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DOI

[10.1016/j.geoderma.2009.09.014](https://doi.org/10.1016/j.geoderma.2009.09.014)

Publication date

2009

Document Version

Final published version

Published in

Geoderma

[Link to publication](#)

Citation for published version (APA):

Zanuzzi, A., Arocena, J. M., van Mourik, J. M., & Faz Cano, A. (2009). Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology. *Geoderma*, 154(1-2), 69-75.
<https://doi.org/10.1016/j.geoderma.2009.09.014>

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Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology

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ARTICLE INFO

Article history:

Received 5 May 2009

Received in revised form 15 September 2009

Accepted 20 September 2009

Available online 25 October 2009

Keywords:

Granular

Intergrain microaggregates

Chelate

Secondary calcite infillings

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 build up of SOM to accelerate the establishment of functional ecosystem characterized by, among others, the presence of healthy soils with granular microstructure.

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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

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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 (Fe²⁺S₂), pyrrhotite (Fe_{0.95}S), 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) (García 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, *Piptatherum miliaceum* (L.) Cosson; thatching grass, *Hyparrhenia hirta* (L.) Stapf; needle grass, *Stipa* sp., sticky fleabane, *Dittrichia viscosa* (L.) W. Greuter; arnica *Paronychia*

suffruticosa (L.) DC; aster, *Helichrysum decumbens* Cambess., gray-green needle grass *Lygeum spartum*, Loefl. ex L.; Mediterranean snow thistle *Sonchus tenerrimus* 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 Cehegín 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 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 equal 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 replicates 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 Cabalceta, 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

Fig. 1. Relative location of the study area.

Table 1

Selected properties of the mine tailings.

pH water	EC (dSm ⁻¹)	EqCaCO ₃ (%)	Total N (g kg ⁻¹)	OC (g kg ⁻¹)	Bulk density (g/cm ³)	Total porosity (%)	Aggregate stability (%)	Texture	Clay (%)	Silt (%)	Sand (%)
2.87 ± 0.12	2.72 ± 0.04	0.20 ± 0.14	0.00 ± 0.00	0.86 ± 0.01	1.05 ± 0.01	76.88 ± 0.71	18.95 ± 0.64	Sandy-loam	3.70 ± 0.28	13.45 ± 3.75	82.85 ± 4.03
Total-extractable metals (mg/kg)				Water-extractable metals (mg/kg)				DTPA-extractable metals (mg/kg)			
Cd	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd	Cu	Zn	Pb
1.03 ± 0.04	42.05 ± 8.41	1500.00 ± 70.7	1254.65 ± 225.78	0.27 ± 0.04	0.34 ± 0.02	6.25 ± 1.06	2.76 ± 0.22	0.10 ± 0.02	0.11 ± 0.01	3.40 ± 0.21	14.85 ± 6.15

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 and 1.2 g TOC kg⁻¹ soil, respectively for the MW+PM and MW+SS treated materials. The amounts of the total nitrogen (N) after 24 months of application were 0.19 and 0.15 g N kg⁻¹ soil, respectively in the MW+PM and MW+SS amended plots. Total porosity was significantly higher in the MW+PM and MW+SS treated materials at 80 and 81%, respectively than the unamended mine waste materials (53%). Coarse fragments were not subtracted from the total volume when porosity was estimated. Aggregate stability of mine waste materials was improved after addition of PM, SS and MW (Table 3).

3.2. Microstructure of unamended and amended mine waste materials

Undisturbed mine waste materials had platy microstructure dominated by planar voids with few vugh 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 compound packing voids (or continuous pore spaces between coarse components). Many single particles (>50 µm) consisted of quartz,

chlorite, iron oxides, gypsum, few dark colored minerals, and intact fragments of laminated mine wastes. Fine materials were few and generally observed as coating on coarse materials.

The microstructures of mine waste materials after the amendments with the MW+PM and MW+SL treatments consisted of intergrain microaggregate (Fig. 2C and D). Compound packing voids were the dominant pores and the microaggregates in between coarse materials (>50 µm) were microcrystalline calcite mixed with monomorphic organic matter. In Fig. 2C, many fragments (~1000 µm) of plant materials with well defined cellular structure were observed while monomorphic (with no recognizable cell structure) organic matter was present in waste materials subjected to the MW+SL treatment (Fig. 2D). Many particles of primary calcite (~250–1000 µm) from marble wastes amendment were observed throughout the thin section (Fig. 2C and D).

Organic matter from pig manure and sewage sludge accumulated in several forms of coarse fragments. Few inherent organic matter accumulations from pig manure occurred as tissues (~1000 µm) (Fig. 3A) and as coarse organic materials surrounded by precipitates of secondary microcrystalline calcite pedofeatures (Fig. 3B).

In MW+PM treated mine waste materials, many monomorphic organic materials together with microcrystalline calcite were observed as infillings in macropores (~1500 µm diameter) between soil aggregates (Fig. 3C and D). In cross-polarized light (Fig. 3D), some of the monomorphic organic pedofeatures appeared like impregnative nodules masking the undifferentiated b-fabric of iron oxides.

