipette method (Soil Survey Staff, 1992). The sand fraction was separated from the clay and silt fractions by wet sieving. The silt- and clay-sized fractions were measured by sedimentation according to Stokes law. The pH and electrical conductivity (EC) were measured in water with a 1:5 soil:solution ratio using an Orion pH meter and a conductivity meter, respectively. The total organic C content was measured according to Walkley and Black wet oxidation method (Soil Survey Staff, 1992). Total N was determined by the Kjeldhal method (Bremner and Mulvaney, 1982). Soil cation exchange capacity (CEC) was determined using a leaching column. The soil of 2 g was transferred into a leaching column followed by leaching with 50 ml of 1 M NH_4OAc at pH 7.0 for an hour, then the cations were measured in the supernatant (Soil Survey Staff, 1992) using an atomic absorption spectrometer (AAS). The CEC was determined in 1 M NH_4OAc (buffered at pH 7.0) after extraction of NH_4^+ as a measure of CEC by 10% NaCl. The Bray 1 method was used to determine soil available P, and that exchangeable Al was extracted by 1 M KCl as described by Van Reeuwijk (1993).

Total elemental analysis of native soil, spoil and tailing was determined using X-ray fluorescence (XRF). Soil, spoil and tailings were finely ground using a ball mill/ pulverizer to pass through a 100-200 mesh sieve as powder. Measurements of major and trace elements were carried out on pressed pellets, prepared following the procedure of Norrish and Chappell (1977). The sample powder was mixed with carboxyl methyl cellulose (CMC) as a binder by lightly ground. Samples were pressed into pellets with boric acid backing in a ring stainless steel, and oven dried at 55°C for about half hour. Elemental composition was determined using X-Ray Fluorescence (Thermo Scientific ARL 9900 Series, 2011 Germany) with a Be tube operating at 60 kV, 40 mA for Ba,Sn, Cd, Ag, Rb,Mo, Zr, Y, Pb, As, Se, Hg, Zr and Y; at 40 kV, 60 mA for Ni, Cu, Co, Si, Al, Fe, Mn, V, Cr, Ti, Ca, K; and at 30 kV, 80 mA for Mg and Na using scintillation counter. The available heavy metals were extracted by 0.05 M $CaCl_2$. The use of $CaCl_2$ in place of 1 M $MgCl_2$ as used by Tessier et al. (1979) was due to native conditions of tailing contain higher Ca than Mg, hence the use of $CaCl_2$ extractant solution is more closely represent the native conditions.

3 RESULTS

3.1 Morphological features of tailing profiles

Mining activities drastically altered soil morphological features (Figures S1 and S2). In tailing derived from sandstone materials, tin mining activities altered the soil morphological features from sandy clay loam texture, dark brown topsoil and yellowish brown subsoil in native soil (TBB4 profile) to sandy texture with stratification of light grey and yellowish grey (TBB1) or of yellowish grey and reddish grey (TBB2) colour throughout profiles (Figure S1). Further, a spoil profile with a mixture of native topsoil and sandy tailing showed a mixture of brown and greyish colours in the topsoil (TBB3 profile), which was underlain by greyish sand and whitish kaolin colours. The presence of yellowish and reddish colours in sandy tailing profiles indicated the initiation of soil formation in post-tin mining areas.

For post-tin mining soils developed from granite parent materials, morphological properties drastically altered from deep solum (> 140 cm), dark greyish brown topsoil and yellowish brown subsoil with sandy clay loam texture (TBB5; Figure S2) in the native soil to loamy sand and grey colour in post-tin mining. These native soil properties disappeared after mining was related to sluice and washing during the separation of heavy tin ore from light sand fractions. The profile of a sandy tailing (TBB6), which has been reclaimed for 26 years using *Acasia mangeum* started a weak soil development as indicated by yellowish colour (iron mobilization and precipitation), the formation of fine soil granular structure, and the growth of many fine roots downward to 60 cm deep (Figure S2). Unfortunately, the formation of fine soil granular structure was not shown by TBB7 profile, a counterpart of TBB6 and just 6 m away. The absence of fine soil granular structure in the TBB7 profile was due to re-mined activities by local traditional miners and abandoned as bare land by 2008 (8 years old of post tin mining), leading to reset back the new start of soil development. The interlayer variations with different colours within a profile indicated the initial accumulation of iron with yellowish grey colour (probably goethite) and it's leaching down the profile.

