Effects of technosols based on organic amendments addition for the recovery of the functionality of degraded quarry soils under semiarid Mediterranean climate: a field study

Authors

Rocío Soria[1], José A. González-Pérez[2], José Mª de la Rosa[2], Layla M. San Emeterio[2,3], Miguel A. Domene[4], Raúl Ortega[1], Isabel Miralles[1,*]

Affiliations

[1]Department of Agronomy & Center for Intensive Mediterranean Agrosystems and Agri-food Biotechnology (CIAIMBITAL), University of Almeria, E-04120, Almería, Spain.

[2]Instituto de Recursos Naturales y Agrobiología de Sevilla, Consejo Superior de Investigaciones Científicas (IRNAS-CSIC), MOSS Group. Av. Reina Mercedes 10, 41012, Seville, Spain.

[3]Med_Soil Research Group, University of Seville, C/ Profesor García González, 1, 41012 Seville, Spain.

[4]Experimental Station Cajamar, Department of Food and Health, E-04710, El Ejido. Almería, Spain.

*Corresponding author: Dra. Isabel Miralles (imiralles@ual.es).

Abstract

This study aims to evaluate the effects of technosols made with different organic amendments to restore degraded soils in a semiarid limestone quarry. The effects on soil quality, functionality and organic matter dynamics of the technosols amended with waste of gardening, greenhouse horticultural, stabilized sewage sludge and two mixtures of sludge with both vegetable composts were assessed. Several physical and chemical properties, humus fractions, soil respiration and molecular composition was performed after 6 and 18 months. Un-amended soils, and nearby natural undegraded soils served as reference. Amended technosols increased water retention capacity, electrical conductivity, total organic carbon and nitrogen, respect to not amended and natural soils. Humus fraction composition was not altered over time. Un-amended soils, very poor in organic matter, did not show any pyrolyzable compounds or labile soil organic matter by thermogravimetry. In contrast, the pyrochromatograms of natural soils showed lignocellulosic materials, polypeptides and a noticeable presence of alkylic compounds. In technosols with both types vegetable compost, the organic matter structure was more complex, showing compounds from lignin-derived and long-chain alkyl, polysaccharides, chlorophyll isoprenoids and nitrogen. In sludge technosol, a set of sterols was outstanding. The mixtures showed a molecular fingerprint of materials derived from the decomposition of the organic amendments that formed them. These signs of the contribution of different organic matter forms derived from the amendments were also reported by the series exothermic peaks found in the calorimetry. This short-term study indicates a clear effect of the amendments on the recovery of soil organic matter and presumably of its functionality. After the amendments application, microbial activity and soil respiration rates increased rapidly but ceased 18 months later. The molecular composition of the organic matter of the soils amended with plant compost was very similar to that of natural, non-degraded soils in nearby areas.

Keywords

Soil recovery, technosols, composting, humic substances, thermal analysis, analytical pyrolysis

1. Introduction

Globally, it is estimated that 33% of the Earth's soil have been degraded by human activity (FAO, 2019). Among different drivers, mining produces serious soil impacts and occupies more than 1 % of the territory (Carabassa et al., 2020a; Šálek, 2012). Specifically opencast mining is a high-impact disturbance to terrestrial ecosystems (Ibarra and De Las Heras, 2005; Smirnov et al., 2021) and causes severe soil degradation, often irreversible (Larondelle and Haase, 2012; Soliveres et al., 2021). This problem is especially sensitive in arid and semi-arid lands due to extreme climatic conditions and scarcity of soil nutrients hinders the cover vegetation development after mining (Gonzalez-Dugo et al., 2005; Josa et al., 2012; Ortega et al., 2020), presenting severe difficulties to recover their functionality (Moreno-de las Heras, 2009).

The soil organic matter (SOM) is considered as determinants of soil quality and health, a concept considered synonymous with the measure of a soil's ability to carry out its ecological functions (Hoffland et al., 2020). SOM responds relatively quickly to changes in both biotic and abiotic conditions, it is key in regulating and restoring the balance of environmental processes occurring in the soil, in what is defined as the "resilience" of the soil to recover from external variations (ECCE, 2005). The development of functional soils with adequate levels of OM and nutrient cycling reactivation is a precondition for ecosystem recovery (Lal, 2015; Moreno-de las Heras, 2009) and the integration of inputs an opportunity to improve soil resilience (Reddy et al., 2020). In this context, the use of organic amendments for the creation of artificially-manufactured prepared soils, called technosols or anthroposols (Larney and Angers, 2012) have been proposed as a possible solution to restore lands degraded by mining (Carabassa et al., 2020b, 2018; Fabbri et al., 2021; Leguédois et al., 2016).

