Factors that affect physicochemical and acid-base properties of compost and vermicompost and its potential use as a soil amendment

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ABSTRACT

Composting and vermicomposting have attracted attention in relation to both waste management and the potential to produce organic amendments that could improve soil quality. The main differences between compost depend on the feedstock, the production process, and the degree of maturity. In the present study, samples of compost of different origin (food and green waste, livestock waste, algae waste, urban waste or sewage sludge) or subjected to different composting methods (traditional or using earthworms) were collected for analysis. Additionally, samples collected at various stages of the composting process were compared (raw material, 15 and 30 days of composting, and final compost). Different analysis and techniques were used to establish the chemical composition, physicochemical and acid-base properties of compost samples and the organic matter extracts. The correlations obtained (between the abundance of acid groups in different extracts of the compost or between the cation exchange capacity and the C/N atomic ratio) would allow for predicting the compost behaviour based on certain characteristics, and a reduction in the number of parameters determined experimentally, thus facilitating comparisons between different compost. In addition, the potential value of the compost as amendment was tested with a Haplic Cambisol from a mining area. The application of compost increased the pH, the organic matter and nutrient content, and promoted seed germination and root growth.

1. Introduction

Waste management is required to maintain natural resources and to protect the environment. Recycling, reuse and valorization of waste are possible solutions potentiating the circular economy (Hollins et al., 2017). Although most of the waste generated by anthropogenic activities is biodegradable, it should not be directly applied because its uncontrolled decomposition can have negative effects on soil systems (Hanc et al., 2019a). Organic matter from waste can be decomposed and stabilized in a process in which microorganisms play an important role. Thus, biodegradable organic residues can be stabilized and repurposed via composting and vermicomposting processes. Both processes are aerobic and bio-oxidative but differ in the involvement of earthworms in vermicomposting. The involvement of earthworms in the composting process promotes the aeration and fragmentation of the organic matter, thus increasing the rate of mineralization (Hanc and Vasak, 2015).

The use of compost and vermicompost to improve soil quality has increased in recent years. Numerous studies have investigated the use of compost as a soil amendment with the aim of immobilising potentially toxic elements or increasing nutrient or organic matter content (Forján et al., 2017; Palansooriya et al., 2020). To use the compost as a soil amendment it should have reached a certain degree of maturity and stability. Maturity is associated with the capacity of a compost to favour plant growth and with the absence of phytotoxic compounds, whereas stability is associated with a decrease in microbial activity during composting (Cerda et al., 2018). The stability is related to the transformation of fresh organic matter into recalcitrant aliphatic compounds and highly humified aromatic structures (Droussi et al., 2009). Different physical, chemical and biological parameters can be used to determine the degree of maturity and stability of compost, including odour, cation exchange capacity, nitrogen and carbon contents or degree of humification (Bernal et al., 1998; Droussi et al., 2009).

The degree of humification of organic matter is related to the production of humic substances (HS) and to the degree of maturity or stability reached during composting (Jurado et al., 2015). As the aim is to yield a stable product rich in humic substances, these substances are

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often extracted from compost for characterization (Amir et al., 2003). Some studies indicate that the humic substances extracted from compost improve the soil properties more effectively than other more conventional amendments (Wu et al., 2021). Humic substances can benefit soil systems by regulating pH, acting as redox agents, complexing metallic ions, and stimulating plant growth (Fuentes et al., 2018; Guo et al., 2019). Thus, humic substances show great potential for elaborating biofertilizers and for removing heavy metals from soils. The contribution of humic substances to the fate and bioavailability of macro and micronutrients and toxic species, such as heavy metals and pesticides, can be attributed to the abundance of aromatic structures and carboxylic and phenolic groups in their structure (Lee et al., 2020). Although there is no much information available on the acid-base properties of HS-like substances and dissolved organic matter from composted material, it is a matter of considerable interest since it can provide useful information to improve the performance of the compost for agronomic purposes in soils and to control the bioavailability, distribution and toxicity of metals in environment (Yan and Korshin, 2014). As concluded by Fernández et al. (2007) the acid-base properties of the HS-like extracted from compost resemble those typical of native soil HS, thus inducing fewer changes in amended soil HS.

Various studies have focused on analysing compost and vermicompost derived from animal and plant waste (Chatterjee et al., 2021; Kucbel et al., 2019). Other studies have compared the composting systems (Soobhany et al., 2017), while others have characterized the HS extracted (Guo et al., 2019), monitored the changes in organic matter throughout the composting process (Lalremruati and Devi, 2021) and, eventually, evaluated the effects of incorporating the resulting material on soils (Forjan et al., 2017; Teodoro et al., 2020).

Since it is not easy to find complete studies including characterization and comparison of compost and their extracts, the present research aims to conduct an integral study of the aforementioned aspects, in order to obtain more detailed information about the products generated by composting and vermicomposting and their potential use as amendment and/or fertilizers. For this purpose, samples of compost and vermicompost were selected to compare both the effect of the composting process and the effect of the feedstock material. The evolution of the organic matter was also monitored at different stages of the composting process. Although soil-compost interactions mainly occur in aqueous media, information about humic-like substances and dissolved organic carbon of these types of material is scarce. We therefore decided to compare the composition and acid-base behaviour of the dissolved organic carbon in the equilibrium solution with the corresponding humic-like extracts. Finally, with the aim of evaluating the effects of the application of stabilized organic residues on degraded soils, compost and vermicompost samples were applied as amendments to an unproductive mine soil.