3.2 Mineralogical composition of tailings

Mineralogical composition of soils at post- tin mining areas was assessed to get an idea of potential inherent nutrient source and heavy metals in weathereable minerals (host-nutrients). Tailings and native soils developing from sandstone contained 70-95% and 81-84% quartz, respectively (Table 1). The corresponding values for tailings and native soils developed from granite were lower, namely 48-73% and 77-80%, respectively. In native soils (TBB4 and TBB5 profiles), the turbid quartz was higher than transparent quarts, irrespective of parent material types, indicating transportation was a dominant process during soil formation.

In contrast to quartz mineral, the tourmaline mineral was considerably higher in tailing deriving from granite (12-22%) than tailing from sandstone (2-10%). The corresponding values in native soil profiles were 5-7% and 2-3%, respectively. Both quartz and tourmaline minerals are well known as mineral resistant to weathering. Opaque mineral was also higher in tailing derived from granite (mostly 9-15%) than tailing from sandstone (1-7%). Further, the tailing profiles deriving from granite (TBB6 and TBB7) contained a small number of orthoclase and sanidine, which were absent in tailing profiles from sandstone (TBB1 and TBB2). Other minerals in small amount were zircon, garnet, epidote and rutile/anatase in all tailings and native soils.

3.3 Soil chemical properties of post-tin mining areas

3.3.1 Total major elemental oxides

Total major and minor elemental compositions (expressed as elemental oxides) as measured by XRF of selected layers of tailing, spoil and native soil profiles are given in Tables 2 and 3. The composition of major elemental oxides of tailing showed much higher SiO_2 content (86-96%) than the native soils (68-76%). The exception for the topsoil of TBB3 spoil profile contained much less SiO_2 (43%) associated with some native topsoil containing 15% clay. In tailings, the oxides of potential major nutrients for crops such as Ca, Mg, K, P, S were very low in each soil layer (< 0.2% altogether), indicating these nutrients are major problems in post-tin mining reclamation.

3.3.2 Total and available heavy metals

The content of total heavy metals showed the presence of Cr_2O_3 in all samples (native soils, tailing and spoil), and SnO in all native soils and some layers of tailing profiles (Table 3). The total concentration of Cr_2O_3 toxic heavy metal was considerably higher in tailing (sand fraction) (204-286 mg kg^{-1}) than the native soils (149-190 mg kg^{-1}), indicating that Cr was occluded in the host-mineral structure. On the other hand, the SnO heavy metal was much higher in the native soil and spoil than in tailings. In addition, the SnO was higher in a native soil deriving from sandstone than the soil from granite.

Total concentrations of other heavy metals such as Pb, Cd, Ni and Hg were not detected in native soils and tailings, except for the TBB3 spoil profile, where Pb was present in the topsoil. The non-heavy metal (trace element) present in high amount was Cl and its concentration was much higher in native soils (1270-1380 mg kg^{-1}) than tailing (370-970 mg kg^{-1}).

The available heavy metals as measured by 0.05 M $CaCl_2$showed the presence of Pb, Cr and Hg in all native soils and tailings, and few samples contained As (Table 4) but their concentration was very low. Although total concentrations of Pb and Hg were not detected in native soils and tailings, they present in small amounts in available forms. The available Pb of soils deriving from sandstone was similar in native and tailing conditions (< 0.30 mg kg^{-1}), which in turn was lower than Pb in native soils and tailings deriving from granite materials (< 1.20 mg kg^{-1}). The higher available Pb in tailings than native soil deriving from granite, indicating that the Pb was inherited from host rocks. This was supported by the total PbO in the granitic rocks was 48 mg kg^{-1} (Table 3).

For Sn available form, it was not detected in both native soils and tailings (Table 4), although its total concentration as measured by XRF was high in native soils (203-418 mg kg^{-1}) (Table 3). This further indicates that the Sn-bearing mineral (cassiterite) was resistant to chemical weathering and Sn heavy metal should not raise concern for health risk in the post- tin mining areas. Other heavy metals such as Cd, Ni, and Co were not detected in both total and available forms of native soils and tailings.