Beside soil degradation, the increase of organic waste worldwide poses a global problem that requires urgent solutions (Hernández et al., 2015). Therefore, recycling and incorporation of organic waste as organic amendments for the regeneration of degraded soils, through the creation of technosols, responds to a strategy of integration into the circular economy (Fabbri et al., 2021; Hueso-González et al., 2018), while promoting to natural capital recovery (Abhilash, 2021; Alba-Patiño et al., 2021). In addition, it leads to a significant increase in OM (Bastida et al., 2008) and contributes to improve the quality and fertility of degraded soils by creating edaphic conditions that facilitate plant colonization (Asensio et al., 2014; Hueso-González et al., 2018).

Numerous studies on recycling organic wastes to amend technosols in mining areas have focused on the use of organic amendments or composts from waste of different origins (Asensio et al., 2013; Watkinson et al., 2017). The application of these organic wastes improves the chemical, physical and microbiological characteristics (Breton et al., 2016; Bukar et al., 2019; Rodríguez-Berbel et al., 2021) and it is effective strategy to soil ensure an immediate OM increase, enrich the soil with humic-like compounds and macro- and micronutrients (Hernández et al., 2015). Likewise, the improvement of the above-mentioned soil properties depends mainly on OM chemical composition provided by organic amendments (Ye et al., 2019). Nevertheless, there is a great variability of the OM composition depending on its origin and nature, affecting its decomposition rate and long-term maintenance (Larney and Angers, 2012; Carabassa et al., 2020b). The SOM quality generally depends on the proportion and distribution of labile and recalcitrant forms, with the highest quality and comparatively more resilient SOM being that with a higher degree of humification, aromaticity and complexity in its molecular structure (Arias et al., 2005). Therefore, understanding the dynamics and molecular composition of OM contributed by organic amendments would provide important information on soil functioning, the evolution of technosols (Pascaud et al., 2016) and their effectiveness in the restoration actions. Due to the complexity of SOM, a combination of chromatographic and thermal analysis tools has been successfully employed to investigate it. Thermal analysis methods, specifically thermogravimetry-differential scanning calorimetry (TG-DSC), have been previously used with success to characterize chemical changes in SOM fractions, degraded plant tissue, and compost (De la Rosa et al., 2008; Dell'Abate et al., 2003; Lopez-Capel et al., 2006). TG-DSC has also been used to compare the proportions of reactive and more stable components in organic matter fractions under contrasting conditions (Lopez-Capel et al., 2005), and to different forms of pyrogenic carbon (Leifeld, 2007). Analytical pyrolysis is an effective tool to characterize the chemical composition, evolution and molecular markers of SOM (Derenne and Quéné, 2015). Specifically, pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS), provides not only value information about the SOM chemical structure (De la Rosa et al., 2008), but also about the origin of the different components and of a wide range of SOM products related to the origin of the analysed material (De la Rosa et al., 2012; González-Vila et al., 2009) and an opportunity to evaluate the evolution and dynamics (Jiménez-Morillo et al., 2016; Picó and Barceló, 2020).

We hypothesize that the different organic amendments applied to the soil severely degraded by the mining activities and subjected to the extreme climatic conditions typical of semi-arid soils will result in a different SOM composition. This, in turn would exert a different evolution in the technosols, conferring distinct physical and chemical properties to the restored soils. Therefore, the main objective of this work is to investigate SOM evolution and its chemical composition at the molecular level, as well as the physical and chemical soil properties in the restored technosols.

