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# **Stability of Organic Matter in Anthropic Soils: A Spectroscopic Approach**

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## **1. Introduction**

### **1.1. Stability of soil organic matter**

The soil organic matter (SOM) plays an essential role in soil biogeochemical processes (Bot and Benites, 2005). Thus, a productive and healthy soil must present a balance among SOM protection and soil biological functioning (Wander, 2004). However, the prediction of organic matter dynamics in soil is hampered by the complexity of SOM distribution and chemical composition (Foereid et al., 2012). The integration of organic inputs in the physicochemically defined organic pools in soil (Six et al., 2002) and their effect on native organic matter has been described to vary with land use, soil physicochemical properties (Strong et al., 2004; Denef and Six, 2005); and composition of the organic inputs (Kimetu and Lehmann, 2010).

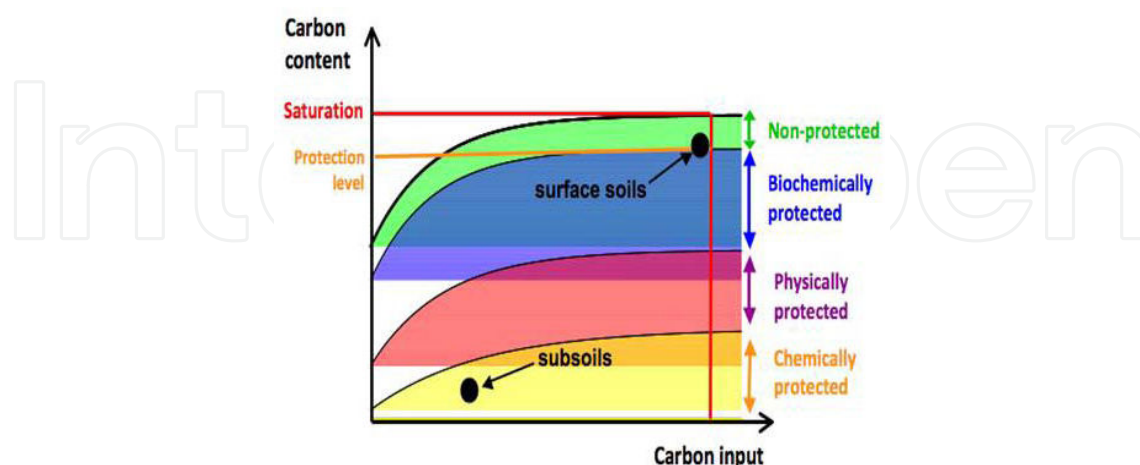
The term soil organic matter refers to all organic substances in the soil: plant and animal residues, substances synthesized through microbial and chemical reactions and biomass of soil micro-organisms. The processes responsible for the stabilization of SOM constitute an essential component of global biogeochemical cycles (Lehmann et al., 2007). Overall, the chemical composition of the organic matter (OM) and the interactions with other soil components such as the mineral phase largely drive the mechanisms for SOM stabilization (Baldock and Skjemstad, 2000), which can be summarized as: (1) biochemical stabilization, (2) physical stabilization and (3) chemical stabilization (Six et al., 2002; von Lützow et al., 2006). The extent of protection offered by each mechanism (Fig. 1) depends on the chemical and physical properties of the mineral matrix and the morphology and chemical structure of the organic matter (Six et al., 2002). Thus, each mineral matrix presents a unique and finite capacity to stabilize organic matter (Baldock and Skjemstad, 2000).

The *physical stabilization* is the preferential location of OM in the soil structure which results in lower access to OM by soil micro-organisms. Thus, integration of OM in soil aggregates reduces the availability of OM for microbial transformation (Six et al., 2002).

The *biochemical stabilization* is a selective enrichment of organic compounds, and refers to the inherent recalcitrance of specific organic molecules against degradation by microorganisms and enzymes. Thus, compounds like lignin, lipids and polyphenols will remain more stable in the soil matrix compared to more labile compounds like polysaccharides and proteins (Six et al., 2002; Kögel-Knabner et al., 2008).

The *chemical stabilization* involves all intermolecular interactions between organic and inorganic substances leading to a decrease in availability of the organic substrate due to surface condensation and changes in conformation, i.e., sorption to soil minerals and precipitation. The chemical stabilization of SOM results mainly from the interaction of SOM with minerals and metal ions (Fig. 1). These interactions include organo-mineral associations such as complexation of organic substances with polyvalent cation bridges, weak hydrophobic interactions (Van der Waals and H-binding) and sorption of SOM to soil minerals (von Lützow et al., 2006; Jastrow et al., 2007). Therefore, some authors have pointed clay fraction as an inhibitor of SOM decomposition (Kleber et al., 2007). For instance, Merckx et al. (1985) described that the stabilization of C and N in soils is positively correlated to the content of clay and silt. Moreover, other authors have indicated that the specific type of clay present in the soil, i.e. clay mineralogy, is most relevant for the capability of a particular soil to stabilize OM (Sollins et al., 1996; Denef and Six, 2005). Consequently, it might be adequate to evaluate specific surface and surface reactivity of soil minerals as predictors of OM stabilization rather than clay content (Baldock and Skjemstad, 2000).