3.3.3 Particle size, organic matter and nutrient availability of post-tin mining areas

Particle size in the fine earth (< 2 mm) of post-tin mining areas was dominated by sand fraction that sharply increased from 57-69% in native soils to 82-96 % in soil tailing (mostly > 90 %) (Table 5). On the other hand, the clay fraction sharply decreased from 27-38% in native soils to less than 14% in tailings and spoil (Table 5). In other words, the soil texture changed from sandy clay loam to sand. Further, organic matter (C and N) and potential P_2O_5 and K_2O were very low status in tailings and spoil, and their content was lower than native soils.

In all cases, the layers of tailing profiles have higher pH (varying from 5.2 to 6.3) than the corresponding layer of native soil profiles (varying from 4.7 to 5.2) deriving from a similar parent material (Table 5). The higher pH of soil tailings than the native soils was associated with the lower exchangeable Al in the former owing to sandy texture, leading to very low ability to retain Al. In native soils, the high clay fraction corresponded to the high exchangeable Al and low pH (Table 6). The available P_2O_5 in tailing was very low (< 4 mg kg^{-1}P_2O_5 according to Bray 1), suggesting the crops would experience a serious P deficiency.

Although potential K_2O as extracted by 25% HCl was very low status in all tailings, there is a good trend for its higher concentration in soils derived from granite parent materials compared to tailings derived from sandstone. This is consistent with the high total K_2O in granite rocks (5.2%) (Table 2). K-bearing minerals were not observed in soil tailings deriving from sandstone.

All exchangeable cations, Ca, Mg, K and Na were very low with the sum of < 0.8 cmol$_c$ kg^{-1} for each layer of soil tailing, and the order of decreasing content was Ca > Mg > Na > K (Table 6). The exchangeable cations in tailings were only slightly lower compared to a corresponding layer of native soil profiles. This indicates exchangeable cations are serious limiting factors for crops in both native soils and tailings. Cation exchange capacity (CEC) drastically decreased from 3.8-6.8 cmol$_c$ kg^{-1} in native soil profiles to 1.0 - 2.3 cmol$_c$ kg^{-1}(mostly < 1.5 cmol$_c$ kg^{-1}) in tailing profiles.

3.4 Characteristics of tin ores and white clay spoil

Properties of tin-host minerals and white clay were assessed using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analyses. The large ore grain of tin (Figure 1a) showed a fresh, clean and smooth surface with elongated grain shape and euhedral crystal edges. The EDX surface chemical composition analysis showed the presence of triple peaks of Sn in the order of decreasing intensity at 3.45, 3.70 and 3.90 KeV, and another Sn peak at 0.5 KeV, indicating the Sn-bearing grain is cassiterite ($Sn0_2$) mineral (Figure 1c). Further, the XRD analysis of the ore grains indicated the presence of three very sharp and slender peaks in the order of decreasing intensity at 3.33, 2.63, and 2.36 Å, confirming the very well crystal structure consisting of cassiterite mineral (Figure 1d). Therefore, the tin ores in this study consisted of mainly cassiterite mineral.

In Bangka, some of the spoils showed greyish white colour with fine texture and sticky consistency, while information of its mineral composition was not available. Hence, it is necessary to examine the mineral constituent of whitish clay and its relation to management as crop media with respect to reclamation measures. The XRD analysis showed the presence of prominent sharp and slender peaks at 7.15 and 3.57 Å, accompanied by less peak intensity at 4.47, 2.56, 2.49, and 2.34Å (Figure 2), indicating the kaolinite mineral. There is also evidence for the kaolinite impurity due to the presence of goethite in the mineral, which is shown by XRD peaks at 4.16 and 2.19 Å. The SEM showed the micro-pores occurring within kaolinite layer arrangement, which are able to store water (data not shown).