2. Materials and methods

2.1. Study site

The area of study is located in a limestone quarry used for the extraction of aggregates in an exhausted mine area with severely degraded soils sited about 15 km from Almería city (SE, Spain). Geographically is located at the position 36 55’ 18’’ N, 2º 30’ 40’’ W between Sierra de Gádor (dolomites and Cenozoic limestones) and intermountain Tertiary basin formed by Tortonian loams (high Miocene) composed mainly by calcareous sandstones and calcitic-gypsiferous mudstones (Luna et al., 2016a). The dominant climate of this area is semi-arid Mediterranean, with irregular temperatures and rainfall. Summers are hot and dry, with maximum temperatures recorded in August of 31 ºC and minimum temperatures of approximately 8 °C in January, and high evapotranspiration rates reaching 1225 mm year-^{1} (data recorded at Alhama de Almería weather station located at 4 km of distance from the study area). The average annual rainfall is 242 mm distributed mainly in autumn and winter. The experimental site was located on an area completely exploited by mining activity and unsloped terrain at an altitude of 362 m. a. s. l. devoid of natural vegetation cover. The resulting post-mining substrate consisted of a mixture of calcareous sandstones rock fragments and loams with clayey texture (Soria et al., 2021), compacted and with high resistance to plants development. In adjacent unexploited locations shallow soils are found over limestones and dolomites with calcareous sandstones and loamy loams or sandy or silty loams forming Regosols (IUSS Working Group WRB, 2015). Native vegetation corresponds to *Macrochloa tenacissima* (L.) Kunth *(=Stipa tenacissima* L.*)* as main species, accompanied by small shrubs such as *Ulex parviflorus* Pourr and *Anthyllis cytisoides* L. among others, as well as dispersed individuals of *Maytenus senegalensis* (Lam.) Exell, *Pistacia lentiscus* L. and *Rhamnus lycioides* L. (Luna et al., 2016b).

2.2. Experimental Design

A total of 18 experimental plots (10 m × 5 m each one) were established in May 2018 on a disturbed site using a random block design. Thus, three experimental plots for each treatment (3 replicates) with five different organic amendments treatments were settled and monitored. First, the topsoil (0-20 cm) of the plots was de-compacted and homogenized using machinery supplied by the mining company CEMEX-Spain. Then, the organic amendments were added in a single dose and the amounts used to prepare technosols were calculated to increase organic matter content by 3% in each plot. These organic amendments consisted of: i) compost from green garden waste (CG) applied with a dose of 28.66 kg m^{-2} (total organic C on dry weight = 40.5 % and moisture = 22.5 %); ii) Sewage sludge waste treated by mesophilic digestion and thermal dehydration at 70ºC (SS) was added at a rate of 14.74 kg m^{-2} (total organic C on dry weight = 66.4 % and moisture = 8.8 %); iii) Vegetable compost from greenhouse vegetables and fruits crop waste (CC) applied with a rate of 34.61 kg m^{-2} (total organic C on dry weight = 43.33 % and moisture = 40 %). In addition, two treatments were designed with mixtures of the above treatments, consisting of: iv) CG + SS (called Mix1) composed of a mixture of CG at a rate of 14.33 kg m^{-2} combined with SS at a rate of 7.73 kg m^{-2}; and v) CC + SS (called Mix2) with a CC amount of 17.30 kg m^{-2} mixed with SS at a rate of 7.73 kg m^{-2}. Untreated plots were used as control (CON) and natural soils taken from nearby area unaffected by mining were chosen as reference ecosystem (NAT) and as a model of the objective to be achieved in this restoration work. 40 plants of *Macrochloa* L. and 10 plants of *Olea europaea* L. var *sylvestris* Brot. were seeded in each experimental plot using a planting pattern of 1 m. These plant species were selected for their high survival rates in previous restorations plans in the same area (García-Ávalos et al., 2018). An initial drip irrigation after planting was carried out in order to ensure the plants survival because in semiarid

Mediterranean ecosystem during the first summer (Ramón-Vallejo et al., 2012; Sánchez et al., 2004). Initially, 3 L per plant were administered, and then 1 L per plant irrigated every two weeks after installation until the end of August, a total of 5 irrigations, thereafter they only received rainwater.

For each experimental plot composited samples made of 10 random subsamples taken from the topsoil layer (0-10 cm) were collected 6 months (T6) and 18 months (T18) after the addition of the organic amendments (17th december2018 and 24th November 2019 respectively). At the same time complete set of samples were also taken from the nearby reference soils (NAT) for comparison purposes. A total of 21 samples in each of the sampling campaigns (3 per treatment, 3 control and 3 of natural soil samples) were collected and taken to the laboratory. All the samples were immediately air-dried at 40 ºC, homogenized and sieved to fine earth (2 mm) A subsample was used for physical and chemical analysis and humic substances insolation and another for thermal and analytical pyrolysis analysis. For the last, an aliquot was taken from each of the three replicates and combined in composite samples representative of each sample and sampling time.

