Catena 160 (2018) 50–56

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Atypical morphology of technosols developed in quarry dumps restored with marble sludge: Implications for carbon sequestration

Mariano Simón[a,*], Inés García[a], Juan A. Sánchez[a], Verónica González[b]

[a] *Departamento de Agronomía, Área de Ciencia del Suelo, Universidad de Almería CITE IIB, Campus de Excelencia Internacional Agroalimentario ceiA3, Ctra. Sacramento s/n, 04120 Almería, Spain*

[b] *LEITAT Technological Center, c/Pallars 179-185, 08005 Barcelona, Spain*

ARTICLE INFO

Keywords:
Marble quarries
Rehabilitation
Marble sludge
Soils
Carbon sequestration

ABSTRACT

Covering the surface of stony slopes with a layer of topsoil is one of the most commonly used techniques to restore quarries. However, in semiarid climates, the topsoil is frequently poor and has limited water availability, which significantly reduces the success of the restoration. The high water-holding capacity of the sludge from the cutting and polishing of marble, as highlighted in previous studies, could contribute to the success of the restoration of marble quarries. In this study, a quarry dump was restored both with and without the addition of marble sludge prior to being covered with topsoil. The aim was to analyse the effect of the sludge on the characteristics and properties of the soils that formed five years after topsoil reposition. In the soils of all plots, a horizon of accumulation of organic matter was formed on the surface, whereas in the plots with sludge, the root growth clearly increased in the contact between the topsoil and the sludge, forming a second organic-mineral horizon at the contact zone of the topsoil and marble sludge layer. The result was the formation of soils with an atypical morphology characterized by two horizons of accumulation of organic matter, one at the surface and another at depth, which encourage the accumulation of organic carbon in the soil (until $363 \pm 62\,\mathrm{g\,C\,m^{-2}\,year^{-1}}$). Therefore, it could be considered that the soils with marble sludge behave as carbon sinks, especially considering that these soils do not seem to have reached equilibrium, and that the organic carbon content could continue to increase over time. Long-term monitoring these plots is needed to better constrain the true extent of carbon sequestration in these soils.

1. Introduction

Stony dump deposits lack soil and have steep slopes, therefore limited water availability, all of which create a high-stress environment for plants and constitute the main problems facing restorers (Clemente et al., 2004; Heneghan et al., 2008), especially in arid or semiarid climates. One of the most frequently used restoration techniques is to cover the surface with a layer of topsoil (approximately 30 cm thick) from areas close to the quarry (Brofas, 2001; Bote et al., 2005; Zhang and Chu, 2010) and then perform hydroseeding with different species (Tormo et al., 2007; García-Palacios et al., 2010). However, in semiarid climates, the pedogenesis is limited, and the soils are poor and have low water-holding capacity, which significantly reduces the success of the restoration (García-Fayos et al., 2000; Oliveira et al., 2011).

During the cutting and polishing of marble, significant quantities of a white sludge consisting of fine particles (silt) of marble are generated. Simón-Torres et al. (2014) used this sludge with high water-holding capacity ($0.256\,\mathrm{kg\,kg^{-1}}$) to restore the dump of a marble quarry, adding an approximately 20-cm-thick layer of marble sludge on the dump prior to providing the topsoil. The results indicated that the mean volumetric water content of the topsoil was 3.6 times lower than that of the marble sludge; thus, in the plots where marble sludge was added, the volumetric water content was considerably increased in the contact zone between the topsoil and sludge (deepest 5 cm of the topsoil and the first 10 cm of the marble sludge). The soil morphology showed a strong increase in the roots in the zone where the volumetric water content was increased, forming a very dark brown horizon that was presumably enriched in organic matter in a few years. A study of the vegetation that developed in this dump restored with marble sludge (Gómez Mercado et al., 2015) highlighted an increase in dry biomass, plant cover and vegetation height and an increase in dry biomass from perennial species such as *Piptatherum miliaceum* L. Coss (with a dense and fasciculate roots system) and *Anthyllis cytisoides* L. (with an ability to fix nitrogen), which would facilitate long-term rehabilitation and accelerate plant succession (Pallavicini et al., 2015; Premrov et al., 2017).

---

[*] Corresponding author.
E-mail address: msimon@ual.es (M. Simón).

http://dx.doi.org/10.1016/j.catena.2017.08.018
Received 20 April 2017; Received in revised form 8 August 2017; Accepted 25 August 2017
Available online 13 September 2017
0341-8162/ © 2017 Elsevier B.V. All rights reserved.

The particular morphology of these soils emphasized the need for a detailed study of their properties to understand their genesis and assess their role as a carbon sink, which is the aim of the present study.

2. Materials and methods

2.1. Studied site

The study was conducted in a dump of the Macael marble quarries (southeast Spain, 37°18′17″N, 2°17′5″W). The mean annual temperature is 16.8 °C, with a mean maximum of 32.0 °C in the summer and a mean minimum of 3.2 °C in the winter. The mean annual rainfall is 454 mm, and the mean annual water deficit (difference between the mean annual precipitation and the mean annual evaporation; Milly, 1994) is -442 mm.

2.2. Restoration of the dump and the soils studied

In early September 2007, the stones of a dump, with an area of approximately 1100 m^2 (48 × 23 m) and a slope close to 72%, were rearranged, and an approximately 20-cm-thick layer of marble sludge was placed over the surface of the dump, save for a 5-m-wide strip in the centre, which served as a control (Simón-Torres et al., 2014). Finally, the dump was covered with a layer of topsoil coming from the soils near the quarries, which were developed mainly on the slates and shales located stratigraphically above the marble. The topsoil thickness ranged from 18 cm to 38 cm, and the marble sludge thickness ranged between 17 cm and 21 cm. To study the restored dump quarry, nine plots of 6 m^2 were selected (3 × 2 m), with three in the central sector where the marble sludge was not added (plots PT) and six in the sector where the sludge was added, three of which were to the west and three to the east of the central sector (plots PTS). In mid-September 2007, three samples of topsoil ($n = 27$) and two samples of marble sludge ($n = 12$) in each plot were collected and analysed. For more information about the studied site and the restoration work on the quarry dump, see Simón-Torres et al. (2014).