DISCUSSION

4.1 Weatherable minerals of post-tin mining areas

The number of weatherable minerals (including feldspar and ferromagnesian minerals) as native nutrient sources in post-tin mining areas is practically depleted, while the resistant minerals (eg. quartz, opaque and zircon) containing no essential crops are predominant. The number of quartz mineral is higher in soil tailings developing from sandstone (70-95%) than tailing from granite parent materials (48-73% quartz) (Table 1). The higher quartz mineral in sandstone materials is related to the nature of fluvial sediment containing higher sand fraction with high quartz composition (Ko, 1986). Other resistant minerals that bear no plant nutrients but occur in considerable amounts are opaque and zircon, further exacerbate nutrient problems. Given that tailing deriving from granite contains some K-bear minerals (orthoclase and sanidine), the K nutrient is slightly better compared to tailing derived from sandstone materials.

In the Dachang district, western China, the tin-cassiterite bearing mineral was formed in a granite-related magmatic-hydrothermal and the rock-forming minerals consisted of quartz (30-32%), K-feldspar (35-40%), plagioclase (20-25 %), biotite (3-6 %) and muscovite (1-2%) (Guo et al., 2018). In native soils (TBB4 and TBB5 profiles) of the present study, the turbid quartz was higher than transparent quarts, irrespective of parent material types, indicating transportation was a dominant process during soil formation. The higher transparent quartz than turbid quartz minerals in tailings suggests that the light sand fractions experienced less transportation. The exception was tailing TBB7 profile deriving from granite has higher turbid quartz than transparent quartz due to several times of re-mining (reworking practices at a tailing pile could mimic transportation processes).

4.2 Soil texture and chemical properties

Tin mining activities have drastically altered soil texture, resulting negative impact attributed mainly by the presence of high volumes of tailings (Nouri et al., 2011). In the present study, sand fraction increased from 57-69% in native soils to 82-96 % in soil tailing (mostly $>$ 90 %) implying that the ability of soil tailing to retain water was very low, leading to extreme limiting factors for crop growth. Similar results reported by Ashraf et al (2010) in post-tin mining in Malaysia containing both gravel and sand as much as 95%. In addition, the high sand fraction of tailing causes high soil temperature during the day time, rapid drainage (high pores), intensive nutrient leaching, low cation exchange capacity to retain nutrients, leading to water stress and insufficient nutrients for crops.

Total SiO_2 content of tailings is very high (92-96%) and agrees well to the predominance of quartz mineral constituent (70-95 %), implying that silica derived mainly from quartz minerals, thereby native nutrient sources for crops are negligible (Table 1). Predominant quartz accompanied by some opaque, zircon and tourmaline minerals, which are mineral resistant to chemical weathering and bear trace if any nutrient for crops, clearly indicated that native nutrient sources were negligible. The low nutrient content is supported by XRF analysis showing extremely low concentrations of total elemental oxides of Ca, Mg, K, P, and S ($<$ 0.2% altogether) in each layer of tailing profiles (Table 2). The implication was many nutrients (if not all) became serious limiting factors for crop growth. Hence for reclamation purposes, the high rate and many types of input (fertilizers) were required to allow plant growth in the sandy tailings.

The exception is the TBB3 spoil profile contains lower SiO_2 in the topsoil (43%) but is high in the subsoil (93%) owing to the presence of significant amounts of silt and clay fractions (their summation was 19%) deriving from native topsoil and mixed with tailing during mining processes. The mixture of tailing and native topsoil contains high oxides of Al_2O_3 (36 %) and Fe_2O_3 (5 %) (Table 2). This observation provides an advantage in tailing management by adding some native topsoil to promote water and nutrient retentions.

The comparison of tailings deriving from different parent materials showed tailing from granite contained higher total K_2O (0.2%) than from sandstone ($<$ 0.05%). The high K_2O in tailing derived from granite was related to the presence of K-bearing minerals (orthoclase, biotite and sanidine) in the granite, while K-bearing minerals were absent in sandstone parent materials. This statement was supported by total elemental analysis of granite rocks that showed the high K_2O content (5.2%, Table 2). This observation is valuable for tailing deriving from granite material and might have more inherent K nutrient source in a long-term period of time.