2.3. Elemental composition, physical and chemical properties of restored technosols

Soil pH and conductivity were determined in distilled water at a soil/solution ratio of 1:2.5 using a water quality meter instrument (LAQUA PH1100, HORIBA, Tokio, Japan). Total organic carbon (TOC) was determined by wet oxidation using the as modified by (Mingorance, 2007). Total nitrogen content (TN) was determined using an elemental analyser TCD detector (ELEMENTAR Rapid N; Elementar Analysensysteme GmbH, Hanau, Germany). C:N ratio was estimated as the ratio of TOC to TN. Soil water retention was determined to pF at -1500 KPa and -33 KPa by the Richards membrane method (Richards, 1941). Carbohydrate content (CH) was determined by cold extraction of 5 g in a soil-to-water ratio of 1:10 (w:v) using the anthrone–sulphuric acid method for soil

CH quantifyication developed by Brink, et al. (1960). The same extract was used to determine the polyphenol content (POL) by the Folin–Denis method (Ribéreau-Gayon, 1968). The absorbance to determine both compounds, CH (625 nm) and POL (750 nm) were measured in a UV-Vis spectrophotometer, (Spectronic Helios Gamma, Thermo Fisher Scientific, Waltham, Massachusetts, USA).

2.4. Isolation and quantification of soil humic fractions

A preparative approach and quantitative C analysis in major humic fractions was performed based in the protocol described in Duchaufour et al. (1975) and Dorado et al. (2003) and the organic C content in the different fractions determined by wet oxidation (Walkey and Black, 1934). In short, a light soil fraction consisting of non decomposed organic particles was first separated by flotation using 5 g soil samples suspended in 2 mol L^{-1} H_3PO_4, centrifuged and the suspension filtered and washed with distilled water. The soil residue was successively extracted with 0.1 mol L^{-1} $Na_4P_2O_7$ shaking for 3 h, and centrifuged of 4,500 rpm during 30 minutes (centrifuge Digicen 21, Ortoalresa, Spain) and further extractied with 0.1 mol L^{-1} NaOH, this process was repeated three times. The total humic extract (THA) was obtained by aggregating the successive alkaline supernatants after centrifugation. Two aliquots of this extract were taken and precipitated with H_2SO_4 (1:1 by volume), centrifuged at 3,000 rpm and the acid-insoluble fraction obtained was used for the quantitative estimation of humic acids (HAs). The acid soluble fulvic acid fraction (FAs) was calculated by difference. The results obtained from the isolation and quantification of HAs and FAs were then used to compare the grade of humification between the different modified technosols 6 and 18 months after the application of the organic amendments.

2.5. Thermal analysis

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) analyses were carried out simultaneously in a Discovery SDT 650 - Simultaneous TG-DSC (TA Instruments, New Castle, Delaware, USA). Briefly, for each sample approximately 20 mg of dry grounded material were placed in previously tared open alumina crucibles under a He flux (flow rate, 50 mL min^{-1}; 10 mL min^{-1} at the micro-furnace) heated and scanned at a rate of 20 K min^{-1} from 50 to 900 ºC. The heat of combustion (Q, in J g−1) and loss-on-ignition in TG_{tot} (%) were determined by integrating the DSC and TG curves (in Wg^{-1}) respectively over the region (50–850 ºC). The area under the TG curves was sub-divided into four sections representing different degrees of resistance to thermal oxidation (De la Rosa et al., 2008): (i) 50–200 ºC, (ii) 200–400 ºC; (iii) 400–600 ºC; and (iv) 600–850ºC. The resulting partial weights are designated as W1–W4, respectively.

2.6. Soil respiration and climatic variables

Soil respiration (SR) was measured in-situ the same days of the soil sample collection (T6 and T18). A portable infrared environmental gas analyzer system with a soil respiration chamber (IRGA) (EGM-4, PP-systems, Hitchin, UK) was used for SR analysis. The chamber had a volume of 1170 cm^3 and a flat surface of 78 cm^2. Measurement time was 90 s to ensure reliability. The CO_2 effluent (SR) measurements were carried out on radometrically located PVC collars in the soil (3 per experimental plot and 3 inserted in natural reference soil) with a diameter of 10 cm and 5 cm high, which were inserted in the soil at a height of 2 to 3 cm above the ground. A total of two soil respiration measurement field campaigns (T6 and T18) were carried out. At the same time, soil moisture (M) and soil temperature (T) were measured at 3 cm depth with a handheld readout sensor ProCheck and GS3 Greenhouse Sensor (Decagon Devices, Inc., Pullman, WA, USA). A pluviometer Rain-O-Matic Small (Pronamic ApS, Denmark) connected to a data logger and placed in the middle of the experimental area recorded rainfall events every 20 minutes for the entire duration of the experiment.