According to Kögel-Knabner et al. (2008), the protection of OM against decomposition by the described mechanisms decreases in the order: chemically protected > physically protected > biochemically protected > non-protected (Fig. 1).



**Figure 1.** Protection of organic matter (OM) in soil. Chemical protection refers to the interactions of OM with minerals; physical protection renders OM poorly accessible to microbes and enzymes; and biochemical protection results from the differential degradability of organic structures. Saturation is thus defined as the theoretical C storage capacity of a soil (adapted from Six et al., 2002).

The complexation of OM with mineral surfaces occurs mostly through ligand exchange, which is an organo-mineral association between OH groups on mineral surfaces and ionized phenolic OH and carboxylic groups of the OM (Korshin et al., 1997). This interaction is particularly relevant in acidic soils with minerals presenting protonated OH groups and is reverted with increasing pH values in soils (von Lützow et al., 2006).

Another important mechanism for organo-mineral association is the formation of polyvalent cation bridges. The presence of negatively charged acidic functional groups (COO<sup>-</sup>) in organic molecules results in repulsion from negatively charged surfaces of clay minerals. However, polyvalent cations function as a cation bridge between those two negatively charged sites (von Lützow et al., 2006). In alkaline and neutral soils, the most abundant multivalent cations are Ca<sup>2+</sup> and Mg<sup>2+</sup> while Fe<sup>3+</sup> and Al<sup>3+</sup> predominate in acid soils, and present higher binding strength. Besides, the role of cation bridges in the stabilization of SOM is particularly relevant for soils with a predominance of 2:1 clays such as smectite and illite (Jastrow et al., 2007).

Adsorption processes also contribute to protect OM against biological degradation (Balesdent et al., 2000). Although feldspars and quartz are the most common minerals in soils, their specific surfaces are rather low (approximately 0.1 m<sup>2</sup>/g), while clay particles provide a significant surface area (specific surface >10 m<sup>2</sup>/g) for the adsorption of OM (Jastrow et al., 2007). Therefore, soils with a high content of clays may provide higher SOM protection than sandy soils, resulting in higher total contents of organic matter (Blanco-Canqui and Lal, 2004). Multivalent cations also contribute to the stabilization of OM by inducing flocculation. Clay particles saturated with multivalent cations remain in a flocculated state, which reduces the exposure of adsorbed organic materials on the clay surface. Thus, flocculation and condensation of organo-mineral complexes can effectively isolate and protect OM from decomposition (Baldock and Skjemstad, 2000). This mechanism has been mainly described for soils with low-charge clays (Jastrow et al., 2007).

Kleber et al. (2007) proposed a conceptual model for organo-mineral interactions in soils, partly based on the self-organizing molecular structure of SOM. These authors suggest that SOM is adsorbed on the mineral surfaces in three discrete zones. Thus, in a contact zone, amphiphilic organic fragments accumulate mainly on charged surfaces through electrostatic interactions, thereby directing hydrophobic parts outwards toward the aqueous solutions. This organization results in a membrane-like bilayer with a hydrophobic core. In the outer region, denominated as kinetic zone, further accumulation of organic fragments likely occurs, and the process is assumed to be mediated by the presence of multivalent cations. However, further research is still necessary to advance our understanding on the dynamics and structure of organo-mineral interactions to validate this zonal concept.

Although abundant research has been previously conducted, the described mechanisms responsible for the reduction of OM decomposition rates, such as sorption of OM to minerals, are not yet well understood. Different stabilization mechanisms may act simultaneously and those proposed in the literature remain speculative and poorly supported by data, mainly due to methodological constraints (von Lützow et al., 2006). Therefore, novel research strategies attempt a better understanding of the mechanisms of OM stabilization in soil by studying the molecular composition of SOM in specific soil fractions. The implementation of spectroscopic techniques (Cory and McKnight, 2005; Lehmann et al., 2010) provides novel and promising

methodological strategies to undertake the challenge of characterizing SOM composition and spatial distribution in soil.

## 1.2. Stability of organic matter in artificial soils

The production of artificial soils or technosols (WRB, 2006) aims to recover landscapes or increase soil productivity. Overall, the addition of soils with organic materials aims to benefit soil quality or increase crop yields by regulating nutrient supply and improving soil structure (Wagner et al., 2007). Addition of single or composite organic wastes is expected to have a positive effect in initiating soil aggregation of structurally degraded topsoils (Wagner et al., 2007 and references therein). For instance, composted or stabilized municipal sewage sludge is frequently applied to soil as organic amendment for restoration purposes. Otherwise, abandoned Fe mine tailings provide a source of Fe-rich mud (FeM), that constitutes an environmental challenge for its adequate disposal, being currently stored in large open-air ponds. A suitable approach might be to use such FeM as a substrate to obtain artificial soils. The Fe oxides and hydroxides present in the FeM might provide a suitable surface for adsorption of organic compounds and may favor the formation of organo-mineral associations, which may result in a pool of chemically stabilized OM. Chemical stabilization by organo-mineral associations is a main mechanism leading to soil aggregation (Kögel-Knabner et al., 2008) and such strategy might result in pools of carbon with long residence time in soil (Macías and Camps Arbestain, 2010).

