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Carbon mineralization in mine tailing ponds amended with pig slurries and marble wastes

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Abstract

Effective application of organic residues to reclaim soils requires the optimization of the waste management to minimize CO_2 emissions and optimize soil C sequestration efficiency. In this study, the short-term effects of pig slurry amendment alone and together with marble waste on organic matter mineralization in two tailing ponds from Cartagena-La Unión Mining District (SE Spain) were investigated in a field remediation experiment. The treatments were: marble waste (MW), pig slurry (PS), marble waste + pig slurry (MW+PS), and control. Soil carbon mineralization was determined using a static chamber method with alkali absorption during 70 days. Soil respiration rates in all plots were higher the first days of the experiment owing to higher soil moisture and higher mean air temperature. MW plots followed the same pattern than control plots, with similar respiration rates. The addition of pig slurry caused a significant increase in the respiration rates, although in MW+PS plots, respiration rates were lower than in PS plots. The cumulative quantities of C-CO_2 evolved from the pig slurry mineralization were fitted to a first-order kinetic model explaining 90% of the data. This model implies the presence of only one mineralisable pool (C_0). The values of the index C_0*constant rate/added C were similar for PS plots in both tailing ponds, but lower in the MW+PS treatment, suggesting that the application of marble reduces the degradability of the organic compounds present in the pig slurry. Thus, the application of marble wastes contributes to slow down the loss of organic matter by mineralization.

Keywords: Carbon mineralization, tailing pond, heavy metal, marble waste, pig slurry

Introduction

In the Region of Murcia (SE Spain) past mining activities have generated large amounts of unconfined wastes accumulated in tailing ponds due to intensive mining activities, especially in the Mining District of Cartagena-La Unión. Although mining activity was abandoned in 1991, tailing ponds still remain in the area. The environmental impacts of such structures generally result from their low pH, high metal content, low organic matter and null vegetation (Conesa et al., 2006). High incidence of wind and water erosion events negatively affects soil, water, vegetation, fauna, and human populations in the surrounding areas (Zanuzzi et al., 2009).

Reclamation is needed to avoid environmental risks. Alkaline materials are commonly used as an amendment for ameliorating the acidic conditions of many acid-generating mine wastes and for immobilising metals such as carbonates, mitigating metal toxicity (Barker, 1997). Organic residues are also

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normally used as amendments because the addition of organic matter can significantly improve the physical characteristics, the nutrient status, stimulate microbial populations and possibly reduce the availability of toxic metals through complexation (Ye et al., 2002).

Soil organic matter is universally recognized to be among the most important factors responsible for soil fertility and land protection from contamination, degradation, erosion and desertification, especially in semiarid areas. Soil organic matter plays a major role in maintaining soil quality, supplying plant nutrients, reducing soil erosion, improving soil structure and water quality, and increasing biomass and vegetal productivity (Stevenson, 1994). A correct management of the application of amendments in soil reclamation relies mainly on two aspects: efficient increase of the soil organic matter and adequate match of the release of mineral nutrients to vegetation demand. Applying organic wastes to soil could represent a useful tool in maintaining and increasing amounts of organic matter (Mondini et al., 2007). Effective recycling of organic residues in soil requires the optimization of the organic waste management in order to minimize CO_2 emissions and optimize soil C sequestration efficiency. Therefore, the knowledge of carbon mineralization dynamics in amended soils is of intrinsic interest. Since the main objective after application of organic amendments is the permanent increment of organic matter, a thorough study on organic carbon stability and mineralization is crucial. Efforts have to be made to use amendments that release nutrients but do not mineralise so fast that organic matter disappears before an adequate development of vegetation cover.

In the current study, the short-term effects of pig slurry amendment alone and together with marble waste on organic matter mineralization in two tailing ponds were investigated in a field remediation experiment.