2.7. Analytical pyrolysis

Analytical pyrolysis (Py-GC/MS) was performed in duplicate using 15 mg of finely grounded composite samples representing each treatment.at 400 °C (1 min) in a micro furnace pyrolysis system (Frontier Lab. model 2020i, Fukushima, Japan) as described elsewhere (Jiménez-Morillo et al., 2020). In short, the pyrolizer was coupled with a GC/MS system (Agilent 6890) equipped with a low polar-fused silica capillary column (Hp 5MS-UI; 30 m x 250 µm x 0.25 µm). The GC was fitted with a mass selective detector (Agilent 5973 MSD) and mass spectra acquired at 70 eV. The following chromatographic conditions were used: the carrier gas was He (flow rate 1 ml min^{-1}), the oven was preheated to 50 °C for 1 min and then increased to 100 ºC at 30 ºC min^{-1}, from 100 to 300 ºC at 10 ºC min^{-1}, and then constant at 300 ºC for the last 10 min. The identification of compounds was achieved by single-ion monitoring (SIM) and by comparison with mass spectra libraries (NIST11 and Wiley7) and published spectra databases.

2.8. Statistical analyses

Significant differences in physical and chemical soil properties, OM fractions and soil respiration (SR) among the different restoration treatments, un-amendment and natural reference soils were studied using two way PERMANOVA analysis ($P > 0.05$), using permutation tests to obtain P values and does not rely on the assumptions of traditional parametric ANOVA (Anderson, 2001). Euclidean distances was used to obtain the samples similarity matrix with to check the effects of the soil restoration treatment and sampling date (T6 and T18) factor on each individual variable. Pairwise test comparisons were made using a multivariate analogue of the t test and by finding the probability levels by permutation (Eldridge et al., 2016) and results with $P < 0.05$ were reported by significant. The total number of permutations used was 999, and the Monte-Carlo test was used when the number of permutations found was less than 100. The statistical package PRIMER + PERMANOVA software (PRIMER-E Ltd., Plymouth Marine Laboratory, UK) for Windows was used for PERMANOVA (Anderson et al., 2008).

3. Results and discussion

3.1 Effect of organic amendments on physical and chemical properties of technosols

In general, the organic amendments changed the physical and chemical properties in restored technosols respect to CON and NAT soils (Table 1). Two-way PERMANOVA analysis showed significant differences ($P < 0.05$) in the physical and chemical soil parameters attending to soil treatment (SS, CG, CC, Mix1, Mix2, CON and NAT) and date of field campaign, but not between the factor interactions (treatment x date) (Supplementary Table 1; ST1).

As expected, the application of organic amendments clearly increased SOM contents in technosols that were maintained during the experiment, which could initially indicate an improvement in soil quality and functionality in technosols in the short term. Higher significant values of TOC and TN content than CON and NAT soils were found for both field sampling periods (T6 and T18). SS, Mix1, Mix2 and CC showed the highest significant ($P<0.05$) TOC and TN results, followed by CG, while for T18 CG showed similar values than the rest of amendments. Probably, there was no significant decrease in TOC and TN due to the continuous input of OM that the soils had from both planted and colonizing annual vegetation (Soria et al., 2021) and by root exudates (Bastida et al., 2006). Other authors such as Carabassa et al. (2018) have also considered that this underestimation of organic carbon could be attributed to biomass inputs from both vegetation. Likewise, CH and POL content were significant higher in the restored soils (Table 1). SS, Mix1 and Mix2 gave rise to the highest values and CC the lowest, followed the same pattern to both sampling campaign, indicating a greater amount of labile OM (Rodríguez-Berbel et al., 2021). Interestingly, CG showed no change in CH content over time. Nevertheless, CH content decreased notably in the second sampling (T18) respect the first campaign (T6), especially in SS, Mix1 and Mix2 that showed a decrease about 67 % to SS of the initial content and approximately a 55 % for mixtures (Table 1). This suggests a depletion of labile forms of carbon, which is in contrast to the behavior of labile OM in CG and CC, whose contents were lower. On the contrary, NAT showed no change in CH content and were non-existent in CON. This is important, considering that the soils of arid and semi-arid zones are poor in OM but with high resistance to biodegradation and high stability (Miralles et al., 2015) and also OM losses aggravated by degradation caused by mining as observed in CON soils where there were no traces of labile forms of OM (Table 1). It should be noted that a slight TOC content was quantified in CON, which could be due to the high active lime in the original soils (Soria et al., 2021) or to the organic amendment carried by the wind to the other experimental plots. In lesser proportion, a detriment of POL was also observed in all restored soils between T6 and T18, however CG content decreased by half, CC had the largest decrease in POL content, while SS and its mixtures had smaller changes.