The objective of this study was to evaluate the chemical composition of OM in artificial soils obtained from organic wastes combined with the FeM at different ratios. The analysis of OM composition at a molecular level and the characterization of the spatial distribution among different pools by Fourier transform infrared spectroscopy (FTIR) can be directly related to SOM stability, soil respiration and OM decomposition rates. Previous research has demonstrated that intensities of distinct peaks obtained by FTIR analysis can be a measure of decomposition of organic carbon in soil (Haberhauer et al., 1998).

Otherwise, dissolved organic matter (DOM) constitutes a highly available carbon source for microorganisms while playing a fundamental role in the mobilisation of organic compounds (Kalbitz et al., 2003). Variations in the composition of the OM present in this pool are an essential component to the knowledge on SOM dynamics (Kalbitz et al., 2000). Therefore, this pool of OM deserves particular attention in our attempt to characterize the evolution of SOM pools. The spectrofluorometric analysis of the soil solution extracted from the different scenarios assayed provides a fingerprinting of the composition of DOM (Cory and McKnight, 2005). Thus, excitation-emission matrix spectroscopy provides the sensitivity to examine subtle changes in DOM fluorescence and provide a valuable insight into variations on the DOM pool composition.

## 2. Materials and methods

### 2.1. Studied area

The studied area is an Fe mine dump in Southeast Spain (Alquife, Granada) planned to be used for residential, leisure and agro-industrial activities. The soil is a degraded technosol with high infiltration rate under a continental Mediterranean climate.



## 2.2. Technosols

A collection of five technosols (Table 1) was obtained by combining a composted mixture (19.4% organic carbon) of sewage sludge from wastewater treatment and olive pruning (SVC) with FeM (44% Fe oxides) and/or a biodiesel byproduct (DRS) with a high concentration of glycerol, following saturation and incubation at 28° C for 30 d. The mineral waste was originated in milling activities carried out in the mine site. A second collection of five technosols was obtained by controlled acidification (H<sub>2</sub>SO<sub>4</sub> 5M) of mixtures as such described for the first set of technosols (Table 1).

Technosol	SVC	FeM	DRS	%OC
T1	100%	-	-	19.4
T2	90%	-	10%	21.0
T3	90%	10%	-	17.5
T4	85%	5%	10%	19
T5	70%	30%	-	13.6

**Table 1.** Composition of technosols.

A second batch of technosols (TS) was prepared with equivalent composition but SVC and FeM were saturated and incubated for 1 week before mixing. For TS3 and TS4, FeM was acidified with H<sub>2</sub>SO<sub>4</sub> 5N during the preconditioning step.

Samples of the different technosols were collected after 2, 9, 20 and 30 d of incubation and stored at -20° C for posterior analysis.

## 2.3. Carbon mineralization rates

To determine carbon mineralization upon application of the technosols in the mine dump, subsamples of soil from two different plots in the dump (AL7 and AL14) were amended at 2% with the different technosols and placed in air tight incubation jars with a volume of 300 mL and moisture content adjusted to field capacity. The lids of the incubation jars were fitted with three-way valves to allow sampling the air from the headspace. The jars were stored in an incubation room at 25° C for circa 120 d. Headspace in the jars was periodically sampled with 60 mL syringes and the CO<sub>2</sub> concentration measured with an infrared gas analyzer (LI-COR; Li-820). The amount of carbon respired was calculated using the ideal gas equation and expressed as percentage of carbon respired relative to the total carbon content in the amended soil.

## 2.4. FTIR-microscopy

Microaggregates-like structures (100-200 µm) were isolated and collected from the different technosols after 2 and 30 d of incubation and analyzed with a Fourier transform infrared spectrophotometer (Varian 620-IR IR microscope) coupled to a microscope (FTIR-microscope)

using a KBr splitter and a liquid nitrogen cooled Focal Plane Array detector for spectrochemical imaging and a CCD camera. The spectra were recorded for the microaggregates-like structures in the mid-infrared range (4000–800  $\text{cm}^{-1}$ ) by combining 32 scans at a resolution of 1  $\text{cm}^{-1}$ . The spectra were recorded in absorbance units. Peak area integration and analysis of the spectral features distribution in the microaggregates were performed using the software Agilent Resolutions Pro. Spectra and image analysis presented were obtained as the average of 5 spectra.

## 2.5. Water soluble organic matter

The fraction of water soluble organic matter (WSOM) was obtained from the technosols sampled at different incubation times, through centrifugation (10 min at 3000 g) using the 'double chamber' method (Bufflap and Allen, 1995). After centrifugation, the soil solution samples were immediately filtered through a 0.45- $\mu\text{m}$  filter. The solutions were analyzed for dissolved organic carbon (DOC) using a TOC-analyser (Analytical Sciences Thermalox). The UV-absorbance was measured with a UV-VIS spectrophotometer (Perkin-Elmer, Lambda 20, quartz cells).