The heavy metals in tailing were mainly Cr_2O_3 and its concentration is lower in native soils than tailing, leading to point out that Cr element was occluded in mineral host structures, i.e., garnet (uvarovite species, $Ca_3Cr_2(SiO_4)_3$) (Table 1). In addition, epidote mineral (Hancockite, $CaPb_2Al_2Fe(SiO_4)_3(OH)$) may host Pb. The dominance of Cr heavy metal may achieve 4695 mg kg^{-1} in serpentinite rocks, corresponding to 533-633 mg kg^{-1} in soil develop on it (Anda, 2012). According to Hudson-Edwards (2003) the information of the mineralogy of heavy metals bearing phases is important in (i) understanding their stability, solubility, mobility, bioavailability and toxicity; (ii) modelling their future behaviour; and (iii) developing remediation strategies. Hence the Cr and Pb heavy metals in this study may have been preserved in mineral structure of garnet and epidote, respectively and led to minimum solubility in soils, corresponding to minimal health risk.

For the Sn heavy metal, it is anticipated to have a high concentration in post-tin mining areas. In fact, Sn concentration is low and only occurs in a few layers of tailings. The low concentration could be explained by Sn-bearing mineral (cassiterite) has been mined as a target tin ore but was not completely removed from the sand fraction during the separation of tin ores. The interesting finding was the much higher concentration of SnO in the topsoil than the subsoil of native soils (TBB4 and TBB5 profiles, Table 3). This trend indicated that Sn host-mineral (cassiterite) was resistant to chemical weathering and immobile in soils, which according to Smeck et al. (1994), the highest concentration of mineral resistant to weathering at the soil surface was due to maximal losses of components susceptible to weathering. The resistance of cassiterite mineral against chemical weathering was evaluated using a scanning electron microscope (SEM), and the result showed grain morphological features with fresh, clean, and smooth surfaces (Figure 1a). These morphological mineral features are indicators of mineral resistant to chemical weathering in the environment (Anda et al., 2009). According to Aleva (1985) cassiterite barely experiences weathering and the solution of cassiterite in surface and soil waters is slight. Cassiterite ($Sn0_2$), the main tin mineral of ores, is both heavy and chemically resistant against weathering, leading to the formation of large deposits or residual concentrations (Sainsbury, 1969; Gama-Castro et al., 2000). The minimal Sn^{2+} translocation and uptake by plants associated with low solubility in soils were also reported by Nakamaru and Uchida (2008) in tin Japanese agricultural soils.

In Chile, Ramirez et al. (2005) reported that Cd, Fe, Mn, Ni, and Pb were mostly occluded in the mineral structure, corresponding to their minimal availability in soils. According to Tessier et al. (1979) the occluded heavy metals were mainly associated with crystal structure of primary and secondary minerals. Therefore, the health risk of Cr, Pb and Sn heavy metals should not be of major concern in the post-tin mining areas, especially in the short-term period. To support this statement the available heavy metals were measured using $CaCl_2$ and the results showed that the heavy concentration is very low in all tailings and native soils, namely (mg kg^{-1}) < 0.5 for Pb, < 0.2 for Cr and not detected for Sn (Table 4).

The elemental composition of tailing also showed the high Cl content in sandy tailing (370-970 mg kg^{-1}) may suggest that Cl element was occluded in the primary mineral structure, probably in quartz or pyroxene mineral. In addition, Cl content was much higher in native soil profiles (1270-1380 mg kg^{-1}) than tailing (370-970 mg kg^{-1}) which is associated with the high clay content to hold Cl, releasing from host-minerals during soil formation processes.

The drastic decrease in soil cation exchange capacity (CEC) less than 2 cmo_c kg^{-1} attributed by tin mining was mainly related with the loss of soil clay fraction during washing to separate tin ores from other refused materials and left behind the accumulation of sand fraction with very low or negligible CEC. However, there is an interesting observation in respect to rehabilitation as revealed by TBB6 tailing profile, which has been reclaimed since 1990 and showed considerably higher CEC (varying from 1.6 to 2.2 $cmol_c$ kg^{-1}) among other profile tailings (< 1.3 $cmol_c$ kg^{-1}). This indicates reclamation practice used *Acacia mangeum* was successful in improving soil CEC by increasing soil organic C and clay content (from 8 to 13%), especially in the uppermost part of the tailing. The low CEC of tailing (< 2 $cmo_c kg^{-1}$) was also reported in tin mining in Malaysia (Madjid et al., 1998).