Material and Methods

The study was conducted in the Cartagena-La Unión Mining District (Region of Murcia, SE Spain), where great mining activities have been carried out for more than 2500 years. The climate of the area is semiarid Mediterranean, with mean annual temperature of 18ºC and mean annual rainfall of 275 mm. The potential evapotranspiration rate surpasses 900 mm year^{-1}. Two tailing ponds generated by mining activities were selected, Gorguel (37º 35' N, 0º 52' W; 7470 m^2), and Lirio (37º 36' N, 0º 49' W; 14600 m^2), since they are representative of the rest of existent ponds in Cartagena-La Unión Mining District: salinity, absence of vegetation, high metal concentrations, low organic carbon content and affection by wind and water erosion. Both tailing ponds were divided in four different field-scale plots with a surface of 25% of the total area. Thus, plots in Gorguel had a surface of ~1868 m^2, while plots in Lirio had a surface of ~3650 m^2. Soil characteristics of the plots in each tailing pond are shown in Table 1.

Table 1. Main soil properties and total heavy metals contents in the different plots established in Gorguel and Lirio tailing ponds. Values are mean ± standard deviation (n=5).

Treatment[a]	pH	EC[b]	Texture	TOC[b]	IC[b]	Nt[b]	Cd	Cu	Pb	Zn
		dS m^{-1}	(% sand, silt, clay)	g kg^{-1}	g kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Gorguel										
MW	7.76	7.62	Loam (47, 37, 16)	13.2	3.23	0.13	24.2	188	5041	12619
PS	7.51	2.64	Sandy loam (61, 32, 7)	11.4	3.06	<dl	29.5	193	4086	12741
MW+PS	7.90	3.87	Sandy loam (57, 35, 8)	14.3	3.05	<dl	32.6	176	3642	10927
CT	7.58	3.31	Sandy loam (76, 17, 7)	11.0	3.07	<dl	32.9	223	4595	12406
Lirio										
MW	5.47	7.65	Sandy loam (67, 32, 1)	2.3	0.05	<dl	48.2.3	159	3945	6757
PS	7.25	3.40	Loamy sand (80, 15, 5)	2.3	1.79	0.01	10.2	176	4177	4912
MW+PS	4.96	2.80	Sandy loam (70, 26, 4)	3.1	0.05	<dl	34.9	159	3598	10074
CT	5.32	5.50	Sandy loam (53, 38, 9)	2.0	0.12	<dl	38.2	203	4093	11851

[a] MW: marble waste; PS: pig slurry; CT: control [b] EC: electrical conductivity; TOC: total organic carbon; IC: inorganic carbon; Nt: total nitrogen. <dl: below detection limit

We used two different amendments (pig slurry and marble waste ($CaCO_3$)) for reclamation purposes, in order to increase soil organic matter and soil nutrients, decrease heavy metals availability, ameliorate soil structure, neutralize potential acidity generated by sulphides, and facilitate vegetation colonization. Each plot in both tailing ponds received a different treatment. The treatments were: marble waste (MW), pig slurry (PS), marble waste + pig slurry (MW+PS), and control (CT), the latter receiving no amendment. The pig slurry came from a pig farm in Pozo Estrecho (SE of Murcia), while marble waste (formed by particles of 5-10 µm diam.) was collected from quarries at the Cehegín region (NE of Murcia). The characteristics of soil amendments are given in Table 2.

Table 2. Main characteristics of the pig slurry (PS) and marble waste (MW) used.

Parameters	PS	MW
pH	7.8	8.0
Electrical conductivity (dS m^{-1})	39.1	2.2
Density (g mL^{-1})	1.0	-
$CaCO_3$ (%)	-	98
Moisture (%)	96.0	1.0
Total N (g L^{-1})	5.1	-
NH_4^+-N (g L^{-1})	4.5	-
Total organic carbon (g L^{-1})	17.8	-

The first activity consisted of tilling the first 50 cm of the surface soil in order to prepare it for the application of the amendments (control plot was also tilled). This activity was needed because of the presence of cementing agents such as oxides and hydroxides of iron, which provoke the formation of crusting, with a thick between 2 and 20 cm, very hardened, forming a coherent mass or strongly cemented. Amendments were mechanically applied. In the MW+PS plots, we first added the marble waste followed by the application of the pig slurry. After the application of amendments, all materials were mixed to a depth of 0-30 cm to incorporate the amendments into the soil. Application of amendments was carried out on 10 September 2010 in Lirio, and on 4 October 2010 in Gorguel.