Variation in the ratio of absorbance to DOC was used to characterize the quality of DOM, through the specific UV absorbance at 254 and 340 nm (Tipping et al., 2009).

## 2.6. Spectrofluorometry

The soil solution samples were diluted such that the absorbance at 254 nm was less than 0.2 prior to the collection of fluorescence spectra (Miller et al., 2010). Fluorescence excitation-emission spectra were obtained for the pore water solutions using a JY HORIBA Fluorolog-3 spectrofluorometer with an excitation range set from 240 to 400 nm and an emission range set from 300 to 500 nm in 2 nm increments. Instrumental parameters were excitation and emission slits, 5 nm; response time, 8 s; and scan speed, 1200  $\text{nm min}^{-1}$ . Spectra were analyzed using the software FluorEssence.

## 2.7. Adsorption of gallic acid on Fe mud

Sorption isotherms were carried out using a batch equilibration method, with 5 g of FeM and 20 mL of an aqueous solution of gallic acid (GA, Sigma Aldrich) at concentrations ranging 5–50 mM. The samples were mechanically shaken end-over-end in a thermostatic chamber at  $20 \pm 1$   $^{\circ}\text{C}$  for 24 h. The samples were centrifuged at 3500 rpm and 15  $^{\circ}\text{C}$  for 15 min. The isotherms were run in duplicate. A GA solution without addition of FeM was used as control, to account for possible degradation during the batch process.

The difference between initial concentration of GA and the concentration of GA remaining in solution after reaching equilibrium was attributed to sorption of GA on FeM. The sorption equilibrium partition coefficient  $K_d$  ( $\text{L kg}^{-1}$ ) was calculated as  $K_d = X / C_e$ , where  $X$  is the concentration of GA in the FeM ( $\text{mg kg}^{-1}$ ) and  $C_e$  is the concentration of GA in the solution at equilibrium ( $\text{mg L}^{-1}$ ). The adsorption experiment was described by the empirical Freundlich equation ( $X = K_f C_e^n$ ), where  $K_f$  is the Freundlich adsorption coefficient ( $\text{L kg}^{-1}$ ) and  $n$  a constant which depends on the adsorbate, the adsorbent and the temperature.

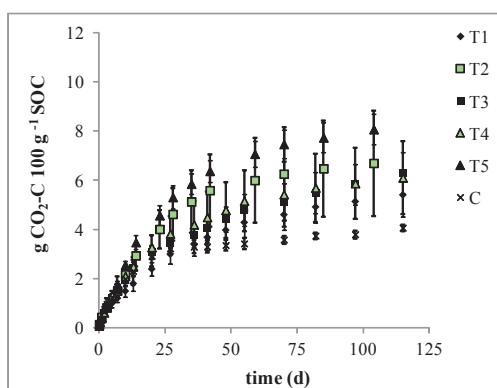
### 3. Results

#### 3.1. Carbon mineralization rates

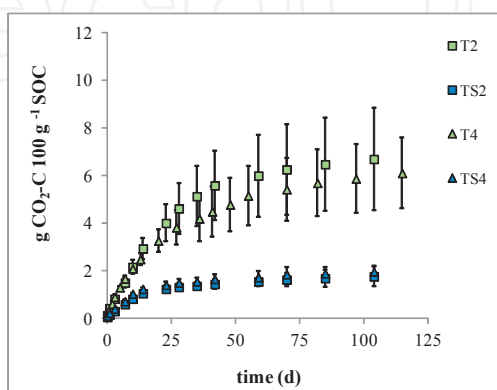
Results obtained from the carbon mineralization assays are summarized in Figures 2-4, which describe cumulative respiration determined for the application of the different technosols to samples of soil collected from the mine dump.

Soil addition with the first batch of technosols (Table 1) increased carbon mineralization rates for all the technosols applied (Fig. 2) compared to control soil (C). For technosols produced solely from SVC and Fe mud, a higher ratio SVC:FeM (T3: SVC:FeM, 90:10) resulted in lower CO<sub>2</sub> production than T5 (SVC:FeM 70:30), regardless the OC content.

The preconditioning step significantly affected carbon mineralization rate. Addition of technosols TS2 and TS4 (saturated) to the dump soil resulted in lower mineralization rates than application of non-preconditioned technosols (Fig. 3). Thus, for technosols obtained solely from SVC/FeM, saturation of wastes before mixing (TS5) significantly decreased the mineralization of OC added to the soil when FeM was acidified during the preconditioning (TS3, Fig. 4).



**Figure 2.** Cumulative CO<sub>2</sub>-C respired for T1-T5 and control soil.



**Figure 3.** Cumulative CO<sub>2</sub>-C respired for T2, T4, TS2 and TS4.



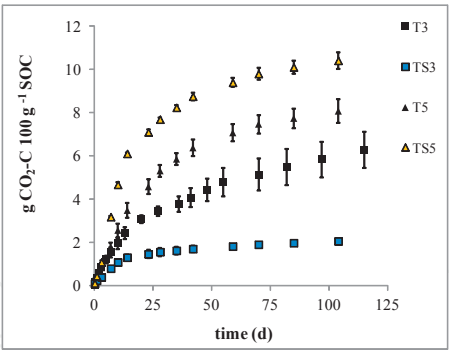


Figure 4. Cumulative CO<sub>2</sub>-C respired for T3, T5, TS3 and TS5.