Organic matter from sewage sludge accumulated as many impregnative nodules of monomorphic organic materials. These nodules were embedded in a dense incomplete infillings in association with microcrystalline calcite (Fig. 3E). 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.

A well-developed typical coating of microcrystalline calcite was observed in mine wastes subjected to the MW+PM treatment (Fig. 3F). The coating was nearly complete with variable thickness from ~1000 to 1500 µm thick.

One of our significant observations was the unique association of organic matter and calcite particles from marble wastes. Few monomorphic organic matter from sewage sludge accumulated as partial organic capping on the surface of calcite amendment in the MW+SL treated mine waste materials (Fig. 4A). Some of these cappings had thickness of ~1000 µm which is sufficient to support the germination

Table 2Selected characteristics of sewage sludge (SS), pig manure (PM), and marble wastes (MW) on dry-weight basis (*n* = 3).

	pH	EC	CaCO ₃	Total N	N-NH ₄	Org C	Moisture content
		(dSm ⁻¹)	(%)	(g kg ⁻¹)	(g kg ⁻¹)	(%)	(%)
SS	7.6	2.5	4.8	50.5	4.8	34.0	80.4
PM	8.6	9.0	19.6	21.7	2.4	32.0	40.3
MW	7.9	2.2	97.9	–	–	–	22.1

Table 3Mean (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).

	Unamended	MW+PM	MW+SS
pH _{water}	2.87 ± 0.12	7.32 ± 0.06	7.33 ± 0.06
Total organic carbon (g kg ⁻¹)	0.86 ± 0.01	2.46 ± 0.67	1.25 ± 0.19
Total nitrogen (g kg ⁻¹)	nd	0.19 ± 0.07	0.15 ± 0.06
Porosity (%)	53 ± 0.71	80 ± 4.01	82 ± 3.32
Aggregate stability (%)	19 ± 0.64	30 ± 2.78	28 ± 4.42

nd – not detectable; *n* = number of replicates.

Fig. 2. Microstructure in mine waste materials before and after organic matter (pig manure, sewage sludge) and calcium carbonate amendments (marble cuttings). (A) – platy microstructure, mine waste materials; (B) – single grain structure of mine waste after mechanical break-up, unamended soil, (C) – single grain to intergrain microaggregate microstructure, organic materials (⬇) inherent in pig manure, and calcite particles (⬆) from marble cuttings, MW+PM treatment; (D) – intergrain microaggregate microstructure, monomorphic organic materials (⬇) from sewage sludge and calcite particles (⬆) from marble cuttings, MW+SS amended soil.

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 Ca²⁺ environment (Römken and Dolfig, 1998). The Ca²⁺ 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 CO₃^{2−} provide hydroxyl to neutralize the acidity from the oxidation of sulphides through the following reactions:

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

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 (ϕ) in pig manure serve as nucleus of precipitation for infillings of secondary calcite ($\circ$), MW+PM treatment; (C, plain light D, cross-polarized light) – infillings of organic matter (ϕ) and secondary calcite ($\circ$) in macropore spaces, MW+PM treatment; (E) – impregnative accumulations of organic matter (ϕ) and infillings of secondary calcite ($\circ$) in pore spaces, MW+SS treatment; (F) – typical coatings of secondary calcite ($\circ$) on pore space, MW+PM treatment.

might be high enough to react with Ca from the marble wastes and resulting to the precipitation of secondary calcite infillings. This process is similar to the accumulation of pedogenic calcite in Canada (Landi et al., 2003). These calcite infillings 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-

tion (e.g., Stevenson, 1994; Sollins et al., 2006). One time addition of pig manure and sewage sludge increased SOM in mine waste deposits from <1.0 to 2.5 g TOC per kg of soil (Table 3). This SOM build up is higher than SOM accumulation from the pioneer plant species alone. In our previous results from sites similar to the study areas (Ottenhof et al., 2007), it took 18 years to accumulate 1.9 g organic C per kg soil from *Phragmites australis*, a pioneer species common in the study area.

With time, the continual addition of SOM from the decomposition of plant remains from pioneer colonizers will result in the invasion by other plants and soil organisms, such as earthworm which are the principal agents in the formation of granular microstructure in soils, i.e., the granular shape originating from the fecal materials (e.g., Brewer, 1976; Pawluk, 1987; van Mourik, 2003). The well developed granular structure on the surface of amended mine wastes (e.g., Fig. 4D) is the result of earthworm activity. The burrowing activities of *Collembola* and *Enchytraeidae* result in the deposition of granular casts in the surface soils (Langmaack et al., 2001). High density of

Fig. 4. Development of soil microstructure in mine waste materials subjected to organic matter (sewage sludge) and calcium carbonate (marble cuttings). (A) – partial monomorphic organic matter coating ($\ominus$) on calcite particle ($\oplus$); (B and C) – seedling establishment on thick monomorphic organic matter ($\ominus$) coating on calcite particle ($\oplus$); (D) – granular microstructure observed in the root zone.

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.

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