2.3. Hydroseeding

At the beginning of October 2007, hydroseeding was conducted with a slurry containing 8 g L^{-1} of mixture of seeds of common native species in the study area (*Agropyron cristatum* (L.) Gaertn., *Cynodon dactylon* (L.) Pers., *Lolium rigidum* (Gaudin) Weiss ex Nyman., *Medicago sativa* L., *Melilotus officinalis* (L.) Pall., *Anthyllis cytisoides* L., *Artemisia campestris* L., *Atriplex halimus* L., *Bituminaria bituminosa* (L.) C.H. Stirt., *Rumex induratus* Boiss & Reut., *Piptatherum miliaceum* (L.) Coss., *Moricandia arvensis* DC. and *Zygophyllum fabago* L.), 35 g L^{-1} of short fibre (100% cellulose) mulch, 7 g L^{-1} of stabiliser (terpene-phenol resins with ethylene-vinyl acetate adhesives) and 15 g L^{-1} of a complex chemical fertilizer, grade 15-15-15 (15% N, 15% P_2O_5, 15% K_2O). The applied dose of this slurry was 3 L m^{-2}.

2.4. Soil morphology in 2013

In May 2013, the soils of the nine selected plots were collected again, thoroughly describing the different horizons (FAO, 2006). Soil morphology was different depending on the addition of marble sludge and the thickness of the added layer of topsoil. The topsoil of the three plots in which marble sludge was not added (PT) were sampled at three depths (Ah, C1 and C2 horizons) without clear morphological differences between them, except for a slight darkening of the surface layer (Fig. 1a). The soils of the plots in which sludge was added were sampled at different depths depending on the thickness of the added topsoil and morphology of each soil. In the soils of the three plots in which the thickness of the topsoil provided was less than or equal to 25 cm (PTS $\leq$ 25), five horizons were sampled (Fig. 1b, d), three of which were located in the topsoil (Ah in the surface, C in the subsurface horizon and A'h in the deepest part of the topsoil in contact with the sludge and with a clearly darker colour) and two in the marble sludge (2C1 with relatively high density of roots and 2C2 with lower density of roots). In the soils of the three plots in which the thickness of the topsoil provided was higher than 30 cm (PTS $>$ 30), six horizons were sampled (Fig. 1c), of which four were located in the topsoil (Ah in the surface, C in the subsurface, a transitional horizon labelled CA and A'h in the deepest part of the topsoil, in contact with the sludge and with a clearly darker colour), including a transitional horizon labelled C/A (Fig. 1d) that was formed by a mixture of A'h horizon (minority) and sludge (majority) and a 2C horizon formed exclusively by the marble sludge. The deepest 5 cm of the topsoil and the first 10 cm of the marble sludge were labelled W layer. The density of roots in the A'h, 2C1 and C/A horizons was estimated visually.

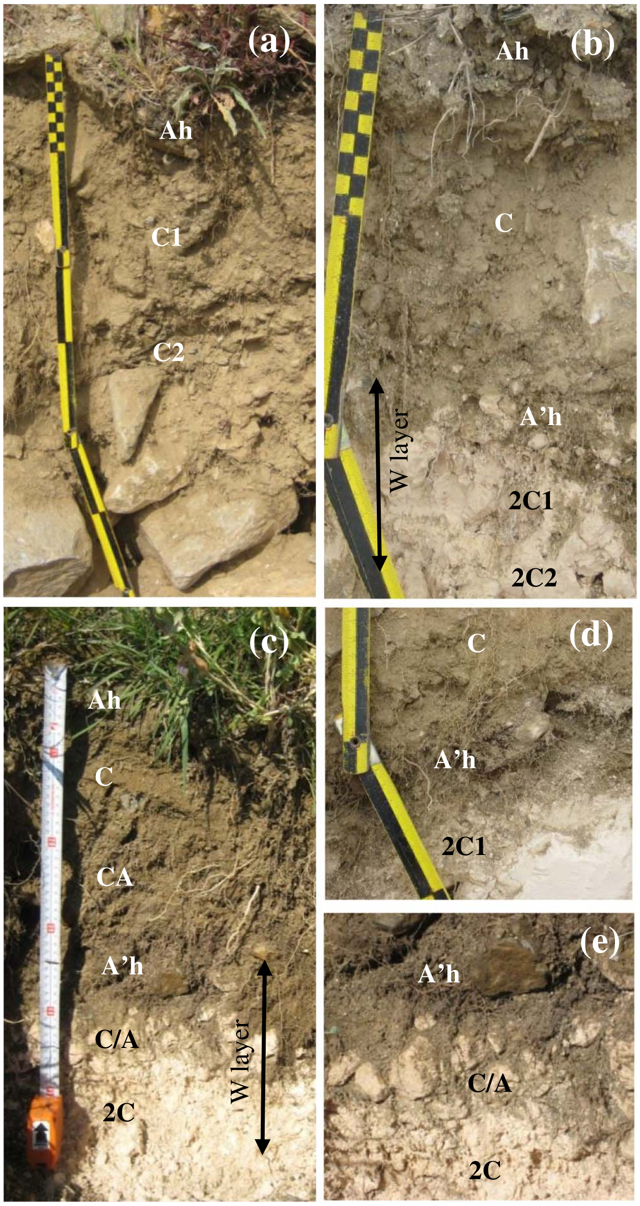

Fig. 1. (a) Soil of the PT plots (without sludge), (b) soil of the PTS $\leq$ 25 plots, (c) soil of the PTS $>$ 30 plots, (d) high growth of roots in A'h and 2C1 horizons of the PTS $\leq$ 25 and (e) detail of the C/A horizon of the PTS $>$ 30 plots.