We applied 4 kg marble m^{-2} and 1.4 kg marble m^{-2} in Gorguel and Lirio, respectively. These doses were calculated using the method proposed by Sobek et al. (1978), which provides an indication of the quantity of lime required to neutralise all the acid according to the sulphides present in the soil. Doses for pig slurry were established by thresholds imposed by legislation regarding the addition of N to soil to avoid contamination by nitrates (Council Directive 91/676/EEC). We applied 3 L pig slurry m^{-2}, corresponding to 60 g C m^{-2}.

Soil carbon mineralization was determined using a static chamber method with alkali absorption (Zibilske, 1994). Soil respiration was determined using white plastic cylinders (25 cm diam., 30 cm height) inserted 2 cm into soil. A sample vial containing 25 mL of NaOH 1 N was hung in the chamber by a wire held in place by a rubber stopper. Surface area of the chamber was 490 cm^2. Five chambers were randomly set out within each plot. Chambers were placed the day of application of amendments up to 43 and 67 days for Gorguel and Lirio, respectively. Alkali traps were replaced every 2-3 days during the first two weeks, and every 7 days from that date. Experiment was interrupted when respiration rates from amended plots equalled control values. Blanks were used in each tailing pond, with vials containing NaOH at the bottom of the chamber not exposed to soil, accounting for residual CO_2 absorbed from the atmosphere. The quantity of absorbed CO_2 was determined by titration (with HCl 1N) to a phenolphthalein endpoint following precipitation of the absorbed CO_2 to $BaCO_3$ with addition of excess $BaCl_2$ (Zibilske, 1994). Soil carbon mineralization was calculated based on exposure time and soil surface area. Cumulative mineralized organic carbon was also calculated to plot these values versus time.

In order to calculate the direct effect of amendments on CO_2-C evolved from soil, the average value of CO_2-C from the control soil was subtracted from each treatment to obtain the increment data (Δ data). This approach supposes that the possible priming effect due to the enhanced decomposition of native soil organic matter will no occur or they are small compared to the mineralization of the organic amendment. Then, in each treatment, the Δ data per treatment were averaged and the cumulative values were fitted to different kinetics functions. The best fits were using a first-order kinetic model $C_{min} = C_0 (1-e^{-K t})$, being C_{min} the carbon mineralized from soil once the control is subtracted (as CO_2-C) in a given time, C_0 the potentially mineralizable pool of organic C, K the mineralization constant rate, and t the time. The fits and kinetic parameters were carried out using the SigmaPlot 10.0 software.

Results

The values of soil respiration rates in all plots were higher the first days of the experiment owing to higher soil moisture due to different rainfall events, and higher mean air temperature (Figure 1). In Gorguel, significant correlations were found between basal respiration rate and soil moisture (r=0.83; P<0.001) and mean air temperature (r=0.52; P<0.01). In Lirio, basal respiration rate was only correlated with mean air temperature (r=0.67; P<0.001). CT plots showed a decreasing trend starting with an average initial soil respiration rate of 0.93 and 1.53 g CO_2-C m^{-2} d^{-1}, for Lirio and Gorguel respectively, and finishing with 0.65 and 1.02 g CO_2-C m^{-2} d^{-1}, for Lirio and Gorguel respectively (Figure 1c,d). MW plots followed the same pattern than CT plots, with similar respiration rates. The addition of pig slurry caused a significant increase in the respiration rates. The highest respiration rates in PS plots were reached during the first days, when most of the easily degradable compounds were not yet depleted.