4.3 Strategy for agro-ecological reclamation of post-tin mining areas

Evaluation of soil characteristics showed the current post-tin mining areas have many severe constraints for crop growth and environmental reclamation. Major constraints included sandy soil texture, the absence or limited weatherable minerals (potential native nutrient sources), the dominance of quartz mineral in tailings, the low water holding capacity, the extreme low in soil organic matter and all nutrients, and nutrient susceptible to leaching. Reclamation of soil capability to retain nutrients and water was prerequisite. We proposed the strategic approach in the view of long-term investment in agroecological reclamation as follows: **(i)** levelling measures of on-site mounds resulted from refused material dumping; **(ii)** building up soil organic matter content (SOM) of sand tailing using green manure or compost to increase soil organic C, supply various nutrients, promote microbial activities and aggregate formation, reduce soil temperature, and increase soil ability to hold water and nutrients; **(iii)** establishing a special cultivation technique. Direct planting on soil tailings with sandy texture dominated by quartz minerals is unlikely to allow crop growth as shown in Fig.3a. Hence, the "pot planting point" technique could be introduced to overcome the unfavourable conditions for crop development. The technique is experimentally being tested in the field and is still collecting more data (Fig.3c). Crop performance using pot planting point technique showed rigorous growth of Paspalum grass (*Paspalum atratum*) (Fig. 3d) and various legumes, namely Gliricidia (*Gliricidia sepium* , Jacq.) (Fig.3b, background), Sesbania (*Sesbania grandifora* (L) (Fig.3b, front), Indigofera (*Indigofera zollingeriana*) (Fig. 3e), Stylosanthes (*Stylosanthes quianensis*) (Fig. 3f) and Lab lab (*Lab lab purpureus*) (Fig.3g). This technique is highly promising to restore soil productivity and ecological recovery in post tin mining areas; and**(iv)** complete fertilizer application and selection of crops with an ability to fix nutrient from the atmosphere. The suggested adaptive legumes with nodules on roots to fix atmospheric N are Indigofera (Figure S3a) and Lab lab (Figure S3b).

Conclusions

Mineral composition of post-tin mining provides strategic roles in providing the potential amount and type of native nutrient sources and heavy metals which are basic information required to determine soil nutrient management in supporting rehabilitation measures.

Post-tin mining areas have many severe constraints for crop development and ecological reclamation. The characteristics of tailings are a dominant sand fraction (up to 96% sand), limited clay fraction (< 14%), dominant quartz minerals, low water holding capacity, extremely low organic matter and all nutrients (especially N, P, K, Ca, Mg, S), slightly acid, and the limited number of weatherable minerals (potential native nutrient sources). Total elemental oxide composition was dominated by SiO_2 (92-96%) deriving from quartz minerals.

Heavy metals were occluded in structures of hot-minerals meaning that they were less availability and low health risk. Heavy metals consisted of mainly Cr and small amounts of Sn, Pb and Hg. Sn availability was minimum in all cases since it was preserved in host-mineral structure (cassiterite) which was resistant to chemical weathering.

Without technology intervention, the reclamation of post-tin mining areas was unlikely and was uneconomically feasible in the short-term. Strategic reclamation includes building up soil organic matter content, establishing pot planting point technique, thoroughly incorporated initial topsoil if it is available, complete fertilizer application and selection of adaptive crops with an ability to fix nutrient from the atmosphere.

Author contributions

M.Anda. designed the research and led the field soil sampling, soil analysis, and writing the manuscript as the main contributor. N.D.Purwantari, E.Suryani, and F. Agus assisted in field soil samplings, designed field rehabilitation techniques and drafting the manuscript, Husnain assisted in designing the field research, managing the financial support, and revising the manuscript.

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REFERENCES

Acosta, J.A., Faz, A., Martinez-Martinez, S., Zornoza, R., Carmona, D.M., & Kabas, S. (2011). Multivariate statistical and GIS-based approach to evaluate heavy metals behaviour in mine sites for future reclamation. *Journal of Geochemical Exploration* , 109:8-17. https://doi.org/10.1016/j.gexplo.2011.01.004.