2.5. Soil analysis

The bulk density (BD) of each soil horizon sampled in mid-September 2007 and May 2013 was estimated using the cylinder of a known volume method (Blake and Hartge, 1986). Samples from all soil horizons collected in both samplings were air dried and sieved to 2 mm, and then the percentages of gravel (> 2 mm) and fine earth (< 2 mm) were calculated. In the fine earth, the particle-size distribution was determined by the pipette method after removing the organic matter with H_2O_2 and dispersion by shaking with $(NaPO_3)_6$ (Loveland and Whalley, 1991). The pH was measured in a 1:2.5 solid-water suspension. A saturation extract of each soil sample was prepared (US Salinity Laboratory Staff, 1954), the liquid phase was vacuum pumped and the electrical conductivity (EC) and the concentrations of selected anions and cations were measured by ion chromatography, atomic absorption spectroscopy (Ca and Mg) and flame photometry (Na and K), respectively. The calcium carbonate equivalent content was estimated manometrically (Williams, 1949), and the cation exchange capacity (CEC) was determined with 1 M Na-acetate at pH 8.2 (Rhoades, 1982). The organic carbon (OC) content was analysed by the wet oxidation method (Mingorance et al., 2007), and the nitrogen (N) content was determined by the Kjeldahl method (Jones, 1991). Humic substances were extracted with $Na_4P_2O_7{\cdot}10H_2O$ and NaOH to pH 13, and the solution was acidified with H_2SO_4 until pH 1, separating humic acids (HA) that precipitate and fulvic acids (FA) that remain soluble (Kononova, 1966). The organic carbon of the HA and FA was determined according to Mingorance et al. (2007). Because the organic carbon was determined in the fine earth, the total organic carbon content in each horizon (TOC) was estimated from the following equation:

$$\mathrm{TOC}\ (\mathrm{g\ m^{-2}}) = th\,(\mathrm{mm}) \times \mathrm{BD}\,(\mathrm{g\ cm^{-3}}) \times \mathrm{OC}\ (\mathrm{g\ kg^{-1}}) \times [(10^3\text{–gravel in g kg}^{-1})/10^3] \quad (1)$$

where *th* is the mean thickness of the horizon, BD is the bulk density and OC is the organic carbon content in the fine earth. Total organic carbon in the soil of each plot (TOCP) was estimated by the sum of the TOC of its distinct horizons. A similar equation was used to estimate the total nitrogen content in the horizons (TN) and soils of each plot (TNP).

2.6. Statistical methods

The data distributions in the different groups of plots (PT, PTS ≤ 25 cm and PTS > 30) were established by calculating the mean values and the standard deviation. Correlation analysis involving different components of the soils were performed, and the coefficient of determination (r^2) and P-value were estimated. The SPSS (PASW Statistics 20) software package was used for all statistical analyses.

3. Results

3.1. Topsoil and marble sludge before hydroseeding

The topsoil used in the restoration and sampled in mid-September 2007 showed a $CaCO_3$ content of approximately 15%, bulk density (BD) of approximately 1.60 g cm^{-3} and high mean gravel content (Table 1). The mean EC values of the saturation extract were < 1.0 dS m^{-1}, and soluble ions were dominated by Ca^{2+} and SO_4^{2-}, with a lower content of Na^+ and Cl^- and trace amounts of Mg^{2+}, K^+ and NO_3^-. The textural class of the fine earth was sandy loam, with low OC and nitrogen content, high sand content and was carbonated. By contrast, the marble sludge was composed almost exclusively of $CaCO_3$, with silt loam texture (around 70% silt) and much lower values of BD, OC and nitrogen compared with the topsoil. The mean EC values were clearly higher than that of the topsoil, although they were < 4 dS m^{-1} (the level at which salinity is considered harmful). Soluble ions were dominated by Ca^{2+}, Na^+, SO_4^{2-} and Cl^-, with lower Mg^{2+}, K^+ and NO_3^- concentrations. The mean pH values were similar in the topsoil and marble sludge, ranging between 8.5 and 8.6.

Table 1
Mean ± standard deviation of the main properties of the topsoil and marble sludge of the samples collected in mid-September 2007.

Properties			Topsoil	Marble Sludge
BD (g cm^{-3})			1.63 ± 0.05	1.23 ± 0.05
Gravel (g kg^{-1})			518 ± 30	nd
Fine earth		Sand (g kg^{-1})	655 ± 55	60 ± 5
		Silt (g kg^{-1})	235 ± 53	687 ± 29
		Clay (g kg^{-1})	110 ± 6	253 ± 27
		$CaCO_3$ (g kg^{-1})	153 ± 12	974 ± 10
		OC (g kg^{-1})	3.5 ± 0.7	0.55 ± 0.05
		N (g kg^{-1})	0.33 ± 0.04	0.06 ± 0.01
		pH	8.5 ± 0.1	8.6 ± 0.2
	Saturation extract	EC (dS m^{-1})	0.56 ± 0.06	2.2 ± 0.1
		Ca^{2+} (mg L^{-1})	83 ± 12	201 ± 10
		Mg^{2+} (mg L^{-1})	11 ± 1	76 ± 4
		Na^+ (mg L^{-1})	34 ± 4	195 ± 6
		K^+ (mg L^{-1})	2.8 ± 0.2	21 ± 2
		SO_4^{2-} (mg L^{-1})	111 ± 10	400 ± 7
		Cl^- (mg L^{-1})	31 ± 4	208 ± 13
		NO_3^- (mg L^{-1})	0.40 ± 0.04	0.29 ± 0.03

BD = bulk density, OC = organic carbon, N = nitrogen, EC = electrical conductivity, nd = not detected.

