Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology
Zanuzzi, A.; Arocena, J.M.; van Mourik, J.M.; Faz Cano, A.

Published in:
Geoderma

DOI:
10.1016/j.geoderma.2009.09.014

Citation for published version (APA):
Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology

A. Zanuzzi a, J.M. Arocena b,⁎, J.M. van Mourik c, A. Faz Cano a

a Sustainable Use, Management and Remediation of Soil and Water Research Group, Agrarian Science and Technology Department, Technical University of Cartagena, Paseo Alfonso XIII, 52, 30203 Cartagena, Murcia, Spain
b Canada Research Chair in Soil and Environmental Sciences, University of Northern British Columbia, Prince George, Canada V2N4Z9

Abstract

Mine tailings are inhospitable to plants and soil organisms, because of low pH and poor soil organic matter contents. Vegetation establishment requires a soil system capable of supporting the nutrient and water requirements of plants and associated organisms. The objective of this study was to understand the influence of added organic and industrial wastes to the formation of soils in degraded landscapes left behind by past mining activities. Specifically, we stimulated the build up of soil organic matter (SOM) and the accumulation of calcite in mine tailing deposits. We amended field experimental plots with pig manure (PM), sewage sludge (SS) in combination with blanket application of marble wastes (MW). Soil samples were collected for physical and chemical analyses, two years after the addition of industrial wastes. Three years after amendments, we took undisturbed samples for micromorphological analysis. Soil pH increased from 2.7 to 7.4 due to dissolution of calcite from MW amendment. The acidity in tailings and low rainfall in the study area precipitated the secondary calcite as infillings within the 0–4 cm layer. Total organic carbon (TOC) increased from 0.86 to 2.5 g TOC kg−1 soil after 24 months since the application of amendments. The build up of SOM resulted to stable SOM–calcite complex as dense incomplete infillings mixed with secondary calcite, and cappings on calcite particles from MW addition. These SOM cappings provide water and nutrient to support initial seedling establishment in mine tailings. We attribute the granular structure of amended materials to soil organisms (e.g., earthworm activity) involved in the decomposition of plant materials. We suggest that any organic matter amendments to acidic mine tailing deposits must be combined with calcium carbonate-rich materials to accelerate the establishment of functional ecosystem characterized by, among others, the presence of healthy soils with granular microstructure.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Mine tailing deposits in southeast Spain are inhospitable to plant growth, because of low carbon and nitrogen contents, high acidity, saline conditions, and elevated contents of metals (e.g., Conesa et al., 2006; Ottenhof et al., 2007). In addition, these tailing deposits pose environmental hazards associated with dam breakage, water and wind erosions, and leaching of acidity and potentially toxic metals into ground water.

Successful re-vegetation is one of the best management techniques available for rehabilitation of mine tailing deposits around the world (e.g., Norland and Veith, 1995; Freitas et al., 2004; Ottenhof et al., 2007; Mendez and Maier, 2008). Phytostabilization minimizes the dispersion of pollutants through wind and water erosions, and improves the aesthetic value of unvegetated landscapes (e.g., Vangronsveld and Cunningham, 1998; Ernst, 2005). However, the establishment of vegetation requires a soil system capable of supporting the nutrient (e.g., Wong, 2003) and water requirements of plants and associated organisms.

Weakly developed soils, if present, in mine tailings ponds often require amendments to improve the fertility level to support vigorous plant establishment. Organic wastes such as sewage sludge or animal manure can be used as slow release nutrient sources (Wong, 2003). Application of lime is a common agricultural and horticultural practice to overcome problems associated with low soil pH (e.g., Soon and Arshad, 2005). Lime also reduces availability of metals in contaminated soils (e.g., Gray et al., 2006). The use of soil amendments and plant cover are cost-effective and environmentally sustainable methods to manage landscapes in mined areas (Tordoff et al., 2000; Wong, 2003). Soil management practices and other human interventions are known to impact soil formation (Dudal et al., 2002).

In southeast Spain, wastes generated by pig and marble industries can provide sources of organic materials (i.e., pig manure and sewage...
sludge) and calcium carbonate, respectively. Addition of organic wastes in mine tailings may promote aggregation favorable for the formation of granular soil structure. In our earlier results (Ottenhof et al. 2007), we argue that soil aggregation from decomposition of SOM from pioneer species represents an early stage of soil formation in mine waste deposits. The soil aggregate is one of the best indicators for a fertile soil because it bridges between the physics and biochemistry of soil systems (Young and Crawford, 2004).