Technosols restored with organic amendments showed an increase of EC and pH values significantly lower than unamended technosols (CON) and natural reference soils (NAT). Results corresponding to EC data showed a more notable reduction in CC and mixtures (Table 1) in T18 respect to T6 that could be attributed to absorption by colonizing halophytic vegetation described in Soria et al. (2021a) or rain washing (Ortega et al., 2020; Ros et al., 2003). SS maintained high EC levels for T18 probably due to the domestic origin of wastes (Domene and Saurí, 2007). The organic amendments also favoured water retention (pF) and water available for plants (Table 1). Zancada et al., (2004) reported an improvement in the water retention capacity of soils after organic amendment application that could be related with a improve a soil structure, stable aggregates and soil porosity related with the increased of TOC (Miralles et al., 2009).

3.1.1. Effect on the addition of organic amendments on the abundance of soil humic fractions

In general, the application of organic amendments was a source of humic substances to soil, such as has been reported by other authors (Albiach et al., 2001; Rodríguez-Vila et al., 2016). The total humic acid content (THA) was similar in restored technosols than natural reference soils (NAT) in both field samplings (T6 and T18) (Table 1). However, the un-amended technosols (CON) did not show the presence of humic substances with exception of a residual FA amount at T18 (Table 1). The content of FAs were higher than HA in all technosols and NAT soils (Table 1), which indicated a low humification rate (Guimarães et al., 2013) in both T6 and T18 field samplings. Although no significant differences were found between organic matter fractions to the different amended technosols (Table 1), CG and CC technosols showed a slight increase in HA and FA from T6 to T18, even comparatively higher than NAT in T18 (Table 1). It is well known that plant residues are mainly formed of substances difficult to degradation, such as lignin or cellulose, with high resistance to biodegradation (Hayes and Swift, 2020). However, some authors consider them as a dominant source of soil humic substances that contributing to improve the structure and composition of OM (Yang et al., 2019). Therefore, plant residue amendments could be favouring humification in CG and CC technosols, indicating a trend towards stabilization of SOM that has been confirmed by other studies of quarry restored technosols (Ojeda et al., 2015). On the contrary, SS not only showed a lower content of humic substances but also losses of FA from T6 at T18, and presented the lower humification degree compared to the rest of technosols (Table 1). The latter suggests that SOM of SS contained greater non-humic substances and materials with lower decomposition resistance than vegetable residues amended technosols (CG and CC) (Asensio et al., 2014; Hayes and Swift, 2020). The addition of the mixtures (Mix1 and Mix2) showed an intermediate degree of humification between SS and vegetable compost-amended technosols (CG and CC) probably due to the OM provided by both types of amendments, one with more recalcitrant compounds and the other more labile. Although increases in humic acids following the application of composted organic amendments have been widely reported in the literature, comparisons of the performance of different residues used are always difficult due to the different characteristics and application rates of the organic amendments (Albiach et al., 2001), especially in the initial stages after their application in restoration processes.

3.2. Effect of organic amendments on soil thermal properties

The results of the thermal analyses are shown in Table 2 and in Figure 1. The addition of the organic amendments increased the total weight loss for all the cases in comparison with the soils from the control plots (28.1–29.4 % Vs. 26.5–26.9 %). This increase corresponds to a greater relative and absolute abundance of very labile OM, intermediate OM and recalcitrant OM (W1, W2 and W3 respectively), at expenses of the reduction in the abundance of mineral-dominated fraction (W4). It is remarkable that the presence of the intermediate and recalcitrant pools of soil OM were considerably multiplied by a factor of 3 to 6 times as a result of the addition of the amendments. Regarding the changes observed between the first and second sampling (T6 and T18) for the amended technosols, the abundance of the most labile and intermediate fraction (W1-W2) were reduced, with the exception of the CG plots, whereas the relative abundance of the most stable fractions increased when comparing similar treatments. Commonly, the low-temperature part of the thermograms (W1) has been linked to the burning of carbohydrates and other aliphatic compounds as simple lipids and amino acids, and consequently associated with the most easily-degradable fraction of the soil OM. Meanwhile, the high-temperature parts (W3 and W4) have been generally attributed to reaction of aromatic compounds or other polyphenols, distinctive of a more humified and stable fraction of the OM (De la Rosa et al., 2008; Fernández et al., 2012).