2. Materials and methods

2.1. Samples

Six compost samples were analysed: four were commercial products (CLW (livestock waste), CUW (urban waste), CSS (sewage sludge) and CVA (algae) and two were produced in traditional composting or vermicomposting systems (CDDW, from domestic waste and CVDW, from domestic waste using earthworms). In addition, with the aim of studying the changes in the organic matter throughout the composting process, samples were obtained at different stages (UW0 (fresh urban waste), CUW15 (after 15 days composting) and CUW30 (after 30 days of composting)), as outlined in Fig. S1 (Supporting Information). A detailed description of the samples is included in Table S1 (Supporting Information).

The compost samples were used to extract the dissolved organic carbon (equilibrium solutions) by adding 150 mL of water to 7.5 g of compost. The resulting suspension was homogenized by an initial vigorous shaking and then equilibrated for 5 days (open atmosphere). The solution was then separated by centrifugation at 6000 rpm.

The humified organic matter was extracted from compost to yield the humic substance-like (HS-like) fractions. The extraction was carried out following the protocol established by the International Humic Substances Society (IHSS) (Swift, 1996).

2.2. Characterization

The compost, equilibrium solutions and HS-like fractions were characterized using common methods for these types of materials. Briefly, C, H, N and S contents were determined in an element analyzer (TruSpec CHN-1000, LecoSC-144DR); ash content was determined gravimetrically by combustion at 650 °C; oxygen content was determined as $O = 100 - (C + N + H + S + ash)$; oxidizable C was determined by Sauerlandt's method (Walkley, 1947) and C in solution was determined using a total organic carbon analyzer (TOC-L CSN Shimadzu); concentrations of the major elements were determined by ICP-OES (PerkinElmer Optima 3300DV); P concentration was determined in the compost and in the equilibrium solution by the molybdenum blue method (Murphy and Riley, 1962); concentration of ammonium in the equilibrium solution was determined with a selective electrode (Elit electrode Nico, 2000); pH and electrical conductivity were measured in the equilibrium solution with a combined electrode (Crison micro pH 2002, pH 0–14) and a conductivity meter (Crison GLP 32), respectively.

Due to the heterogeneity of the samples, all the analysis were replicated until a standard deviation below 10% was achieved. The bivariate Pearson correlation analysis was conducted with SPSS 25 to evaluate the relationship between the different physico-chemical parameters analysed. Significance was assumed if $p < 0.05$.

2.3. Acid-base properties

Acid-base titrations were conducted with the equilibrium solutions (~5 g solid/L) and of the different HS-like fractions (0.1 g HS/L), following the protocol proposed by López et al. (2012). The titration of the equilibrium solutions was conducted at 0.1 M ionic strength in KNO_3. The titration of the HS-like fractions was also conducted at 0.01 M to obtain the intrinsic parameters of protonation. Because of the high pH of the equilibrium solutions, two aliquots were taken from the same sample to study protonation (titration with 0.1 M HCl) and deprotonation (titration with 0.1 M KOH).

2.4. Application of the amendments

Compost samples were applied to an unproductive mine soil, with the aim of evaluating the efficacy of these samples as soil amendments. The soil was a Haplic Cambisol (Ch2) collected in a uranium mine site (Mina Fé, Saelices el Chico, Spain) and characterized by Arán et al. (2020). The compost samples were applied as individual amendments by manually mixing the soil and compost. Thus, 150–200 g of soil were amended with the amount of compost required to reach a variable content between 2% and 10% (w:w). The soil-compost samples were then incubated at room temperature for 2–3 weeks, during which the moisture content was maintained at between 50 and 70% of the water holding capacity. At the end of the incubation period, the samples were dried, and the pH, C and N contents, total P, Olsen P, and the exchange cations were determined by standard methods (Sparks et al., 1996). A sample of unamended soil was used as a control.

Aqueous equilibrium solutions were made from the compost and the amended samples by the same method as outlined above. The resulting equilibrium solutions were used in germination assays on filter paper, following a similar protocol to that described by Di Salvatore et al. (2008). The ryegrass *Lollium perenne* was selected for use in the assays since it is relatively insensitive to high concentrations of metal, as usually observed in mine soils (Teodoro et al., 2020). Twenty *Lollium*

perenne seeds were placed on three layers of filter paper held in Petri dishes (120 × 20 mm) and watered with 8 mL of equilibrium solution or distilled water (control). The Petri dishes were then sealed and placed in a germination chamber, where they were held at 22 °C, in darkness, for 7 days. Then, the germinated seeds were counted, and the root length was measured. Seeds were considered to have germinated when the root was at least 1 mm long. Each treatment was carried out in triplicate. To facilitate comparison of the results of the germination assays, the percentages of relative radicle growth (RRG), relative seed germination (RSG) and germination index (GI) was calculated (Walter et al., 2006). The normalized residual elongation (NRE) index was also determined (Bagur-González et al., 2011):

$$RRG(\%) = \frac{Mean\ root\ length\ in\ sample}{Mean\ root\ length\ in\ control} \times 100 \qquad (1)$$

$$RSG(\%) = \frac{Number\ of\ seed\ germinated\ in\ sample}{Number\ of\ seed\ germianted\ in\ control} \times 100 \qquad (2)$$

$$GI(\%) = \frac{RRG \times RSG}{100} \qquad (3)$$

$$NRE = \frac{Mean\ root\ length\ in\ sample - Mean\ root\ length\ in\ control}{Mean\ root\ length\ in\ control} \qquad (4)$$