The objective of this study was to understand the influence of combined addition of organic and industrial wastes to stimulate the formation of soils in degraded landscapes left behind by mining activities. Specifically, we investigated the accumulation of organic matter and calcium carbonate from pig manure, sewage sludge in combination with marble wastes added to acidic and nutrient poor mine waste material. The information on the spatial association of organic matter and calcite will be useful to enhance phytostabilization of mine tailing ponds in southeast Spain (and other places in the world) through alternative disposal of industrial wastes.

2. Materials and methods

2.1. Study area

The Cartagena–La Unión Mining District covers an area of ~50 km² with an elevation range from 0 to 110 masl, and is located on the eastern part of the Murcia province, southeast Spain (Fig. 1). The semiarid climate is a typical Mediterranean, with annual average temperature of 18 °C and an annual rainfall of ~200–300 mm. This mining area was an important center for the extraction of mineral ores such as sphalerite [(Zn, Fe)S], galena (PbS) and pyrite [pyrite (FeS₂), pyrrhotite (Fe₀.₉₅S)], and marcasite (Fe²⁺S₂) for more than 2500 years, until its closure in 1991. Minerals identified in mine wastes include quartz, other silicates (e.g., muscovite, chlorite, and feldspars), sulfates (e.g., gypsum, anglesite, and alunite), carbonates (e.g., calcite, siderite, and cerussite), and sulfides (e.g., galena and pyrite) (Garcia et al., 2008). We selected the Brunita tailings pond to represent a typical mine waste deposit characterized by laminated deposits of acidic materials, and of extremely low contents of carbon and nitrogen (Table 1).

Vegetation in the study areas is generally absent and at best patchy and sparse when present. Plants observed in isolated parts of the tailings are millet rice, Piparttherum miliaceum (L) Cosson; thatching grass, Hyparrhenia hirta (L) Stapt; needle grass, Stipa sp., sticky fleabane, Dittrichia viscose (L) W. Greuter; Arnica Paronychia suffruticosa (L) DC; aster, Helichrysum decumbens Cambess., gray-green needlegrass Lygeum spartum, Loefl. ex L.; Mediterranean snow thistle Sonchus tenerinus L.; Mediterranean salt brush, Atriplex halimus L., bean caper, Zygophyllum fabago L.; rock phagnalon Phagnalon saxatile L. Cass. (Conesa et al., 2006; Zanuzzi, 2007).

2.2. Field experiment

We established 20 field plots, each with an area of 4 m², in a completely randomized design to evaluate influence of the combined additions of industrial and organic wastes in soil development in mine waste deposits. The blanket application of marble waste was necessary to correct the high acidity in the study area. The pig manure came from a pig farm in the Cuevas de Reillo (SE of Murcia Region), sewage sludge was taken from the Cartagena wastewater plant, and marble waste was collected from quarries at the Cehegin region (NE of Murcia). The particle size distribution in marble waste was 26% < 2 mm and the rest from 2 to 5 mm in size. Selected properties of the industrial wastes used in the experiment are given in Table 2.

We applied three rates of pig manure or sewage sludge additions combined with a blanket application of calcium carbonate from the marble industry. The three treatments were: (1) Control – no amendment, (2) MW + PM – marble wastes + pig manure, and (3) MW + SS – marble wastes + sewage sludge. There were three replications in each treatment. Rates of organic amendments (dry-weight) were calculated based on the bases of the European and Spanish nitrogen legislations (Council Directive 91/676/EEC, 1991; Real Decreto 261/1996) while the amount of marble waste addition (162.5 t ha⁻¹) was equivalent to the amount of calcium carbonate required to raise the pH to 7 (Sobek et al., 1978). Each plot (4 m²) received an equivalent of 7.7 kg C from the blanket application of MW.

Quantities of PM addition were 6.25, 12.5 and 25 t PM ha⁻¹ whereas the rates of SS consisted of 5, 10, and 20 t SS ha⁻¹. The equivalent C additions from PM were 0.86, 1.7 and 3.4 kg C per plot while SS amendments supplied 0.69, 1.4 and 2.8 kg C in each plot. Amendments were manually applied. First, we added marble wastes and let it dry for 24 h. Then, we mixed the materials with the soil to a depth of 0–15 cm. Following this, we applied the organic amendments using the same procedure. There were three replications for each combination of amendments. After the addition of soil amendments, plots were exposed to the semi-arid climatic conditions in the study area for long-term observations.