3.2. Dissolved organic carbon: concentration and composition

Total organic carbon content and UV-absorbance analysis performed for the water soluble organic carbon collected from the technosols indicated that DOC from technosols prepared with SVC+FeM (90/10) was highly humified, as suggest by SUVA and extinction coefficients values at 254 and 340 nm (Fig. 5 and 6).

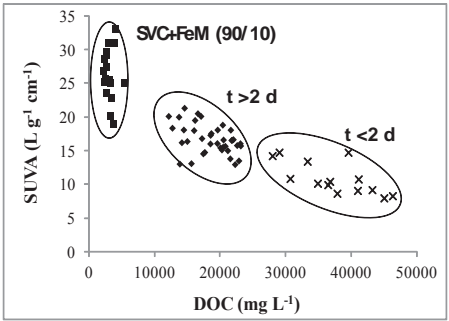


Figure 5. Relationship SUVA-DOC. Squares, technosol prepared with SVC+FeM (90/10); diamonds, rest of technosols after incubation time > 2 d; X, rest of technosols after 2 incubation days.

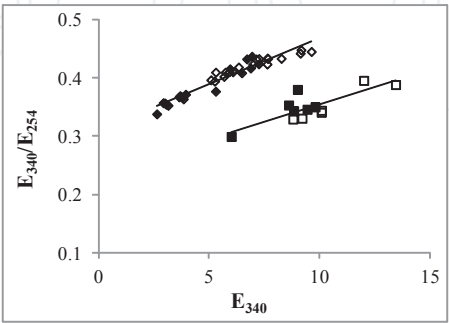


Figure 6. Relationship ratio of extinction coefficients at 340 and 254 nm and the extinction coefficient at 340. Full squares, T3, T9 (t=2d ); empty squares, T3, T9 (t=30 d); full diamond, T1-T2, T4-T8, T10-T12 (t=2 d); empty diamond, T1-T2, T4-T8, T10-T12 (t=30 d).

Table 2 summarizes the values determined for the different fluorescence indexes derived from the spectrofluorometric analysis. Overall, higher humification index values (HIX) were derived for increasing concentration of FeM in a particular technosol, which confirms higher humification of the water soluble organic carbon. The freshness index values ( $\beta:\alpha$ ) confirmed the expected predominance of recently derived DOC. Besides, the high fluorescence index values determined (FI) indicated that DOC was originated from intense microbial activity.

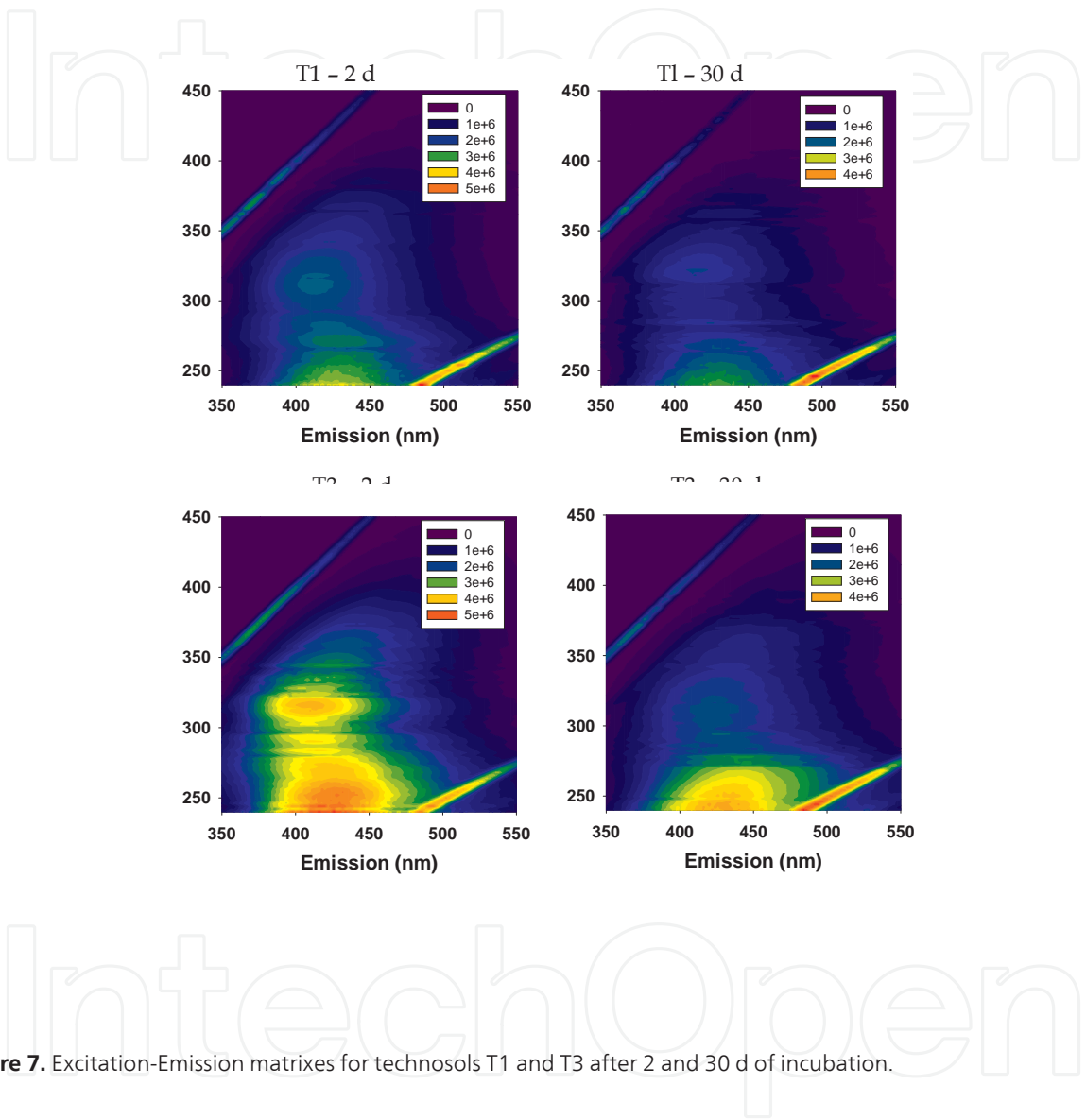
Overall, preconditioning the materials prior to the production of the technosols resulted in higher values of the HIX, likely due to an increase in organo-metal interactions, while changes on the  $\beta:\alpha$  and FI values were neglectable. Variation of the fluorescence indexes over time was not conclusive.