Anda, M., Chittleborough, D.J. & Fitzpatrick, R.W. (2009). Assessing parent material uniformity of a red and black soil complex in the landscapes. *Catena, 78* , 142-153.

https://doi.org/10.1016/j.catena.2009.03.011.

Anda, M. (2012). Cation imbalance and heavy metal content of seven Indonesian soils as affected by elemental compositions of parent rocks.*Geoderma, 189-190* , 388–396.

https://doi.org/10.1016/j.geoderma.2012.05.009.

Aleva, G. J. J. (1985). Indonesian fluvial cassiterite placers and their genetic environment. *Journal of the Geological Society London* , 142, 815-836. https://doi.org/10.1144/gsjgs.142.5.0815.

Ashraf, M.A., Maah, M. J., & Yusoff, I. (2010). Study of Water Quality and Heavy Metals in Soil & Water of Ex-Mining Area Bestari Jaya, Peninsular Malaysia. *International Journal of Basic & Applied Sciences,* 10, 7-23. https://doi=10.1.1.207.5843&rep=rep1&type=pdf

Barney, G.O. (1980). The Global 2000 Report to the President of the United States. Pergamon Press, New York.

Bremner, J.M., & Mulvaney, C.S. (1982). Nitrogen-total, In: Page, A.L., Miller, R.H., Keeney, D.R. (Eds.), Methods of Soil Analyses, Part 2. Chemical and Mineralogical properties. Monograph No.9, 2nd Edition. American Society of Agronomy and Soil Science Society of America, Madison, WI, USA, pp. 595–624.

Dudka, S., & Adriano, D.C. (1997). Environmental impacts of metal ore mining and processing: a review. *Journal of Environmental Quality,* 26:590-602.

https://doi/abs/10.2134/jeq1997.00472425002600030003x

Fryer, M., Collins, C.D., Ferrier, H., & Colvile, R.N., Nieuwenhuijsen, M.J. (2006). Human exposure modelling for chemical risk assessment: a review of current approaches and research and policy implications. Environtal Science & Policy, 9, 261-74.

https://doi.org/10.1016/j.envsci.2005.11.011

Gama-Castro, J. E., Solleiro-Rebolledo, E., & VallejoGomez, E. (2000). Weathered pumice influence on selected alluvial soil ´ properties in west Nayarit, Mexico. *Soil and Tillage Research* 5, 143-165. https://doi.org/10.1016/S0167-1987(00)00114-8.

Guo,J¸ Zhang,R., Sun,W., Sun,W., Ling, M., Hu, Y., WU, K., Luo, M., & Zhang, L. (2018). Genesis of tin-dominant polymetallic deposits in the Dachang district, South China: Insights from cassiterite U–Pb ages and trace element compositions.*Ore Geology Reviews*, 95, 863-879. https://doi.org/10.1016/j.oregeorev.2018.03.023

Hudson-Edwards, K.A. (2003). Sources, mineralogy, chemistry and fate of heavy metal-bearing particles in mining-affected river systems.*Mineralogical Magazine* , 67, 205-217.

https://doi.org/10.1180/0026461036720095

Ko, U.K. (1986). Preliminary synthesis of the geology of Bangka Island, Indonesia. *GEOSEA V Proceedings Vol.1, Geol. Soc. Malaysia, Bulletin 20,* August 1986; pp. 81-96

Komnitsas K., & Modis, K. (2006). Soil risk assessment of As and Zn contamination in a coal mining region using geostatistics. *Science of the Total Environment* , 371, 190-6.

https://doi.org/10.1016/j.scitotenv.2006.08.047

Li, Z., Ma, Z., van der Kuijp,T.J., Yuan,Z., & Huang, L. (2014). A review of soil heavy metal pollution from mines in China: Pollution and health risk assessment. *Science of the Total Environment* , 468-469, 843-853. https://doi.org/10.1016/j.scitotenv.2006.08.047

Majid, N.K., Paudyal, B.L.K., & Shebli, Z. (1998). Survival and Early Growth of Acacia mangium, Ceiba pentandra and Casuarina equisetifolia on Sandy Tin Tailings. *Pertanika Journal Tropical Agricultural Science* , 21, 59 – 65.