2.3. Sample collection and analyses

Composite soil samples from 5 sub-samples (from center and 4 corners) were collected in each treatment plot including control after 24 months after the application of organic and marble wastes. Each sample was about 200 g and taken from the 0 to 15 cm layer. Samples were air dried and passed through a 2-mm sieve prior to laboratory analyses.

Soil pH was determined in a 1:1 water/soil and 1 N KCl/soil ratio following the method given in the National Soil Survey Center (2004). Electrical conductivity was measured on the saturated extract (Bower and Wilcox, 1965). Total nitrogen was determined using the Kjeldahl method (Duchaufour, 1970), while organic carbon was determined using a Shimadzu TOC Analyzer and the calcium carbonate equivalent (inorganic carbon) was estimated using a Bernard calcimeter. Samples were pre-treated with 10% HCl to remove carbonates. Total porosity was estimated using bulk and real density (Henríquez and Cahalaceta, 1999), while aggregate stability was analyzed by wet sieving (Díaz et al., 1994).

2.4. Micromorphological analysis

Undisturbed soil samples were collected prior to the addition of industrial wastes and three years after treatment applications. We used
Kubiëna boxes to take one undisturbed sample from each treatment. Thin sections from undisturbed soil samples were prepared according to the technique described by Jongerius and Heintzberger (1975). Ten thin sections (5 cm × 7.5 cm) were described under an Olympus BH-2 polarizing microscope following the the concepts and terminology in Brewer (1976), Bullock et al. (1985) and Stoops (2003).

2.5. Statistical evaluation

We used Statistix 8.0 (Analytical Software, 2003) to conduct ANOVA on dependent parameters collected from the three replicates for each treatment. F-value with a probability of <0.05 was considered to be statistically significant.

3. Results

3.1. Selected physical and chemical properties of soils

We combined the data from three rates of pig manure and sewage sludge amendments due to the lack of significant differences among the rates of application. Soil pH increased from 2.7 in the unamended treatment to 7.4 for both the MW+PM and MW+SS treated materials (Table 3). The total organic carbon (TOC) increased from 0.86 to 2.5 t soil, respectively for the MW+PM and MW+SS treated materials. The amounts of the total nitrogen (N) after amendments (after Zanuzzi, 2007) (n = 3).

3.2. Microstructure of unamended and amended mine waste materials

Undisturbed mine waste materials had platy microstructure dominated by planar voids with few vug type pore spaces (Fig. 2A). Many coarse materials (>50 μm) were embedded in a dense mass of fine materials with undifferentiated b-fabric composed mostly of iron oxyhydroxides and opaque minerals. There were few large (>1000 μm) rock fragments. Upon mechanical mixing, single grain microstructure dominated the unamended sample (Fig. 2B). The pore spaces were dominated by planar voids with few vugh type pore spaces (Fig. 2A). The coating was nearly complete with variable thickness from ~1000 to 3000 μm thick.

One of our significant observations was the unique association of organic matter masked the b-fabric of dark minerals, perhaps iron oxides. A well-developed typic coating of microcrystalline calcite was observed in mine wastes subjected to the MW+PM treatment (Fig. 3F). Size of organic nodules ranged between 50 and 250 μm in diameter. Some monomorphic organic matter masked the b-fabric of dark minerals, perhaps iron oxides.

Table 2

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>EC (dSm⁻¹)</th>
<th>CaO₂ (%)</th>
<th>Total N (g kg⁻¹)</th>
<th>N-NH₄ (g kg⁻¹)</th>
<th>Org C (%)</th>
<th>Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>75</td>
<td>0.22</td>
<td>50.5</td>
<td>4.8</td>
<td>34.0</td>
<td>80.4</td>
<td></td>
</tr>
<tr>
<td>PM</td>
<td>86</td>
<td>3.02</td>
<td>21.7</td>
<td>2.4</td>
<td>32.0</td>
<td>40.3</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>79</td>
<td>2.22</td>
<td>97.9</td>
<td>-</td>
<td>-</td>
<td>22.1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3

Mean (and standard error) of selected properties of mine waste deposits after 24 months since pig manure (PM), sewage sludge (SS) and marble wastes (MW) amendments (after Zanuzzi, 2007) (n = 3).