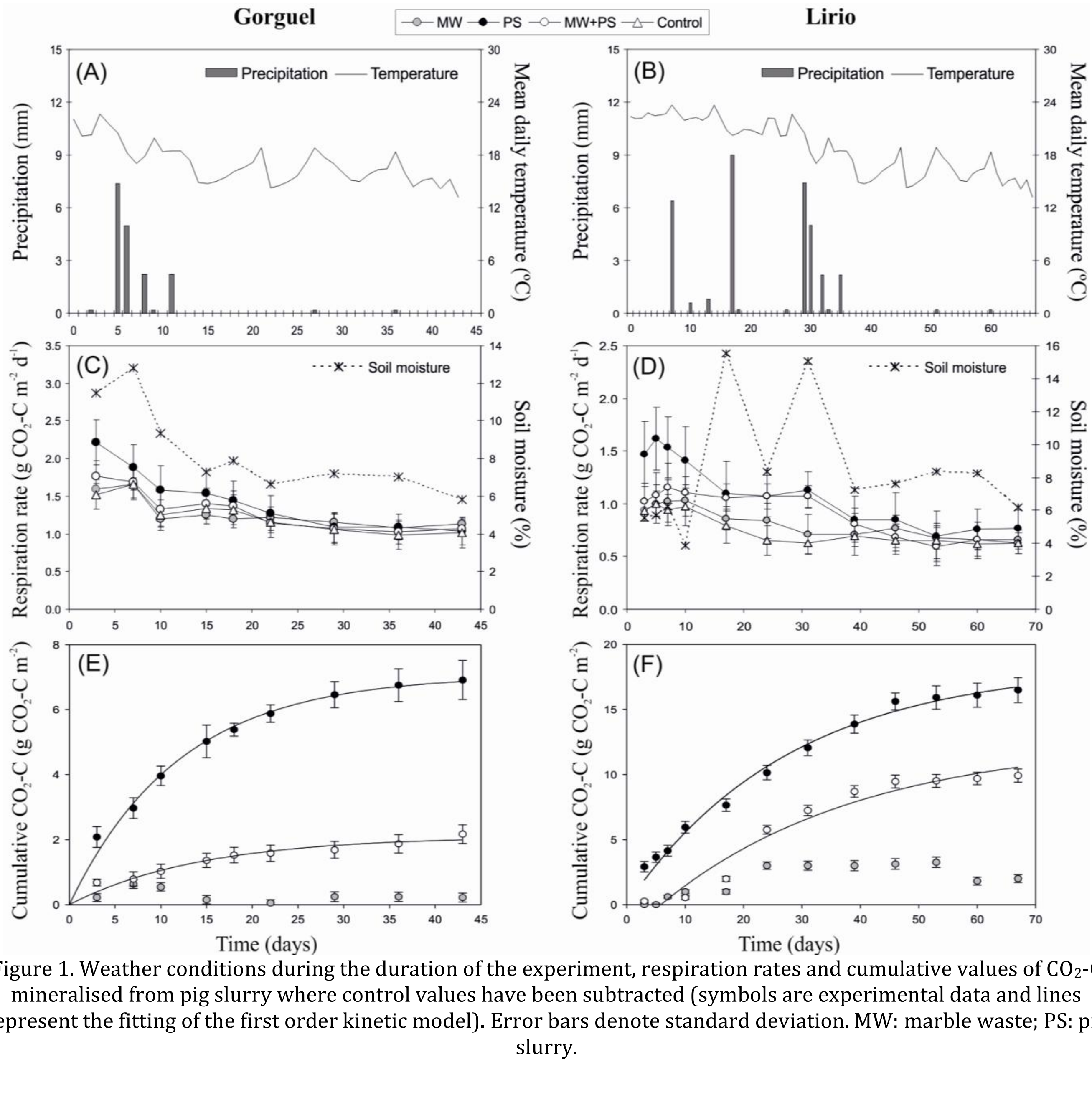

Figure 1. Weather conditions during the duration of the experiment, respiration rates and cumulative values of CO_2-C mineralised from pig slurry where control values have been subtracted (symbols are experimental data and lines represent the fitting of the first order kinetic model). Error bars denote standard deviation. MW: marble waste; PS: pig slurry.