3. Results and discussion

The results and discussion of physicochemical characterization, acid-base properties and application of the compost as soil amendment are presented in different sections. Within each section, different subsections are devoted to the results from compost, equilibrium solution and HS-like fractions, respectively. In each sub-section, results are displayed into three discussion blocks:

● Origin: Samples of different feedstock subjected to a similar composting process: CLW, CUW, CDDW and CSS; CVA and CVDW
● Process: Samples of the same feedstock subjected to different composting processes: CDDW (traditional composting) and CVDW (vermicomposting)
● Maturation: Samples obtained at different times throughout the composting process: UW0, CUW15, CUW30 and CUW

3.1. Characterization

3.1.1. Compost

The results of the chemical analysis are included, along with the values of other relevant parameters, in Table 1. Results for the Pearson's correlation between these parameters are shown in Table S2 (Supporting Information), while the metal contents of the different compost are shown in Table S3 (Supporting Information). The percentage of carbon in the samples produced by a traditional composting process with different types of waste material varied between 22.8 and 34.0%. The sample with the highest content of carbon corresponded to that obtained from a combination of green and food waste (CUW). The sample with the lowest percentage of carbon was produced from livestock manure (CLW). Comparison of samples CDDW and CVDW, produced from similar feedstock and subjected to traditional composting or vermicomposting, respectively, revealed a substantial increase in both the total and oxidizable carbon due to the vermicomposting process. The vermicomposting process reduces the proportion of carbon that can be oxidised relative to traditional composting: 75.4% and 81.0%, respectively. Analysis of the changes in the carbon content during the composting process (UW0, CUW15, CUW30 and CUW) revealed a decrease in both the total and oxidizable carbon, particularly during the maturation stage, i.e. oxidizable carbon was 86.1% of the total carbon at the end of the process, while it remained above 95% during the initial decomposition stage.

The C/N ratio (Table 1) is widely used as an indicator of compost maturity. Thus, various studies report that values below 20 indicate that the maturity of the compost is acceptable, but those compost showing a C/N ratio below 15 are recommended for agronomic use (Soobhany et al., 2017). The C/N ratio ranged between 8.6 (CSS) and 12.8 (CLW) for the samples produced from different types of feedstock. A value of 8.5 was found for sample CVDW, lower than that determined for sample CDDW (10.3) produced by a different composting process. This finding appears to be consistent with previous studies and can be attributed to the earthworms, which supply N and may mineralize the organic nitrogen in the form of mucus excretions and nitrogenous excrements during vermicomposting along with the loss of organic matter (Negi and Suthar, 2018). Although the C/N ratio in the raw sample UW0, mainly constituted by a mixture of green and food waste, is low relative to the optimal values for a composting process to be considered effective (20 < C/N < 30), other authors showed this type of waste may be effectively broken down by the composting process (Kumar et al., 2010; Wang et al., 2019). As the composting process advanced, the values of the C/N ratio decreased due to the loss of carbon as CO_2, caused by the

Table 1
Chemical composition of the compost samples. Percentages in parentheses are calculated based on the total content.

		%C	%C$_{oxi}$	%N	C/N	%S	P-total (mg/kg)	P-Olsen (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	K (mg/kg)	CEC cmol (+)/kg
Compost	CLW	22.8	17.8 (77.8%)	1.8	12.8	0.7	13,505	3452 (25.6%)	78,040	18,230	11,410	30,187	149.7
	CUW	34.0	29.3 (86.1%)	2.7	12.6	0.2	5002	279 (5.6%)	77,470	3739	4830	12,237	167.0
	CDDW	23.3	18.8 (81.0%)	2.3	10.3	0.2	2513	251 (10.0%)	16,100	3621	618.1	7597	95.3
	CSS	31.3	30.9 (98.6%)	3.6	8.6	1.1	21,021	508 (2.4%)	19,880	5200	2150	4269	51.5
Vermicompost	CVA	29.7	27.5 (92.4%)	2.4	12.5	0.4	5512	1386 (25.1%)	13,100	4516	2807	10,247	136.7
	CVDW	43.9	33.1 (75.4%)	5.2	8.5	0.4	4152	297 (7.2%)	9632	4430	1089	14,577	98.8
Maturation	UW0	40.4	38.6 (95.4%)	2.5	15.9	0.2	3129	295 (9.4%)	25,670	2520	4300	10,063	127.6
	CUW15	38.9	36.9 (95.0%)	2.8	13.8	0.3	3950	255 (9.0%)	28,420	2637	4531	8878	96.3
	CUW30	35.2	34.8 (98.9%)	2.7	12.9	0.3	4717	474 (10.0%)	43,100	3451	5190	10,737	108.7

%C$_{oxi}$: percentage of oxidizable carbon.

decomposition or breakdown of the compostable organic components. As indicated by Bernal et al. (1998), the greatest decrease occurred during the active phase, while the maturation stage scarcely influenced the ratio.