Technosol	Incubation (d)	HIX	$\beta:\alpha$	FI
T1	2	5.25	0.68	2.17
T1	30	5.72	0.66	2.09
T3	2	7.25	0.60	1.99
T3	30	7.16	0.58	1.88
T4	2	4.62	0.7	2.18
T4	30	6.14	0.67	2.12
TS1	2	4.91	0.74	2.19
TS1	30	5.51	0.67	2.25
TS3	2	6.85	0.60	1.96
TS3	30	7.13	0.62	1.91
TS4	2	6.57	0.58	2.21
TS4	30	7.46	0.58	1.82

HIX: Humification index.  $\beta:\alpha$ : freshness index. FI: Fluorescence index.

**Table 2.** Spectroscopic analysis.

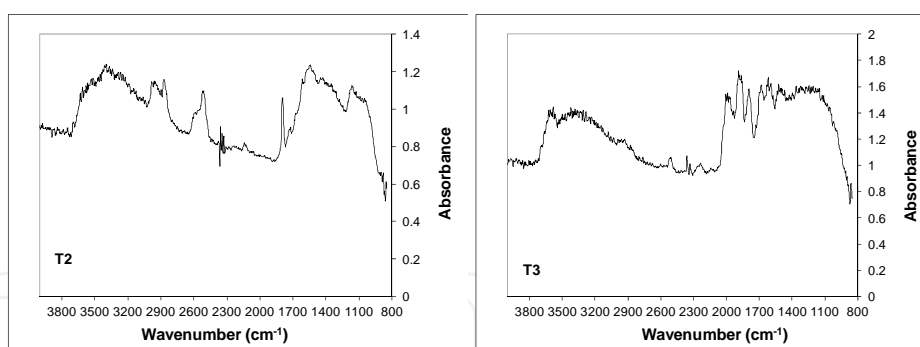
Otherwise, results from the excitation emission matrixes (Ex/Em) collected for T1 and T3 (Fig. 7) indicated a substantial increase in the fraction of UV (Ex/Em 260/400-460) and visible (Ex/Em 320-360/400-460) humic-like organic matter for T3 compared to T1, which suggest the presence of a pool of highly stable, low degradation rate OM. Moreover, the strong increase in fluorescence intensity suggests that the added OM might complex metal ions in solution, which can result in a protective effect for DOM against rapid mineralization. The attenuation of the signal at Ex/Em 320-360/400-460 over time suggest the precipitation of organo-metal complexes in the solid phase.



**Figure 7.** Excitation-Emission matrixes for technosols T1 and T3 after 2 and 30 d of incubation.

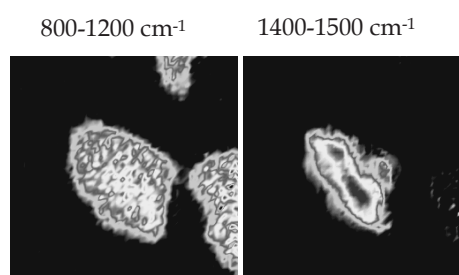
**3.3. FTIR-microscopy**

Spectra obtained for microaggregate-like structures (Fig. 8) showed a consistent absence of aliphatic-C ( $2900\text{ cm}^{-1}$ ); the presence of aromatic compounds-C assigned to signals at  $1400\text{--}1500\text{ cm}^{-1}$  and at  $1600\text{ cm}^{-1}$ ; and aromatic overtones at  $1790$ ,  $1865$  and  $1998$  (T3, Fig. 8), according to previous literature (Demyan et al., 2012). Polysaccharide-C were identified in the fingerprint region (between  $800$  and  $1200\text{ cm}^{-1}$ ) while peak at  $3620\text{ cm}^{-1}$  are related to the presence of clay like compounds (Lehmann et al., 2007). Additionally, a peak at  $3700\text{ cm}^{-1}$  was obtained for the analysis of T5, which might also be related to clay-like compounds.