3.2. Soils properties in 2013

The $CaCO_3$ content and particle-size distribution of the horizons sampled in May 2013 (Table 2) were similar to those of the original material from which they were formed (sampled in 2007). Thus, the $CaCO_3$ content and texture in the Ah, C, CA and A'h horizons, were similar to those of the topsoil (Table 1), whereas those in the C/A and 2C horizons were similar to those of the marble sludge. By contrast, the other soil properties showed greater differences.

The mean OC and N content in the Ah and A'h horizons of the soils sampled in 2013 (Table 2) increased considerably compared with the topsoil sampled in 2007 (Table 1). This increase was clearly different depending on the plot and the type of horizon (Fig. 2a). In the PT plots, the ratios between the mean values of OC and N content in the Ah horizons and those of the initial topsoil were 1.4 for the OC and 1.2 for the N; in the PTS ≤ 25 plots, these ratios were 2.5 for OC and 2.2 for N, whereas the PTS > 30 plots were 2.8 for OC and 2.4 for N. However, the largest increases in OC and N occurred in the A'h horizons, in which the prior ratios were 5.2 for OC and 3.9 for N in the PTS ≤ 25 plots, and 7.1 and 5.2, respectively, in the PTS > 30 plots. In the C, CA and 2C horizons of the PTS plots, the OC and N contents were also clearly higher than those of the topsoil and marble sludge sampled in 2007.

This increase in OC and N resulted in a strong increase of the TOCP and TNP (Fig. 2b) in the PTS ≤ 25 (1648 ± 303 g C m^{-2} and 156 ± 27 g N m^{-2}) and PTS > 30 plots (2852 ± 401 g C m^{-2} and 283 ± 35 g N m^{-2}) compared with the PT plots (757 ± 77 g C m^{-2} and 68 ± 6 g N m^{-2}). Because the carbon sequestered for each soil is the difference between the carbon content in 2013 and 2007 (prior to hydroseeding) and the treatment was extended by a period of 68 months, the rate of carbon and nitrogen sequestration in the soils of the plots with marble sludge ranged between 187 ± 38 g C m^{-2} year^{-1} (PTS ≤ 25) and 363 ± 62 g C m^{-2} year^{-1} (PTS > 30) and between 17 ± 3 g N m^{-2} year^{-1} (PTS ≤ 25) and 36 ± 5 g N m^{-2} year^{-1} (PTS > 30), which were clearly higher than those observed in the PT plots (16 ± 1 g C m^{-2} year^{-1} and 0.9 ± 0.3 g N m^{-2} year^{-1}).

The decomposition of the organic matter resulted in the formation of humic compounds with relatively high molecular size, as indicated by the highest HA concentration in relation to FA in all the horizons

Table 2
Selected properties of the horizons sampled in 2013 in each plot.

						Fine earth							
Plot	Horizon	Depth (cm)	BD (g cm^{-3})	EC (dS m^{-1})	Gravel	Sand	Silt	Clay	$CaCO_3$ (g kg^{-1})	OC	N	HA	FA
1PT	Ah	0–7	1.59	0.71	514	653	237	110	137	4.8	0.39	0.93	0.37
	C1	7–17	1.68	0.45	487	634	241	125	158	3.7	0.34	0.53	0.46
	C2	17–27	1.63	0.39	552	629	242	129	151	3.6	0.34	0.53	0.52
2PT	Ah	0–8	1.58	0.80	625	661	224	115	144	4.5	0.38	0.82	0.35
	C1	8–18	1.70	0.48	573	645	237	118	152	3.8	0.34	0.42	0.35
	C2	18–28	1.67	0.40	600	637	230	133	151	3.7	0.34	0.42	0.35
3PT	Ah	0–7	1.60	0.73	558	700	233	67	132	5.1	0.43	0.90	0.36
	C1	7–17	1.67	0.47	621	669	251	80	152	3.7	0.35	0.45	0.31
	C2	7–28	1.68	0.44	660	638	248	114	146	3.6	0.35	0.40	0.33
1PTS ≤ 25	Ah	0–5	1.59	1.02	682	689	258	53	125	8.0	0.71	1.16	0.51
	C	5–16	1.63	0.69	661	671	230	99	140	5.4	0.50	0.84	0.59
	A'h	16–21	1.55	1.65	639	648	262	90	222	16.3	1.61	2.10	0.81
	2C1	21–26	1.23	1.71	14	78	682	240	881	3.1	0.28	0.50	0.41
	2C2	26–36	1.25	1.92	nd	73	701	226	963	1.7	0.16	0.14	0.28
2PTS ≤ 25	Ah	0–8	1.59	1.14	605	662	241	97	119	8.6	0.88	1.87	0.65
	C	8–20	1.66	0.65	648	662	238	100	142	5.6	0.54	0.76	0.53
	A'h	20–23	1.64	2.37	618	659	227	114	197	18.1	1.69	2.31	0.95
	2C1	23–28	1.19	1.71	nd	81	725	194	871	3.8	0.36	0.67	0.61
	2C2	28–37	1.21	1.67	nd	69	705	226	973	1.7	0.16	0.17	0.26
3PTS < 25	Ah	0–8	1.65	1.42	619	701	218	81	126	9.7	0.89	2.42	0.87
	C	8–20	1.68	0.63	575	655	254	91	135	5.8	0.55	0.81	0.68
	A'h	20–25	1.63	2.54	668	594	292	114	230	20.2	1.84	3.16	1.09
	2C1	25–30	1.24	1.66	17	69	718	213	881	4.4	0.42	0.66	0.69
	2C2	30–41	1.27	1.75	nd	61	742	197	973	1.3	0.12	0.13	0.23
1PTS > 30	Ah	0–9	1.69	1.04	703	674	237	89	151	8.3	0.83	0.85	0.60
	C	9–19	1.65	0.68	674	681	242	77	147	4.4	0.44	0.56	0.50
	CA	19–27	1.64	0.83	640	713	229	58	143	10.6	0.98	2.68	0.78
	A'h	27–33	1.60	2.90	664	664	258	78	285	23.1	2.61	5.43	1.53
	A/C	33–38	1.31	1.96	21	196	649	155	853	5.1	0.48	0.66	0.56
	2C	38–49	1.24	1.87	nd	73	680	247	958	1.5	0.15	0.15	0.24
2PTS > 30	Ah	0–8	1.63	1.31	589	728	186	86	138	9.4	0.89	2.56	0.81
	C	8–18	1.69	0.87	613	703	205	92	146	5.9	0.55	0.93	0.73
	CA	18–27	1.67	0.95	608	689	214	97	140	9.5	0.86	0.69	0.65
	A'h	27–33	1.62	3.06	579	650	254	96	312	24.4	2.79	6.27	1.36
	A/C	33–38	1.42	2.19	23	161	697	142	837	6.1	0.58	0.79	0.75
	2C	38–47	1.25	1.84	nd	58	730	212	960	1.7	0.16	0.15	0.28
3PTS > 30	Ah	0–8	1.59	1.47	649	694	215	91	151	12.1	1.12	2.52	0.80
	C	8–18	1.68	0.85	631	668	250	82	159	5.9	0.57	0.72	0.62
	CA	18–28	1.70	0.91	682	649	271	80	147	10.4	0.95	0.48	0.44
	A'h	28–34	1.63	2.96	619	606	308	86	326	27.2	2.79	5.74	1.86
	A/C	34–39	1.35	1.93	19	172	684	144	861	6.9	0.66	0.78	0.66
	2C	39–48	1.22	1.76	nd	63	707	230	970	1.5	0.14	0.13	0.24