The cation exchange capacity (CEC) has been widely used to evaluate the maturity of the compost and the degree of humification of the organic matter, as functional groups that increased the CEC are generated during this process. Thus, high CEC values may be related to a higher maturity degree and to the increase of humic substances in the compost. Pearson correlation analysis indicated a positive correlation between CEC and the C/N ratio when compost feedstock was considered. Thus, samples with the highest C/N ratio, CLW and CUW, showed larger CEC values (Fig. 1). The CEC increased during the composing process, as observed by comparison of the uncomposted material (UW0) and the final product (CUW) (Table 1). After the first cycle of composting, the CEC decreased (comparing UW0 and CUW15) and then increased gradually with composting time. A negative correlation between CEC and C/N ratio has been found with composting time (or composting maturity), similar to that found by Harada and Inoko (1980), although in their study the range for the C/N ratio was larger. This trend appears to indicate that after the first composting cycle, the carbon is mainly derived from humified organic matter, in which the acid sites are occupied by exchange cations. As the composting process advances, the formation of humic substances is favoured, increasing the content of carboxylic and phenolic groups. The Pearson correlation analysis also showed that a negative correlation exists between total P and C/N or C, pointing out to the mineralization of the organic P forms.

3.1.2. Equilibrium solutions

The values of the parameters used to characterize the equilibrium solutions of the samples are given in Table 2. The concentrations of the metals determined in the equilibrium solutions are included in Table S4 (Supporting Information). The pH of the equilibrium solutions ranged between 6.3 and 8.5. The lowest values corresponded to the two vermicompost samples. Comparison of the compost and vermicompost samples made from the same feedstock showed that the pH of the equilibrium solution was lower after vermicomposting. During the composting process, the pH increased slightly in the first cycle and then increased sharply, by approximately one unit, in the second cycle, before remaining almost constant throughout the maturation stage. This increase of pH can be attributed to the decomposition of organic components like proteins, amino acids or peptides and the release of ammonium ions or volatile ammonia (Jamroz et al., 2020).

The electrical conductivity (EC) was used as an indicator of salinity, in order to evaluate any potential problems on using the compost as soil amendment. The EC should remain below 4 mS/cm to be tolerated by plants (Lasaridi et al., 2006). This value was only exceeded in sample CLW, due to high concentrations of sodium and potassium. On the other hand, this parameter did not follow any clear pattern throughout the composting process. However, the EC was much lower in the commercial product than in the uncomposted sample, and the largest decrease occurred during the first composting cycle, suggesting a significant reduction in the amount of soluble salts in the composted material. The pH and EC were correlated in mature compost samples, which may be explained by differences in pH-dependent occupation of acid sites in the organic matter by cations (Fig. 2). The relationship was again different in the composted and vermicomposted samples. The pH of sample CSS was lower than expected from the EC, which can be explained by the high concentration of NH_4^+ in this sample (159.1 mg/L) relative to the other samples (between 4.6 and 21.2 mg/L).

The major elements that mobilize into the equilibrium solution are shown in Fig. S2 (Supporting Information). The highest percentages generally corresponded to Na and K, except in sample CSS, in which Na, K and Mg occurred in almost the same proportion (~20%). The presence of a high concentration of Na in solution may be problematic regarding the use of compost as a soil amendment as this cation is rapidly absorbed by plants, thus preventing absorption of Ca and Mg (Kucbel et al., 2019). Comparison of the compost and vermicompost produced from the same waste material (CDDW and CVDW) revealed very similar results regarding the major elements released to the solution, suggesting that the feedstock is the main factor responsible for the availability of the major elements. In general, the concentration of major cations of the water extracts of the samples collected at the different stages of the composting process decreased with the composting time, which was also observed by Jamroz et al. (2020).

The sample with the highest concentration of dissolved organic carbon was that obtained from livestock waste (CLW), even though the carbon content of the compost was low. The percentage of oxidizable carbon was lowest in the solid sample of this compost, which led to the percentage of dissolved organic carbon being the highest. The equilibrium solution samples with the lowest content of dissolved organic carbon were CDDW and CVA. Comparison of the uncomposted sample (UW0) and the final composted sample (CUW) revealed a marked decrease in the dissolved organic carbon of the water extracts. Very similar findings have been reported by different authors (Said-Pullicino et al., 2007; Hunce et al., 2020; Jamroz et al., 2020). This can be
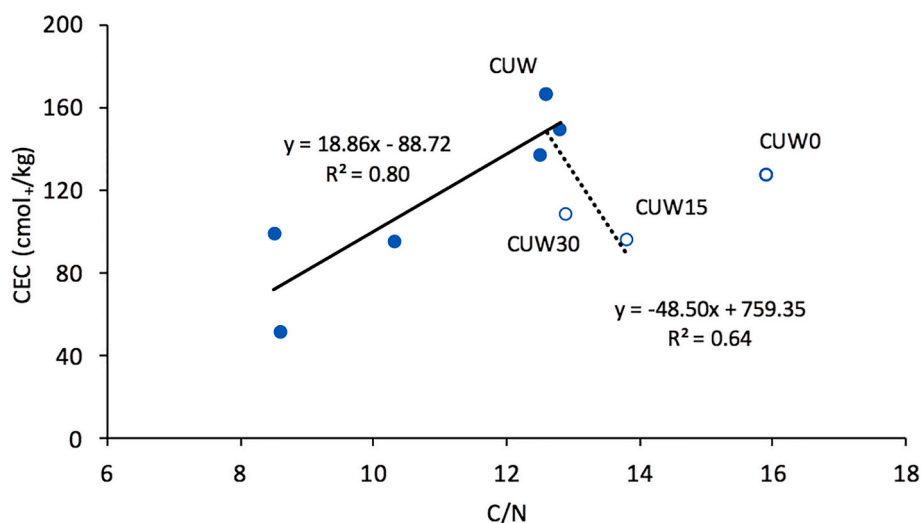

Fig. 1. Correlation between cationic exchange capacity (CEC) and C/N ratio of the compost. The solid line corresponds to the positive correlation observed for compost of different feedstock (filled symbols) and the dashed line shows a negative correlation during the composting process (empty symbols).