The DSC curves show some differences in the biomass that forms CG and CC amendments. CG is dominated by biomass decomposed over 360 ºC followed by a exothermic shoulder at 530 ºC, which could be typically attributed to cellulose and lignin respectively. The absence of those signals at the DSC of CON samples indicate the lack of plant remains in those plots. The shift of the exothermic signal from 360–370 to 385 ºC for the NAT samples suggests a greater thermal stability of the native soil OM conforming the remaining cellulose than of the used amendments. However, the signal corresponding to highly recalcitrant OM is negligible, which would indicate in general a rapid and complete removal of humified OM in native soils. The greatest weight loss corresponded in all cases to the mineral fraction (included in W4), especially for NAT and CON samples (raging between 86 and 90 % of the total loss). The DSC endothermic peak present over 740–750 ºC would indicate the abundance of dolomites.

3.3 Effects on soil respiration rates

Soil respiration (SR) measured in the field showed higher rates for all technosols amended and natural reference soils (NAT) in the first campaign 6 months after application (T6), while in the second campaign measured 18 months later (T18) it presented a significant reduction resembling CON and NAT soils (Figure 2). Un-amended soils (CON) showed significantly lower SR rate in both measurement campaigns (Figure 2) due to its lack of

OM. Soil temperature and humidity were similar at both times (Figure 2), as expected, taking into account that both field measurements were carried out under similar environmental conditions, without rainfall events in the previous 5 days, and similar average daily temperatures (11.1 °C for T6 and 12.2 °C for T18; data from RAIFALL003, Junta de Andalucía). Therefore, the different results for SR measurements could be attributed to different chemical composition of technosols and depending on the type of organic amendment applied (Ray et al., 2020). For the first campaign (T6), SS presented the higher significant ($P < 0.05$) SR, followed by Mix1, Mix2 and CC that presented similar values than NAT, while CG had the lowest significant values. The high SR rates could be due to the high initial CH content observed in T6, especially in SS (Table 1), which presented to the high mineralization rates, as well as a priming effect that has previously been discussed in Soria et al., (2021a). This initial SOM mineralization and decomposition could be caused by stimulating microbial activity where there were dormant microbial communities, that could have responded with a rapid growth of their populations in response to exogenous of labile C input (Kuzyakov et al., 2009), or by microorganisms provided by organic amendments (García et al., 2017; Rodríguez-Berbel et al., 2021), that would have consumed the most labile fractions in T6. This decreased of microbial activity “hot spot” (Kuzyakov, 2010) in T18 could suggested a possible MOS stabilization and an increased presence of recalcitrant fractions after depletion of easily decomposable OM (Bastida et al., 2013). Although SS had a TOC content similar to CC, Mix1 and Mix2, the high CH content could have favored mineralization and slowed down humification processes since it presented a comparatively lower HA/FA ratio than the others (Table 1). On the contrary, the low SR rates in CG could be due to the presence of a more recalcitrant OM, less available for the soil microbiota. However, in the second measurement campaign (T18), the RS rate was low and similar to that of NAT, probably due to the depletion of the more labile fractions. Interestingly, NAT showed a high SR rate in T6, probably caused by a contribution of root exudates or plant biomass provided by the abundant natural plants.

3.4. Effect of organic amendments addition on the molecular composition of soil organic constituents by analytical pyrolysis

The labelled pyrograms obtained from the soil samples in the two sampling periods are depicted in Figure 3. The relative distribution of the main groups of compounds identified for each sample are shown in Figure 4. The pyrolysis performed directly on the control degraded soils (CON) did not produced any appreciable pyrolysis compound, probably due to the extremely low OC content. However, by pyrolysis the natural soil of the area (NAT) produced a complex and varied molecular assemblage with 61 compounds identified and a clear lignocellulose signature that include guaiacyl (G) units (5.3 %) and polysaccharide (PS) derived compounds (25.2 %), mainly furan derivatives that may came from the cellulose but also from the microbial activity. A well resolved alkyl series from C14 to C30 (ALK; 9.9 %) derived mainly from epicuticular plant waxes (Eglinton et al., 1962) and nitrogen compounds (N; 23.7 %) from peptides and proteins were also found. A conspicuous high proportion of aromatic compounds with unknown origin (ARO; 35.1 %) are also part of the NAT pyrolysate. This, together with the relative low content of lignin methoxyphenols and of SOM in general, may point to accelerated humification processes with active ligninolytic activities yielding a wide variety of aromatic and polycyclic aromatic compounds (phenols, benzenes, indenes and naphthalenes) (Ceccanti et al., 2007). This NAT SOM structure remained mostly unchanged during the two sampling periods (Figure 3).