BD = bulk density, EC = electrical conductivity, OC = organic carbon, N = nitrogen, HA = humic acids, FA = fulvic acids.

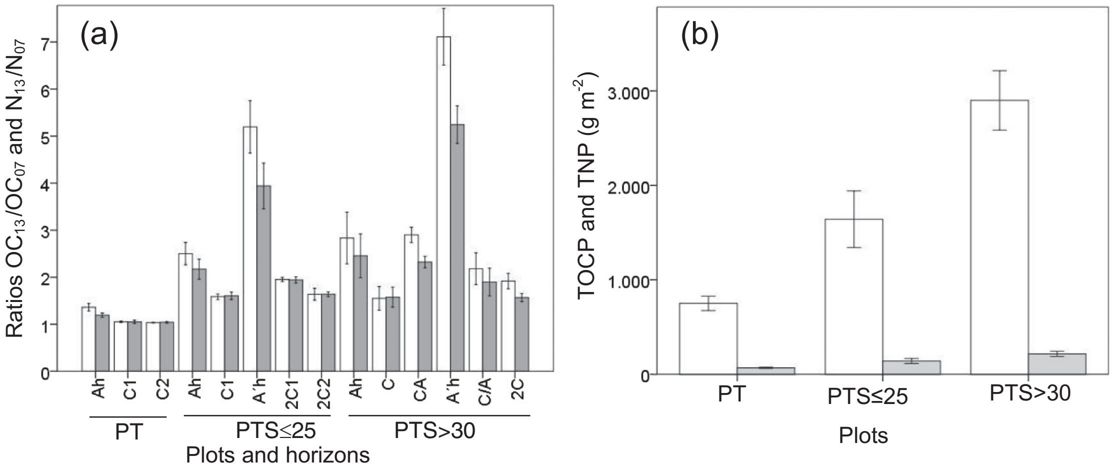

Fig. 2. (a) Mean value and standard deviation of the ratios between the OC (white) and N (grey) content in the soils sampled in 2013 and in the initial topsoil (OC_{13}/OC_{07} and N_{13}/N_{07}, respectively), (b) mean and standard deviation of the total organic carbon (white) and total nitrogen (grey) in the plots studied (TOCP and TNP, respectively).

sampled (Table 2). The HA + FA/OC ratio ranged from 0.23 to 0.27, without significant differences between horizons. However, the HA concentration increased in relation to FA concentration as the OC content increased. Thus, the HA/FA ratio was significant and linearly related to the OC content by the following equation:

$$\mathrm{HA/FA} = 0.762 + 0.134\ \mathrm{OC}\ (\mathrm{g\ kg^{-1}}) \quad r^2 = 0.713 \quad P < 0.001 \tag{2}$$

The mean pH values did not show large differences in most horizons, ranging between 8.6 and 8.8. Only the mean pH of the A'h horizons showed a clear decrease, with values of approximately 8.3 in the PTS ≤ 25 plots and approximately 7.8 in the PTS > 30 plots. The pH values were significant and linearly related to the OC content by the following equation:

$$\mathrm{pH} = 8.8\text{–}0.034\ \mathrm{OC}\ (\mathrm{g\ kg^{-1}}) \qquad r^2 = 0.780 \qquad P < 0.001 \tag{3}$$

The CEC was also significantly related to the OC content through a linear equation:

$$\mathrm{CEC}\ (\mathrm{cmol_+kg^{-1}}) = 0.755 + 0.519\ \mathrm{OC}\ (\mathrm{g\ kg^{-1}}) \qquad r^2 = 0.797 \qquad P < 0.001 \tag{4}$$