Table 2
Chemical characterization of the equilibrium solutions.

		DOC (mg/L)	%C	NH_4^+ (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	PO_4^{3-} (mg/L)	pH	EC (μS/cm)
Compost	CLW	861	9.7	21.2	22.5	38.9	552.0	1363.6	124.1	8.5	6020
	CUW	548	3.7	7.8	28.0	8.8	175.4	349.2	29.5	7.7	2840
	CDDW	115	1.2	4.6	28.6	12.3	17.3	149.5	45.2	6.9	883
	CSS	698	4.5	159.1	95.7	55.8	21.1	55.0	29.0	7.6	3850
Vermicompost	CVA	111	0.8	14.1	80.7	66.1	114.2	431.0	241.4	6.7	3280
	CVDW	717	4.3	11.1	17.8	15.1	26.7	333.2	70.3	6.3	1370
Maturation	UW0	1187	6.2	10.8	197.0	62.3	207.9	349.9	110.2	6.4	3870
	CUW15	429	2.3	13.2	133.1	37.4	194.3	322.0	80.4	6.8	3030
	CUW30	430	2.5	10.1	64.1	24.9	225.6	533.1	60.0	7.9	3300

DOC: dissolved organic carbon. %C: oxidizable C released to the solution. EC: electrical conductivity.
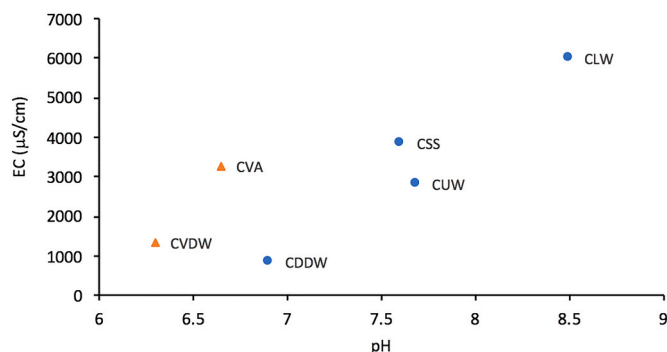
Fig. 2. Variation of the electric conductivity (EC) as a function of the pH in the equilibrium solution of the compost samples.

explained by the biochemical transformations of the organic components through composting. Initially, the concentration of the more labile organic components is relatively high. These components, with hidrophylic character, are mainly composed of polysaccharides, proteins, peptides, and amino acids. As the composting process advances, the mineralization, re-polymerization and condensation of these labile components, lead to the formation of HS-like components, resistant to degradation and with lower solubility (Jamroz et al., 2020).

Semi-empirical relationships between parameters determined by UV–visible spectroscopy are often used to characterize organic matter in solution. These include the correlation between the coefficient of molar absorptivity at 280 nm (ε_{280}) and the percentage aromaticity (% aromaticity = 0.05 x ε_{280} + 6.74) and between this coefficient and the molar mass (molar mass = 3.99 x ε_{280} + 490) (Fuentes et al., 2006). The lowest values of ε_{280} corresponded to the uncomposted sample UW0 and sample CSS (Table S5, Supporting Information), which is representative of an immature compost. The highest value corresponded to sample CDDW, followed by the two vermicompost samples (CVA and CVDW). In the equilibrium solutions of the mature samples, except that of sample CSS, the percentage aromaticity was between 20 and 27%, which agrees the presence of hydrophobic moieties, more resistant to degradation, at the end of the composting process (Jamroz et al., 2020). Accordingly, the relative aromaticity of the DOC increased throughout the composting process, from 10.5% to 20.1%. These results suggest that these semi-empirical parameters are good indicators of the degree of humification and maturity of the soluble organic matter.

3.1.3. HS-like fractions

As in other studies with compost (Fuentes et al., 2018; Veeken et al., 2000), the protocol used for extracting the HS-like components is that recommended by the IHSS for extracting humic substances from soil. This protocol yields good results when applied to mature organic matter but is probably not as effective for immature organic matter. It is therefore possible that the method will quantify carbohydrates, proteins and amino acids as HS-like compounds, even though these are

precursors of HS-like compounds and have not yet decomposed.

The percentages of major elements and the corresponding atomic ratios for the HS-like fractions extracted are shown in Table 3. Analysis of the extraction yields of HS-like components reveals that sample CLW had the highest content of HS-like compounds (42 g/kg of compost). The total carbon content was lowest in this compost, but the DOC was highest. Analysis of these data revealed a correlation between the amount of HS-like compounds extracted from the compost of different origin and the percentage of organic carbon in the equilibrium solution (Fig. 3 a). Inclusion of the other samples in the same plot shows that the concentration of DOC present in the equilibrium solution provides a good estimate of the content of HS-like compounds. The only exception is sample CVA, for which a lower DOC was measured. Although organic matter humification should occur as the composting process advances (Amir et al., 2010; Li et al., 2017), the extraction yield of HS-like compounds was very high for the fresh material at the beginning of the composting process. After the first composting cycle, the percentage of HS-like compounds extracted increased and then remained almost constant throughout the maturation stage. This agrees with the loss of organic carbon with the composting time (Table 1). The decrease of HS-like substances may be consequence of the mineralization rate and decomposition rate of labile HS constituents, which may be higher than the HS formation rate at the initial stages of the composting process (Chen et al., 2021; Wang et al., 2019). Also, this can be explained by considering that the protocol used extracts small organic acids as HS-like compounds. In addition to the previously mentioned correlation, the relationship between the yield of HS-like compounds and the pH of the equilibrium solution distinguished the two types of process: composting and vermicomposting (Fig. 3 b).