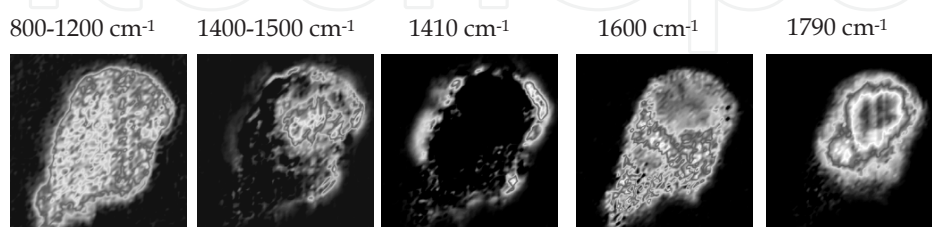


**Figure 8.** FTIR spectra collected for technosols T2 and T3.

Analyzing the distribution of such spectral features in soil microaggregates revealed polysaccharides homogeneously dispersed on the surface of the microaggregates, as depicted for T1 (Fig. 9) and T3 (Fig. 10). Otherwise, distribution analysis for T1 and T3 (Fig. 9 and 10) suggested the presence of cores of aromatic compounds (Wan et al., 2007).

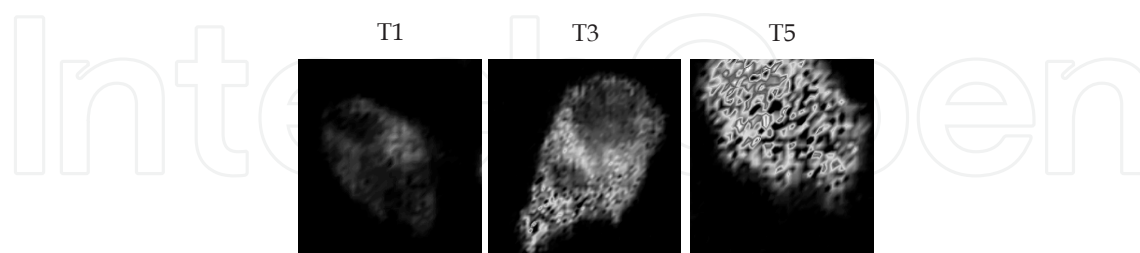


**Figure 9.** Distribution of polysaccharides ( $800\text{--}1200\text{ cm}^{-1}$ ) and aromatic compounds ( $1400\text{--}1500\text{ cm}^{-1}$ ) in a microaggregate from T1 (without FeM).



**Figure 10.** Distribution of chemical compounds in a microaggregate from T3 (SVC plus 10% FeM) obtained from FTIR spectra. Polysaccharides at  $800\text{--}1200\text{ cm}^{-1}$ , aromatic compounds at  $1400\text{--}1500$ ,  $1600$ ,  $1410$  and  $1790\text{ cm}^{-1}$  and organo-mineral associations at  $1410\text{ cm}^{-1}$ .

The distribution of clay-like compounds in the microaggregates isolated from T1, T3 and T5 indicates an increasing presence of such compounds for higher concentrations of FeM in the technosols (Fig. 11).

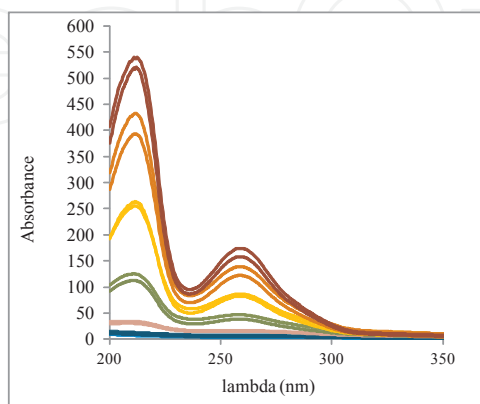


**Figure 11.** Distribution analysis for the signal recorded at  $3620\text{ cm}^{-1}$  in microaggregates from the three technosols.

Thus, a weak signal was detected for T1 that might be related to oxidized compounds that overlap with the signal corresponding to clay-like compounds, while a strong signal was obtained for T3 and T5, consistently with the different ratios of FeM in their composition. Moreover, the distribution of clay-like compounds obtained for T3 (Fig. 11) overlaps with the distribution depicted for aromatic compounds ( $1600\text{ cm}^{-1}$ , Fig. 10), which confirms the presence of organo-mineral associations.