McKinney, J., & Rogers, R. (1992). Metal bioavailability.*Environmental Science and Technology* , 26, 1298-1299. https://doi.org/10.1021/es00031a603

Nakamaru, Y., &Uchida, S. (2008). Distribution coefficients of tin in Japanese agricultural soils and the factors affecting tin sorption behavior. *Journal of Environmental Radioactivity,* 99, 1003–1010. https://doi.org/10.1016/j.jenvrad.2007.11.012

Nouri, J., Lorestani, B., Yousefi, N., Khorasani, N., Hasani, A. H., Seif, S., & Cheraghi, M. (2011). Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead–zinc mine Hamedan, Iran.*Environmental Earth Science* , 62, 639-644. https://doi.org/10.1007/s12665-010-0553-z

Norrish, K., & Chappell, B.W. (1977). X-ray fluorescence spectrography. In: Zussmann, J. (Ed.), Physical Methods in Determinative Mineralogy. Academic Press, London, pp.201-272.

Oves, M., Khan, M.S., Zaidi, A., & Ahmad, E. (2012). Soil contamination, nutritive value, and human health risk assessment of heavy metals: an overview. *In:* Zaidi, A., Wani, P.A., Khan, M.S., (Eds.), Toxicity of Heavy Metals to Legumes and Bioremediation. pp.1-27. Springer-Verlag Wien, New York.

Ozkan, S., & Ipekoglu, B. (2002). Investigation of environmental impacts of tailings dams. *Environmental Management and Health,*13, 242–248. https://doi.org/10.1108/09566160210431042

Pinto, M.M.S.C., Silva, M.M.V.G., da Silva, E.A.F., Dinis, P.A., & Fernando Rocha, F. (2017). Transfer processes of potentially toxic elements (PTE) from rocks to soils and the origin of PTE in soils: A case study on the island of Santiago (Cape Verde). *Journal of Geochemical Exploration,* 183, 140-151. https://doi.org/10.1016/j.gexplo.2017.06.004

Ramirez, M., Massolo, S., Frache, R., & Correa, J. A. (2005). Metal speciation and environmental impact on sandy beaches due to El Salvador copper mine, Chile. *Marine Pollution Bulletin* , 50, 62-7. https://doi.org/10.1016/j.marpolbul.2004.08.010

Sainsbury, C. L. (1969). Tin resources of the World. Geological survey bulletin 1301. United States government printing office, Washington DC.

Schwartz, M.O., Rajah S.S., Askury, A.K., Putthapiban, P., & Djaswadi, S. (1995). The Southeast Asian Tin Belt. *Earth-Science Reviews* , 38, 95-293. https://doi.org/10.1016/0012-8252(95)00004-T

Smeck, N.E., Torrent, J., & Barron, V. (1994). Interactions and weathering losses of iron and phosphorus in Palexeralfs of southern Spain. *Soil Science Society of America Journal* , 58, 1723-1729. https://doi/abs/10.2136/sssaj1994.03615995005800060021x

Soil Survey Laboratory Staff. (1992). Soil Survey Laboratory Methods Manual. Soil Survey Investigation Report No. 42, Version 2.0, USDA.

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals.*Analytical Chemistry* , 51, 844-851.

https://doi.org/10.1021/ac50043a017

USGS. (2018). Mineral Commodity Summaries: Tin. Released January 2018.

https://minerals.usgs.gov/minerals/pubs/commodity/tin/mcs-2018-tin.pdf. Accessed February 22, 2019.

Van Reeuwijk, L.P. (1993). Procedures for Soil Analysis, 4th ed. International Soil Reference and Information Centre, Wageningen, The Netherlands.

Zhou, J.M., Dang. Z., Cai. M.F., & Liu CQ. (2007). Soil heavy metal pollution around the Dabaoshan mine, Guangdong province, China.*Pedosphere* , 17, 588-94. https://doi.org/10.1016/S1002-0160(07)60069-1

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