Analysis of the HS-like fractions revealed a greater carbon content in the humic acid (HA) than in the fulvic acid (FA) fraction, whereas the latter is richer in oxygen. Regarding the content of other elements, generally the proportion of nitrogen was much higher in the HA extracted from mature compost. Changes in the N content and C/N ratio for the HA extracts during composting, is consisting with previous studies, and might be attributed to the degradation of labile OM molecules and the transformation to saturated structures (Li et al., 2017). Comparison of the HS-like compounds extracted from compost and vermicompost from the same feedstock showed that the nitrogen content was higher in the vermicompost, which can be attributed to the fact that the solid sample also contained more nitrogen due to the direct action of earthworms. The atomic ratios in the FA and HA fractions obtained from the mature compost were plotted in a van Krevelen diagram, along with the ratios reported in other studies (Fig. S3, Supporting Information). We can see that the samples are more widely dispersed in the FA fraction than in the HA fraction. Generally, the HAs are displaced towards lower values of the O/C ratio. This is usually attributed to the enrichment in oxygenated acidic groups for the FA fraction, which is expected to be higher in this fraction. This also agrees with the aromaticity degree, which is generally higher in the HA-like fraction (Fig. S4, Supporting Information). The variation in the atomic ratios during the different stages of composting is similar to that reported in previous

Table 3
Chemical characterization and extraction yield of the HS-like obtained with the extraction protocol of the IHSS.

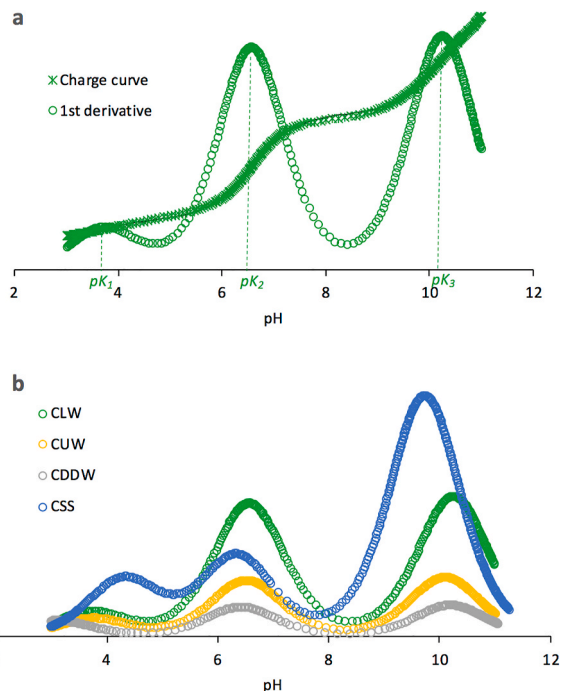|		Fulvic Acid-like								Humic Acid-like							
		Yield (g/kg)	%C	%N	%H	%O	C/N	O/C	H/C	Yield (g/kg)	%C	%N	%H	%O	C/N	O/C	H/C
Compost	CLW	7.0	35.4	3.4	3.4	56.1	12.3	1.2	1.1	34.9	55.2	6.0	5.7	33.4	11.4	0.4	1.2
	CUW	3.3	40.8	4.4	6.0	47.8	10.9	0.9	1.8	21.1	54.5	6.7	6.1	31.7	9.4	0.4	1.3
	CDDW	4.2	38.4	2.6	3.1	55.5	17.1	1.1	1.0	19.0	50.6	4.9	4.5	39.5	12.0	0.6	1.1
	CSS	4.8	40.9	6.1	5.8	45.0	7.9	0.8	1.7	23.8	58.5	5.8	8.3	25.5	11.8	0.3	1.7
Vermicompost	CVA	2.3	49.7	3.7	5.4	40.1	15.6	0.6	1.3	33.4	53.5	3.7	5.5	36.2	16.8	0.5	1.2
	CVDW	4.7	39.8	3.2	3.6	52.9	14.5	1.0	1.1	26.4	52.7	6.1	4.6	36.1	10.0	0.5	1.1
Maturation	UW0	2.2	52.2	6.2	6.2	34.6	9.9	0.5	1.4	33.1	59.8	5.4	8.0	26.1	12.8	0.3	1.6
	CUW15	2.7	52.3	5.2	6.1	35.7	11.8	0.5	1.4	19.8	54.4	5.4	6.9	32.4	11.7	0.4	1.5
	CUW30	2.4	50.3	4.3	5.7	38.8	13.8	0.6	1.3	21.9	54.6	5.6	5.7	33.1	11.3	0.5	1.3
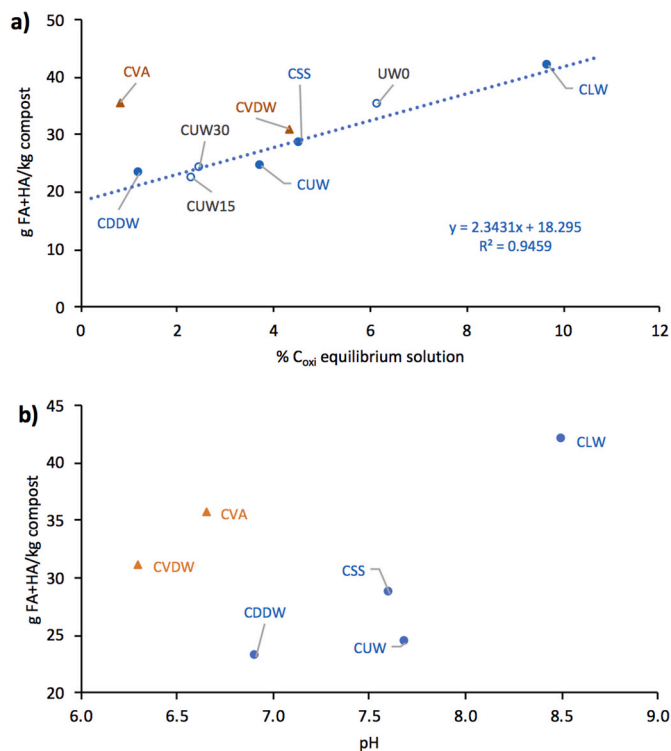
Fig. 3. Relationship of the yield in the HS-like extraction and a) the oxidizable carbon (C_{oxi}) content in the equilibrium solution and b) the pH of the equilibrium solution.