### 3.4. Adsorption of gallic acid on Fe mud

Results from batch adsorption assays confirmed the capability of FeM to adsorb gallic acid ( $300\text{ mmol kg}^{-1}$ ), probably through interaction of the carboxyl and phenolic groups with the Fe oxide surface, as determined by the decrease in the signals at 220 and 270 nm for increasing concentrations of FeM in solution (Fig. 12). The adsorption constant derived,  $K_d=231.5\text{ L kg}^{-1}$ , indicates high adsorption of the acid in the FeM  $n=0.1$ , weak sorption of the second layer.



**Figure 12.** Gallic acid solution UV spectra.  $K_d=231.5\text{ L kg}^{-1}$ , high adsorption of the acid in the FeM  $n=0.1$ , weak sorption of the second layer.



## 4. Discussion

Fresh organic inputs applied to a harsh environment such as a mine dump in the arid Mediterranean climate can be expected to be rapidly mineralized, as previously described by Novara et al. (2012). The evolution of DOM in a particular soil largely determines the SOM stability and protective capacity of the soil. Hence, the aromaticity and fluorescent properties of DOM provide an adequate characterization of this pool of OM, which allow adequately predicting carbon mineralization rates and protective capacity for a given soil scenario (Murphy et al., 2010).

The extent and rate of DOM biodegradation and humification were in agreement with previous studies (Kalbitz et al., 2003). The increase in DOM with low aromaticity upon addition of such amendments might enhance the microbial activity in the soil, but poor beneficial effects can be expected in the long term due to the short residence time of the OM added. The application of composite amendments including a source of metal ions might contribute to a longer permanence of OM in the soil (Kaiser and Kalbitz, 2012), which will largely benefit soil quality in the long term. Thus, application of composites with a low percentage of FeM resulted in higher humification indexes. Moreover, soil preconditioning by acidification and incubation under saturated conditions promoted the formation of organo-metal complexes, which resulted in lower mineralization rates (Kaiser and Kalbitz, 2012).

Otherwise, the presence of FeM in the artificial soils provides a pool of Fe oxides and Fe and Al hydroxides that presents a clay-like behaviour (Lehmann et al., 2007). This was confirmed by peak position at  $3620\text{ cm}^{-1}$  in spectra collected for T3 (Fig. 10-11). The slight signal recorded for T1 can be attributed to hydroxyl groups in the SVC. Therefore, the incorporation of FeM in the production of technosols results in organo-mineral associations, due to complexation of Fe with phenol/carboxyl groups, which contributes to the protection and stabilization of fresh inputs of organic carbon. Complexation of fulvic acids with Fe oxides surfaces has been linked to the occurrence of a band around  $1410\text{ cm}^{-1}$  (Gu et al., 1994). For technosols from SVC+FeM, distribution analysis suggests that such complexes locate in the edges of the microaggregate as depicted for T3 in Fig. 10. However, the protection is limited by the low adsorption capacity of this FeM, which can be attributed to a negatively charged surface (pH=8.5). Organic compounds present in the fresh inputs such as gallic acid (pH=3.5) might induce short-term acidification on the Fe oxide surface, which could allow the adsorption of carboxyl and phenolic groups (Ni et al., 2011). However, increasing the ratio of FeM in the technosol might counteract such effect, resulting in lower protection effect, which explains the higher mineralization rate determined for such technosols.

Polysaccharides were ubiquitous on the microaggregates analyzed and homogeneously dispersed on the surface of the microaggregates, which is consistent with an increase in the microbial activity due to the addition of fresh inputs of organic carbon (Six et al., 2004). The presence of cores of aromatic compounds in the microaggregates-like structures analyzed was consistent with hypothesis previously established in the literature for the formation of aggregates (Six et al., 2002; Six et al., 2004; Wan et al., 2007).

Overall, the results obtained with this study have demonstrated that successful production of technosols as organic amendments to ameliorate soil quality might highly benefit of the incorporation of a mineral substrate at an optimized ratio. The spectroscopic characterization

of DOM and soil aggregates provides a low cost, effective analysis to determine the effect of a particular amendment in soil structure and OM stability.

## 5. Conclusions

The production of technosols from low-cost wastes provides a suitable strategy for wastes disposal while providing a valuable resource for plant sustaining in soil. Application of composite amendments to degraded soils might constitute a highly effective approach for increasing soil health and productivity and a suitable alternative to conventional strategies based on single organic amendments. Moreover, such composites constitute a balanced soil amendment, which involves a compromise between enhancement of soil biological activity and the establishment of pools of stabilized organic matter.

The approach presented provides general guidances for designing optimized mixtures of C-rich organic materials through characterization of the DOM pool, soil aggregates, and the potential of the composites for chemical stabilization of OM. Thus, spectrophotometric fingerprinting of DOM and molecular characterization of OM in soil aggregates have been demonstrated to provide soil quality benchmarks to develop technosols tailored for an specific environmental scenario.

Rehabilitation plans can be designed according to soil-plant requirements as well as safe and effectively cost means for disposal wastes. Fe-enriched amendments might constitute an essential component for technosols, playing a key role in the chemical stabilization of organic matter in soil.

Overall, an optimized combination of mineral and organic wastes may result in a pool of chemically stabilized organic matter. The proposed technosols present a significant potential to create a sink of C while providing an inexpensive in-situ strategy for wastes disposal.

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