<table>
<thead>
<tr>
<th></th>
<th>Unamended</th>
<th>MW+PM</th>
<th>MW+SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>pHwater (70°C)</td>
<td>2.87 ± 0.12</td>
<td>7.32 ± 0.06</td>
<td>7.33 ± 0.06</td>
</tr>
<tr>
<td>Total organic carbon (g kg⁻¹)</td>
<td>0.86 ± 0.01</td>
<td>2.46 ± 0.67</td>
<td>1.25 ± 0.19</td>
</tr>
<tr>
<td>Total nitrogen (g kg⁻¹)</td>
<td>nd</td>
<td>0.19 ± 0.07</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>53 ± 0.71</td>
<td>80 ± 4.01</td>
<td>82 ± 3.32</td>
</tr>
<tr>
<td>Aggregate stability (%)</td>
<td>19 ± 0.64</td>
<td>30 ± 2.78</td>
<td>28 ± 4.42</td>
</tr>
</tbody>
</table>

nd = not detectable; n = number of replicates.
of seeds (Fig. 4B, C) and eventually, plant establishment. In places where seedlings were growing for a significant period of time, we observed the presence of well-developed granular structure (Fig. 4D).

4. Discussion

4.1. Mechanisms of organic matter and calcite accumulations

The combination of organic matter with marble wastes develops some unique interaction between the functional groups in organic matter and calcite. The acidic nature of mine wastes promotes the rapid dissolution of added calcite in periods of occasional precipitation. However, due to the low rainfall (200–300 mm yr\(^{-1}\)) in the study area, secondary calcite precipitates as dense incomplete infillings in compound packing voids created during the application of the amendments (Fig. 3C, D, E). These calcite infillings in macropores serve as accumulation zone for organic matter from the pig manure or sewage sludge additions mobilized in periods of rainfall events. The affinity of organic materials to calcite is well established in the literature. Organic acids such as oxalate are known to precipitate as calcium oxalate in calcareous soils (Ström et al., 2001). Liming increases hydrophobic and carboxylic groups in organic matter (e.g., Karlik, 1995; Andersson et al., 2000) and precipitates high-molecular weight SOM due to flocculation or adsorption by cation bridging in a high Ca\(^{2+}\) environment (Römkens and Dolfing, 1998). The Ca\(^{2+}\) bridge with organic matter results in the formation of stable Ca–SOM complexes (or chelate), thus the accumulation of SOM in mine waste materials amended with industrial wastes rich in organic matter and calcite.

Inherent fragments of organic matter in pig manure enhance the accumulations of calcite in the amended waste materials (Fig. 3A, B). These tissue residues of plant materials serve as nuclei of precipitation for secondary calcite accumulation. We think that the process of accumulation is similar to the chelate formation discussed above. However in this situation, the organic fragments are stationary and the calcite precipitates around it; this is the opposite of chelation in the first case where secondary calcite serves as the accumulation zone for dissolve organic matter.

Organic matter also accumulates as coatings around iron oxides and other dark colored minerals (Fig. 3D). These organic matter coatings form when the functional groups in SOM chelate with positively charged iron in iron oxide minerals (e.g., McBride, 1994; Jones and Edwards, 1998). The process is similar to the calcium–SOM complex with calcite, where chelate reaction is with iron rather than calcium. Flocculation of organic acids from percolating solutions is promoted by additional trivalent cations such as iron and aluminum (Lundstrom et al., 2000; Chantigny, 2003) present in iron oxides and other dark colored minerals in the area studied.