Fig. 4. a) Charge curve and proton affinity distributions in the Dissolved Organic Matter (DOM) of the equilibrium solution of sample CLW as a function of pH. b) Proton affinity distributions in the DOM of the equilibrium solution of compost samples of different origin as a function of pH.

studies (Amir et al., 2010; Hanc et al., 2019b). Both fractions are displaced towards higher values of the O/C atomic ratio, which may be related to an increase in acidic groups throughout the composting process due to the gradual transformation of polysaccharides and other similar compounds into oxygenated compounds such as carboxylic and phenolic compounds (Hanc et al., 2019b).

3.2. Acid-base properties

3.2.1. Equilibrium solutions

Acid-base titrations were conducted to evaluate the concentration and type of acid groups present in the dissolved organic matter (DOM). The charge curve for sample CLW, resulting from the difference in the mmoles of acid or base consumed in the titration of the sample and those consumed by the electrolyte is shown in Fig. 4 a. The figure includes the derivative obtained from the charge curve, in which three well-defined peaks were observed. All samples, except CSS, showed similar behaviour independently of the composting process and the feedstock material (Fig. 4 b and Fig. S5, Supporting Information). Despite the scarcity of information, Sciubba et al. (2015) also identified the presence of three

types of acid positions on the DOM extracted from compost and attributed these to carboxylic groups in amino acids (pKa between 2 and 3), carboxylic groups in organic acids (pKa between 4 and 6) and phenolic hydroxyl groups, hydroxyl in carbohydrate units and amino groups from amino acids (pKa between 8 and 11), respectively. The pH interval in the present study only enabled observation of positions type 2 and type 3 identified by Sciubba et al. (2015).

The 3-site Langmuir isotherm was used to obtain the acid-base parameters of the DOM (equation (5)):

$$Q = Q_0 + \frac{M_1}{1 + K_1[H^+]} + \frac{M_2}{1 + K_2[H^+]} + \frac{M_3}{1 + K_3[H^+]} \tag{5}$$

where K_i represents the protonation constant of the different groups, M_i represents the abundance of each type of group, and Q_0 is the charge due to occupation of the acid sites by cations that must be displaced by protonation. The model fitting results are shown in Table 4. For correct interpretation it should be noted that the charge generated on the organic matter is due to the deprotonation of acid sites and it is therefore negative. The Q_0 value shown in Table 4 can be interpreted as a net positive charge that is occupying acid sites, as positive charges are

Table 4

Acid-base parameters of the dissolved organic matter in the equilibrium solutions from compost samples of different feedstock and different composting stages. Errors associated to the fitting are also shown.

	CLW		CUW		CDDW		CSS		CVA		CVDW		UW0		CUW15		CUW30	
$\log K_1$	3.67	0.02	3.69	0.03	3.06	0.03	4.24	0.02	3.27	0.07	3.45	0.02	4.50	<0.01	3.99	0.05	3.57	0.07
(*)M_1	0.09	<0.01	0.06	<0.01	0.06	<0.01	0.18	<0.01	0.04	<0.01	0.08	<0.01	0.42	<0.01	0.05	<0.01	0.03	<0.01
$\log K_2$	6.56	<0.01	6.51	0.01	6.42	0.01	6.27	0.01	6.55	0.01	6.65	0.01	6.05	0.01	6.54	0.01	6.65	0.01
(*)M_2	0.43	<0.01	0.18	<0.01	0.10	<0.01	0.25	<0.01	0.08	<0.01	0.33	<0.01	0.16	<0.01	0.24	<0.01	0.25	<0.01
$\log K_3$	10.25	<0.01	10.11	0.01	10.17	0.01	9.65	0.01	10.00	<0.01	10.33	0.01	9.73	0.01	10.06	0.01	10.08	0.01
(*)M_3	0.45	<0.01	0.19	<0.01	0.10	<0.01	0.74	<0.01	0.10	0.01	0.21	<0.01	0.27	<0.01	0.22	<0.01	0.21	<0.01
(*)Q_0	−0.48	<0.01	−0.23	<0.01	−0.14	<0.01	−0.40	<0.01	−0.10	<0.01	−0.36	<0.01	−0.52	<0.01	−0.26	<0.01	−0.26	<0.01
R^2	0.9997		0.9997		0.9999		0.9998		0.9996		0.9993		0.9998		0.9994		0.9991	
RMSE	0.0055		0.0024		0.0009		0.0062		0.0013		0.0052		0.0035		0.0041		0.0050	
(*)M_T	0.96		0.44		0.25		1.17		0.22		0.62		0.85		0.52		0.50	

(*) Parameters in mmol/g$_{compost}$. M_T corresponds to the total abundance of acid positions.

usually used to facilitate data handling.