Similar to the OC and N concentrations, the EC values (Table 2) and the concentration of ions in the saturation extracts (Fig. 2) were clearly higher in the A'h horizons followed by the C/A and 2C horizons. Both parameters were also higher in the Ah horizons than in the C horizons. In the C and 2C horizons, the EC values and ion concentration were in the vicinity of those of the topsoil and marble sludge, respectively. In the PT plots, Ca^{2+} and SO_4^{2-} were the dominant ions, whereas in the PTS plots, in addition to Ca^{2+} and SO_4^{2-}, clear increases in the Mg^{2+}, Na^+ and Cl^- concentrations were observed, especially in the A'h, C/A and 2C horizons. The NO_3^- content was minor ($< 2\ \mathrm{mg\ L^{-1}}$) and significant, and linearly related to the OC content by the following equation:

$$\mathrm{NO_3^-}(\mathrm{mg\ L^{-1}}) = 0.287 + 0.060\ \mathrm{OC}\ (\mathrm{g\ kg^{-1}}) \qquad r^2 = 0.892 \qquad P < 0.001 \tag{5}$$

4. Discussion

The soils of the PT plots were Hyperskeletic Leptosols according to the IUSS Working Group WRB (2006), with < 20% fine earth average over a depth of 75 cm from the soil surface. The only distinctive feature of these soils was the formation on the surface of an Ah horizon, with a slight increase in the OC content compared to the underlying C horizons.

The soils of the PTS plots were Spolic Technosols, with 20% or more of solid substances from an industrial manufacturing process in the upper 100 cm from the soil surface. The morphology of these soils was characterized by the formation of two Ah horizons, one at the surface and another at depth, separated by a C horizon. The formation of the subsurface Ah horizons is atypical and is not considered in the Guidelines for Soil Description (FAO, 2006), which only considered the formation of a subsurface organic horizon when it is formed by illuviation (Bh). To distinguish between both horizons, the one located at depth was labelled A'h.

Both horizons were formed by accumulation of organic matter and N. The Ah horizon was mainly derived from organic remains from the aerial part and superficial roots of vegetation, and the A'h horizon was presumably linked to the high root density observed throughout its thickness (Chirinda et al., 2014). The higher moisture content in the W layer as a result of the high water-holding capacity of the sludge (Simón-Torres et al., 2014), must have been the trigger that favoured the development of perennial species, such as *Piptatherum miliaceum* (L.) Coss (Gómez Mercado et al., 2015), which shows a dense and fasciculate system of roots whose development gave rise to the formation of the A'h horizon.

The greater accumulation of OC and N in the A'h horizons from the PTS > 30 plots compared to those from the PTS ≤ 25 plots would be justified by the increase in moisture content in the W layer by increasing the thickness of the added topsoil (Simón-Torres et al., 2014). The greater development of the A'h horizons of the PTS > 30 plots compared with the PTS ≤ 25 plots, as evidenced by their higher OC content and greater average thickness (Table 2), would justify the formation of transitional CA and C/A horizons in the soils of these plots, the first with an intermediate OC content between the overlying C horizon and the subjacent A'h horizon and the second formed by fragments of the 2C horizon surrounded by the A'h horizon material (Fig. 1e). These transitional horizons reveal that the development of the A'h horizons would progress both towards the surface and with depth. Because the marble sludge acts as a reservoir of water that stimulates the development of the roots, the depth at which it should be placed to be more effective would be related both to the climatic conditions and the water-holding capacity of the added topsoil (Simón-Torres et al., 2014).

The highest OC content in the A'h horizons compared to the Ah horizons could be related to the different degree of decomposition of the organic matter in both horizons. This decomposition resulted in the predominance of humic compounds with a relatively high molecular size (HA), which intensified with increasing OC content (Eq. (2)). The high HA concentration and the youth of litter (up to 5 years old) suggest that the humic compound originated from the derived lignin (Kang and Felbeck, 1965) and represents the early stages of the humification process (Simón et al., 1994). The structural complexity of the lignin (polymer of phenylpropane units) makes it resistant to microbial degradation, especially in terms of sunlight deficiency (Austin and Ballaré, 2010). In addition, the lignin-derived compound forms a barrier that limits the access of enzymes to more labile organic compounds (Pauly and Keegstra, 2008). Therefore, the absence of sunlight in the A'h horizons as a result of its location away from the soil surface could justify the slowdown of the organic debris decay and the higher accumulation of OC in these horizons. However, although the organic debris decay was small, the C/N ratio was also relatively low (approximately 12 in the Ah horizon and approximately 14 in the A'h horizons), which could be justified by the increases in the PTS plots of biomass from *Anthyllis cytisoides* L. (Gómez Mercado et al., 2015), which is a leguminous plant with nitrogen-fixing ability.

The increase in OC content resulted in a decrease in pH (Eq. (3)) and an increase in CEC, the former due to the acidity of the formed humic compounds and the latter because the negative electric charges tend to be located on the surface of the organic matter at a higher concentration than on any other solid surface of the soil. Similarly, the increase in OC resulted in an increase in EC (Table 2) and dissolved ion concentrations (Fig. 3), indicating that the root development involves a more intense suction of the soil solution and soluble ions tend to concentrate in the root environment. Because EC and the concentration of soluble ions, especially Mg^{2+}, Na^+ and Cl^-, were clearly higher in the marble sludge than in the topsoil (Table 1 and Fig. 3), the largest increase of these parameters in the A'h horizons in relation to the other horizons formed in the topsoil reveals that the water retained in the 2C horizons was suctioned by the roots of the A'h horizons.