The technosols amended with vegetable compost from green house (CC) showed a pyrolysate with a remarkable high N compounds (26.0 %) and lignocellulose with compounds derived from lignin guaiacyl (G) and syringyl (S) structures (19.8 %) and cellulose (PS) derived compounds (c. 8.9 %), including anhydrosugars, furan and cyclopentane derivatives. In addition, high content of chlorophyll derived ISO were found (15.1 %) whereas the amount of aromatic compounds was intermediate (ARO: 14.2 %) and less than a half that in the NAT soil (Figure 4f). The substrate amended with the green garden waste (CG) is characterized by a high relative content of ARO (47.1 %) and N (20.4 %) compounds (Fig. 4a). The pyrolizate produced by the technosol with sewage sludge waste (SS) produced high amounts of N (30.6 %) and ARO (29.2 %) compounds, but also included high relative content of alkyl material (ALK: 15.8 %), esterols (EST: 12.0 %) including faecal sterols (coprostanols) and fatty acids (FA: 1.1 %), reflecting the origin of the amendment (Kruge et al., 2010) (Fig. 4c). The pyrolysis of the technosols amended with mixtures of SS and CG (MIX 1) and CC (MIX2) showed the main chemical features of the biomass added. Both mixtures showed EST and FA as markers from the SS waste and the general plant biomass imprint that included lignin methoxyphenols (G and S), PS, ALK and ISO (Figure 4d and 4e). After amending the CON, unrestored, soil with the three materials and mixtures, the OM structure of the resulting technosols resembled that from the NAT soil. The general chemical structure is preserved in the timeframe of this experiment with no appreciable major changes seen by analytical pyrolysis.

4. Conclusions

The application of recycled organic waste composts as amendment on degraded soils from quarrying in a semi-arid climate to form technosols rapidly improved the physical, chemical and microbiological properties and increased SOM levels in the formed technosols. All technosols amended resulted in improved soil functionality and soil quality in the short term compared to un-amended plots. Nevertheless, the SOM composition from vegetable compost amended plots was the most similar to non-degraded natural plots in only 6 months after the amendment. The studied parameters indicated a rapid recovery of microbiological activity and SOM diversity, which were maintained for at least 18 months and therefore this practice could be a valid solution to accelerate the processes of restoration and recovery of quarry mine soils in semi-arid climates, as well as improve their resilience.

Technosols amended with compost from plant residues showed a more recalcitrant SOM, lower soil respiration rates and a higher degree of humification than the sludge-amended technosols, indicating that the nutrient reserve and fertility of the restored soils could be guaranteed in the longer term with plant residues compost. In contrast, the sludge-amended technosols produced a higher respiration rate in the study at 6 months after application associated with their high labile OM content and a rapid initial consumption of nutrients. However, the soil respiration rates sharply decreased 18 months after the application of the composts, which suggested that despite the easily decomposable OM is consumed the presence of recalcitrant OM is maintained, being a long-term reserve of OC and N. In addition, sludge technosols showed the lowest degree of humification in both periods. The mixtures showed intermediate properties of both types of amendments (sludge and vegetal composts), but they showed the highest decomposition of the more labile fractions at the beginning of the experiment. The labile fractions present at the sludge composts would have favored microbiological activity at the short term, but the mixtures maintained intermediate OM contents 18 months later because of the presence of more resilient compounds from the plant composts. These findings were confirmed by thermogavimetric and analytical pyrolysis studies. These analyses showed that 6 months after the amendment the restored technosols with plant compost were composed by a combination of labile and recalcitrant OM similar to natural (undisturbed) soils, which was maintained one year later. In conclusion, the application of vegetable compost from greenhouse crop residues and garden pruning waste were the most suitable for restoring the functionality of degraded soils from quarrying in a semi-arid climate, similar to undisturbed soils (native) by mining activity. Therefore, these findings are still preliminary and further studies are needed to confirm long-term developments.

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