The respiration peaks were reached the fifth day after the beginning of the experiment in Lirio (1.62 g CO_2-C m^{-2} d^{-1}) and the third day in Gorguel (2.22 g CO_2-C m^{-2} d^{-1}) to continuously decrease up to reach values similar to control at the end of the experiment (Figure 1c,d). In MW+PS plots, respiration rates were lower than in PS plots. Respiration rates were only positively correlated with arylesterase (r=0.75; P<0.001) and MBC (r=0.63; P<0.001), and negatively correlated with exchangeable Cd (r=-0.51; P<0.05), exchangeable Cu (r=-0.63; P<0.001) and exchangeable Pb (r=-0.70; P<0.001).

The cumulative quantities of CO_2-C evolved from the pig slurry mineralization (Figure 1e,f) were fitted to a first-order kinetic model explaining more than 90% of the experimental data. In Table 3 the potentially mineralisable C pools from the pig slurry estimated by the model are shown. These data are approximately equivalent to 30, 25, 12 and 4% of the organic carbon added for PS in Lirio, MW+PS in Lirio, PS in Gorguel and MW+PS in Gorguel, respectively. The mineralization constant rate (K) was higher for Gorguel plots than for Lirio. The values of the index C_0*K/added C were similar for PS plots in both tailing ponds, but lower in the MW+PS treatment, mainly for Gorguel. The cumulative quantities of CO_2-C released at the end of the experiment were positively correlated with sand content (r=0.87; P<0.01) and negatively correlated with IC (r=-0.85; P<0.01), pH (r=-0.83; P<0.01), clay content (r=-0.92; P<0.001) and total Zn (r=-0.82; P<0.01).

Table 3. Parameters of first order kinetic model ($C_{min} = C_0\,[1-e^{-K\,t}]$) fitted to the cumulative values of CO_2-C mineralised from pig slurry.

	Lirio		Gorguel	
	PS[a]	MW[a]+PS	PS	MW+PS
C_0 (g C m^{-2})	18.41	15.05	7.06	2.10
K (d^{-1})	0.0358	0.0293	0.0834	0.0697
C_0 * K/added C	0.0109	0.0074	0.0098	0.0024
R^2 adj	0.99	0.95	0.98	0.92
F	944 (P<0.001)	112 (P<0.001)	523 (P<0.001)	102 (P<0.001)

[a]PS: pig slurry; MW: marble waste

Discussion

Respiration rates were influenced by weather conditions, microbial size and availability of heavy metals, also reported in literature (e.g. Conant et al., 2000; Kao et al, 2006; Nwachakwu and Pulford, 2011). Mineralization of organic carbon was lower in Gorguel than in Lirio, despite applying the same quantity of slurry. This could be due to higher pH, higher carbonates content (expressed as inorganic carbon), lower sand content and higher clay content, inferred by the correlations study. Carbonates and clays stabilize organic carbon and make it more inaccessible for microbial attack (Bernal et al., 1991). Saviozzi et al. (1993) suggested that the use of the index C_0*K/added C is as an indicator of degradability for organic materials, being lower in MW+PS plots. Thus, the application of marble reduces the degradability of organic compounds. This is of special interest to enhance carbon accumulation in reclaimed soils, since the protection of soil C is an integral part of C sequestration (Shrestha and Lal, 2006). No differences with CT were observed in MW plots in terms of C mineralization. Thus, the application of carbonates seems to be useful to stabilize fresh and very labile organic matter, such as that supplied by pig slurries, rather than that long-term stabilized in soil. The percentages of PS mineralised C were lower than those found by Pardo et al. (2011) in mine soils (74-98% after 56 d of lab incubation), likely due to constraint climatic conditions in field experiments and higher heavy metals content. Metal binding to organic matter may offer some protection from microbial degradation (Merckx et al., 2001). Thus, despite no acidity corrections are needed, the combined application of pig slurry with marble wastes also helps to stabilize organic matter and minimize carbon losses as CO_2.

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