The increase in OC content in the soils of the PTS plots resulted in a high rate of carbon sequestration (between $187\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$ and $363\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$), which was on the order of those obtained by Ahirwal et al. (2017) in reclaimed coal mine soils with *Prosopis juliflora* (Sw.) DC. ($260\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$) and De Deyn et al. (2011) in a grassland improved with the addition of fertilizer and legume seeds ($317\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$) and was considerably higher than those obtained by Franzluebbers (2005) in pastures ($140\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$) and Baumert et al. (2016) in *Jatropha curcas* L. systems ($62\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$). Therefore, considering that most carbon sequestration calculations are conducted in the first 25–30 cm of the soil, which underestimate the amount of carbon sequestered (Olson and Al-

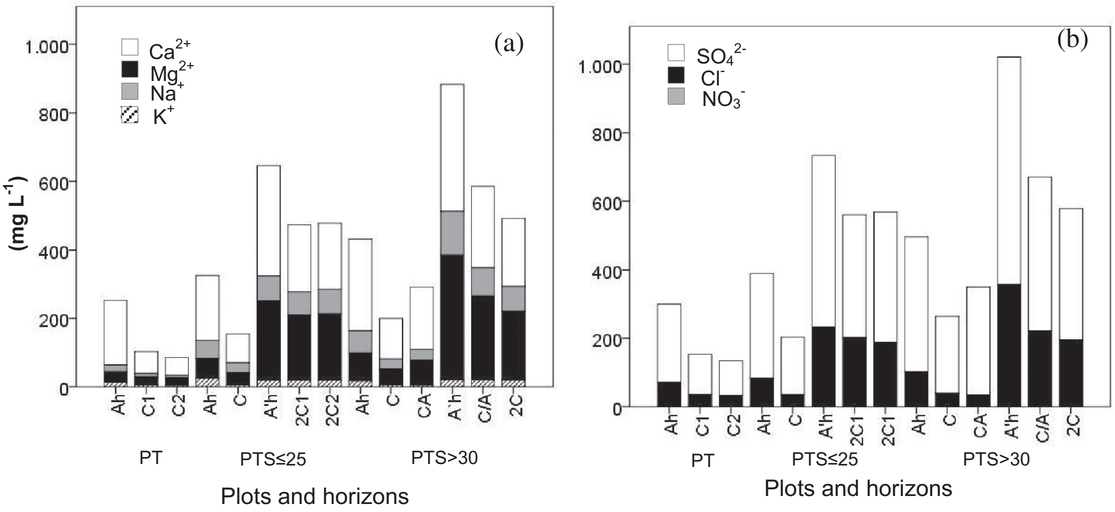

Fig. 3. Mean concentration of selected cations (a) and anions (b) in the saturations extracts of the horizons of the studied plots.

Kaisi, 2015; Premrov et al., 2017), but were made across the depth of the soil in our case, it could be surmised that the soils with marble sludge behave as carbon sinks, especially because these soils have not yet reached equilibrium and the OC and N content can continue to increase over time. Thus, medium or long term monitoring of these plots is required to constrain the true extent of carbon sequestration in quarry dumps restored with marble sludge.

The increased concentrations of OC, nitrogen and soluble ions and CEC values in the soils from the PTS plots suggest an enhancement in fertility (especially in the A'h horizons), which would presumably contribute to accelerating plant succession and the development of the ecosystem (Kalinina et al., 2015; Bätz et al., 2015). These benefits indicate that the sludge from the marble industry would be a beneficial resource for improving the restoration of this type of stone slopes. However, these results have been obtained under very specific conditions; hence, it is necessary to implement this restoration technique in different weather conditions and topsoil characteristics, to extend the knowledge of the benefits of restoring quarry dumps with marble sludge.

5. Conclusion

In the restoration of this type of quarries, marble sludge addition prior to topsoil addition promoted root growth, especially in the contact zone between the topsoil and sludge, where an organic-mineral horizon away from the soil surface was formed. The result was the formation of soils with an atypical morphology characterized by the formation of Ah horizons both at the surface and at depth, and a rate of OC sequestration similar or higher than those reported by other authors, indicating that the soils restored with marble sludge can behave as carbon sinks. Moreover, the addition of marble sludge increased soil fertility, suggesting that both the vegetation and ecosystem could accelerate their evolution. Monitoring these plots is necessary to more accurately assess the effect of marble sludge on ecosystem evolution and the ability of soils to sequester carbon.

Acknowledgements

This study was funded by the project P07-RNM-03303 (Andalusian Government and European Regional Development Founds) and the contract of collaboration UAL-CTAP F08/06. We would also like to thank CTAP for the restoration work at the dump deposit.

References

Ahirwal, J., Maiti, S.K., Reddy, M.S., 2017. Development of carbon, nitrogen and phosphate stocks of reclaimed coal mine soil within 8 years after forestation with *Prosopis juliflora* (Sw.) Dc. Catena 156, 42–50.

Austin, A.T., Ballaré, C.L., 2010. Dual role of lignin in plant litter decomposition in terrestrial ecosystems. Proc. Natl. Acad. Sci. U.S.A. 107, 4618–4622.

Bätz, N., Verrecchia, E.P., Lane, S.N., 2015. Organic matter processing and soil evolution in a braided river system. Catena 126, 86–97.

Baumert, S., Khamzina, A., Vlek, P.L.G., 2016. Soil carbon sequestration in *Jatropha curcas* systems in Burkina Faso. Land Degrad. Dev. 27, 1813–1819.

Blake, G.R., Hartge, K.H., 1986. Bulk density. In: Klute, A. (Ed.), Methods of Soil Analysis. Part I. Physical and Mineralogical Methods. American Society of Agronomy, Inc., Madison (WI), pp. 363–375.

Bote, D., Valladares, F., Matesanz, S., Tena, D., 2005. Importancia de la tierra vegetal en la restauración de desmontes. Revista Montes 80, 19–24.

Brofas, G.L., 2001. Reclamation of lands disturbed by mining activities. Protection of the natural environment and restoration of degraded areas. In: 9th Annual Conference of HFA, Hellenic Forestry Association, Kozanipp. 52–66.

Chirinda, N., Roncossek, S.D., Heckrath, G., Elsgaard, L., Thomsen, I.K., Olesen, J.E., 2014. Root and soil carbon distribution at shoulderslope and footslope positions of temperate toposequences cropped to winter wheat. Catena 123, 99–105.