4.2. Stimulated soil formation through enhanced accumulation of soil organic matter

Marble wastes are the principal cause of increase in pH from 2.3 to 7.4 in amended mine wastes. The dissolution of calcite and the hydrolysis of CO\(_3^{2-}\) provide hydroxyl to neutralize the acidity from the oxidation of sulphides through the following reactions:

\[
\text{CaCO}_3(s) + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \quad (1)
\]

Eq. (1) is a reversible reaction and results in the precipitation of secondary calcite as infillings (e.g., Fig. 3D) and coatings around inherent fragments of organic matter from pig manure (e.g., Fig. 3A). In the microenvironments where the degradation of organic matter from PM and SS takes place, the amount of carbonic acid production
might be high enough to react with Ca from the marble wastes and resulting to the precipitation of secondary calcite in fillings. This process is similar to the accumulation of pedogenic calcite in Canada (Landi et al., 2003). These calcite fillings serve as accumulation zones for dissolved organic matter from PM and SL amendments, thus increasing SOM. Increase in pH reduces the solubility of elevated levels of metals such as Zn and Pb, thus reducing the toxicity of mine waste materials to plants and organisms. The reduction in metal contents is due to the reaction of OH\(^-\) produced from reactions following Eq. (1) with metals to form stable metal–hydroxide complexes or the formation of metal carbonate precipitates (e.g., McBride, 1994; Gray et al., 2006; Sheoran and Sheoran, 2006).

Soil organic matter also builds up through SOM capping on calcite particles. In some cases, SOM cappings are sufficiently thick to support the nutrient and water requirements of early plant colonizers (Fig. 4B, C). Organic matter is known to increase nutrient and water holding capacity of soils to favor plant establishment and microbial coloniza-

![Fig. 3. Accumulations of organic matter and calcite in mine waste materials subjected to organic (pig manure and sewage sludge) and calcium carbonate amendments. (A and B) — inherent tissue residues of plant materials (⇩) in pig manure serve as nucleus of precipitation for infillings of secondary calcite (⇧), MW+PM treatment; (C, plain light D, cross-polarized light) — infillings of organic matter (⇩) and secondary calcite (⇧) in macropore spaces, MW+PM treatment; (E) — impregnative accumulations of organic matter (⇩) and infillings of secondary calcite (⇧) in pore spaces, MW+SS treatment; (F) — typic coatings of secondary calcite (⇧) on pore space, MW+PM treatment.](image-url)
earthworm and abundance of fecal materials are common in fertile and productive ecosystems (Wardle et al., 2004).

In this study, we determined the increase in soil porosity from 53 to 80% (Table 3) via the presence of the granular (or aggregated) structure. Initially, mine waste deposits were extremely compacted, and the addition of organic and industrial wastes promoted by the establishment of a plant cover that we believed was responsible for the increased porosity. The good aeration and water holding capacity often associated with soils with granular microstructure are the results of compound packing voids (e.g., Fig. 2C, D). Compound packing voids are characterized by interconnected pores formed in-between soil aggregates (Stoops, 2003). The size and continuity of pore space influence several properties and soil forming processes. Earthworms were not observed in the plots. Transport of water-soluble elements that are essential to plants, hydraulic conductivity, and the rate of diffusion of compounds and gases into and out of the soil aggregates are all affected by the soil pore system.

5. Conclusions

Addition of pig manure, sewage sludge and marble wastes accelerated the soil development in mine waste deposits in southeast Spain. The soil pH increased to above 7.0 and SOM content to 2.5 g TOC per kg soil by a single addition of combined industrial and organic wastes. Secondary calcite and chelate formations and the subsequent formation of granular microstructure are the principal soil forming processes stimulated by organic and industrial wastes amendments of mine waste deposits.

We think that we are the first to report the unique formation of organic matter capping on calcite particles in mined areas. This is a significant finding because it clearly illustrates the effectiveness of organic amendments when combined with calcite to accelerate the SOM accumulation in acidic materials in mined areas. The knowledge on the accelerated build up of SOM can be utilized to promote the transformation of mine tailing ponds into a functional ecosystem characterized by, among others, the presence of healthy soils with granular microstructure. For soil rehabilitation purposes, we strongly suggest that organic amendments to mine tailings deposits must be combined with calcium carbonate (e.g., marble waste) to accelerate the build up of soil organic matter. We believe that our results can be extended to other inhospitable environments created from the exploitation of natural resources.

Acknowledgements

We acknowledge the Fundación Séneca of Comunidad Autónoma Región de Murcia (Spain) for the financial support to Dr. A. Zanuzzi and J.M. Arocena, and Natural Sciences and Engineering Research Council and the Canada Research Chair program (Canada) for grants to J.M. Arocena. Words of appreciation are also due to Selim Kapur and 3 anonymous reviewers who provided valuable suggestions to improve the quality of the manuscript.

References