Clemente, A.S., Werner, C., Máguas, C., Cabral, M.S., Martins-Loução, M.A., Correia, O., 2004. Restoration of a limestone quarry: effect of soil amendments on the establishment of native Mediterranean sclerophyllous shrubs. Restor. Ecol. 12, 20–28.

De Deyn, G.B., Shiel, R.S., Ostle, N.J., McNamara, N.P., Oakley, S., Young, I., Freeman, C., Fenner, N., Quirk, H., Bardgett, R.D., 2011. Additional carbon sequestration benefits of grassland diversity restoration. J. Appl. Ecol. 48, 600–608.

FAO, 2006. Guidelines for Soil Description, 4th edition. (Rome).

Franzluebbers, A.J., 2005. Soil organic carbon sequestration and agricultural greenhouse gas emissions in the southeastern US. Soil Tillage Res. 83, 120–147.

García-Fayos, P., García-Ventoso, B., Cerdà, A., 2000. Limitations to plant establishment on eroded slopes in southeastern Spain. J. Veg. Sci. 11, 77–86.

García-Palacios, P., Soliveres, S., Maestre, F.T., Escudero, A., Castillo-Monroy, A.P., Valladares, F., 2010. Dominant plant species modulate responses to hydroseeding, irrigation and fertilization during the restoration of semiarid motorway slopes. Ecol. Eng. 36, 1290–1298.

Gómez Mercado, F., de Haro Lozano, S., Delgado Fernández, I.C., Simón Torres, M., 2015. Using marble sludge increase the success of dump deposit restoration under Mediterranean climate. Ecol. Eng. 84, 305–310.

Heneghan, L., Miller, S.P., Baer, S., Callaham Jr., M.A., Montgomery, J., Pavao-Zuckerman, M., Rhoades, C.C., Richardson, S., 2008. Integrating soil ecological knowledge into restoration management. Restor. Ecol. 16, 608–617.

IUSS Working Group WRB, 2006. World Reference Base for Soil Resources 2006. World Soil Resource Reports no. 103. FAO, Rome.

Jones Jr., J.B., 1991. Kjeldahl Method for Nitrogen (N) Determination. Micro-Macro Publishing, Athens, Georgia.

Kalinina, O., Goryachkin, S.V., Lyuri, D.J., Giani, L., 2015. Post-agrogenic development of vegetation, soils, and carbon stocks under self-restoration in different climatic zones of European Russia. Catena 129, 18–29.

Kang, K.S., Felbeck, G.T., 1965. A comparison of the alkaline extract of tissues of *Aspergillus niger* with humic acids from three soils. Soil Sci. 99, 175–181.

Kononova, M.M., 1966. Soil Organic Matter. Its Nature, Its Role in Soil Formation and in Soil Fertility, Second Ed. Press. Oxford, Pergamon.

Loveland, P.J., Whalley, W.R., 1991. Particle size analysis. In: Smith, K.A., Mullis, C.E. (Eds.), Soil Analysis: Physical Methods. Marcel Dekker, New York, pp. 271–328.

Milly, P.C.D., 1994. Climate, soil water storage, and the average annual water balance.

Water Resour. Res. 30, 2143–2156.

Mingorance, M.D., Barahona, E., Fernández-Gálvez, J., 2007. Guidelines for improving organic carbon recovery by the wet oxidation method. Chemosphere 68, 409–413.

Oliveira, G., Nunes, A., Clemente, A., Correia, O., 2011. Effect of substrate treatments on survival and growth of Mediterranean shrubs in a revegetated quarry: an eight-year study. Ecol. Eng. 37, 255–259.

Olson, K.R., Al-Kaisi, M.M., 2015. The importance of soil sampling depth for accurate account of soil organic carbon sequestration, storage, retention and loss. Catena 125, 33–37.

Pallavicini, Y., Alday, J.G., Martinez-Ruiz, C., 2015. Factors affecting herbaceous richness and biomass accumulation patterns of reclaimed coal mines. Land Degrad. Dev. 26, 211–217.

Pauly, M., Keegstra, K., 2008. Cell-wall carbohydrates and their modification as a resource for biofuels. Plant J. 54, 559–568.

Premrov, A., Cummins, T., Byrne, K.A., 2017. Assessing fixed depth carbon stocks in soils with varying horizon depths and thicknesses, sampled by horizon. Catena 150, 291–301.

Rhoades, J.D., 1982. Cation exchange capacity. In: Page, A.L. (Ed.), Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties. American Society of Agronomy, Inc., Madison (WI), pp. 149–157.

Simón, M., García, I., Gil, C., Polo, A., 1994. Characteristics of the organic matter of Mediterranean high-mountain soils. Geoderma 61, 119–131.

Simón-Torres, M., del Moral-Torres, F., de Haro-Lozano, S., Gómez-Mercado, F., 2014. Restoration of dump deposits from quarries in a Mediterranean climate using marble industry waste. Ecol. Eng. 71, 94–100.

Tormo, J., Bochet, E., García-Fayos, P., 2007. Roadfill revegetation in semiarid Mediterranean environments. Part II: topsoiling, species selection, and hydroseeding. Restor. Ecol. 5, 97–102.

U.S. Salinity Laboratory Staff, 1954. Diagnosis and Improvement of Saline and Alkali Soils. Handbook 60. US Department of Agriculture, Washington DC.

Williams, D.E., 1949. A rapid manometric method for determination of carbonate in soils. Soil Sci. Soc. Am. Proc. 13, 127–129.

Zhang, H., Chu, L.M., 2010. Rehabilitation of quarries in Hong Kong. In: 2010 International Conference on Environmental Engineering and Applications (ICEEA 2010), pp. 214–217.