DOM containing the highest and lowest number of acid sites (M_T) is that corresponding to samples CSS and CVA, respectively. In all cases, the most acidic groups are the least abundant, whereas the abundance of the other two types of groups was very similar (Table 4). Again, sample CSS is the exception. The presence of some cations in the solution may alter these results, as we attributed the consumption of acid/base to the protonation/deprotonation of the acid sites in the organic matter, without considering possible hydrolysis reactions and/or precipitation of cations. The possible effect of hydrolysis reactions may be important in samples such as CSS, due to the high concentration of NH_4^+ (Table 2).

The log K values (Table 4) did not follow any trend in relation to the origin of the compost. However, in the vermicompost samples, the DOM contains more acid groups when the original material contains a high proportion of manure (i.e. sample CVA). The result of applying the different composting processes to similar types of material, as in samples CDDW and CVDW, demonstrates that vermicomposting generates DOM with higher content of functional groups, although these groups show a less acidic character. Similar results were found by Campitelli et al. (2012), when studying the HA extracted from compost and vermicompost obtained from rabbit manure. The content of carboxylic and phenolic groups was higher for the HA extracted from the vermicompost, while the acidity constants were slightly lower. Sample CSS was once again an exception, as it yielded the highest log K value for the first type of sites (4.24 relative to a mean value of 3.43 ± 0.27 for the other samples) and the lowest values for sites 2 and 3 (6.27 and 9.65 relative to mean values for the other samples of 6.54 ± 0.08 and 10.17 ± 0.13, respectively).

The same type of comparison can be carried out for the DOM of the samples obtained at the different stages of composting (Fig. S6, Supporting Information). There were notable differences in the curves of the fresh material and the material collected at the different stages of the process. The modelling parameters showed a decrease in the number of acid sites during composting (Table 4), indicating differences between DOM at the beginning of the process, when labile organic matter is also mobilized into the solution, and that after the first composting cycle. The variation in the acidity of the groups with the composting time also indicated a clear difference between UW0 and the other samples, as it corresponded to the highest log K value for the first site (4.50 relative to a mean value for the other samples, of 3.75 ± 0.22) and lower values for sites 2 and 3 (6.05 and 9.73 compared with 6.57 ± 0.08 and 10.08 ± 0.03, respectively). The most acidic groups were the most abundant in UW0 (almost 50% of the total), whereas they became the least abundant after the first composting cycle. The high abundance of these sites in sample UW0 is attributed to the contribution of amino acids, which disappear as the organic matter matures.

3.2.2. HS-like fractions

As expected, the FA charge was larger than the HA charge over the entire pH range (Fig. 5 and Fig. S7, Supporting Information). The distribution of affinities indicates the presence of two types of acid sites, while in the case of DOM three different acid sites were obtained. These acid sites can be attributed to carboxylic and phenolic groups (Milne et al., 2001; Plaza et al., 2005). The charge generated due to the deprotonation of the acid groups can be described by equation (6):

$$Q = Q_0 + \frac{M_1}{1 + (K_1\,[H^+])^{m_1}} + \frac{M_2}{1 + (K_2\,[H^+])^{m_2}} \tag{6}$$

where K_i is the protonation constant of the carboxylic and phenolic groups, M_i is the abundance of each type of acid site, and m_i represents the width of the distributions. The parameters obtained by fitting are shown in Table S6 (Supporting Information). The Q_0 values are not shown as they are equal or close to zero. The results show that the model provided a good fit to the experimental data and demonstrate that the total number of acid sites (M_T) is greater in the FA fraction. The ratio
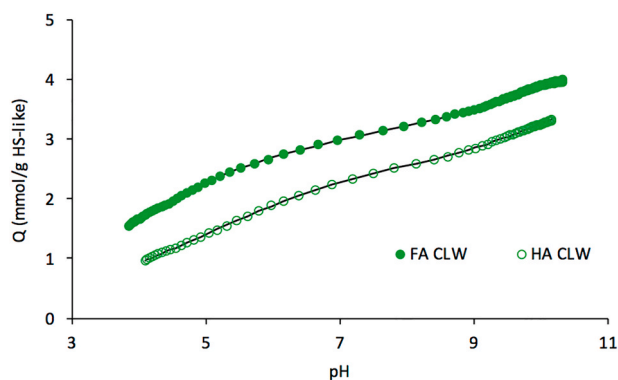
Fig. 5. Charge curves of the HS-like of sample CLW as a function of pH. Symbols represent experimental data obtained from potentiometric titrations and lines represent fits with equation (6).

between the total number of sites in both fractions (M_T (FA)/M_T (HA)) was around 1.1 for the HS-like extracted from the compost samples, with the exception of sample CSS, which has a value slightly higher than 2, and around 1.5 for the corresponding extracts from vermicompost.

To enable comparison with DOM, the site abundance of the HS-like fractions is expressed in mmol of charge per g of compost, by using the extraction yield (Table 3). Considering the different solubility of the HS-like extracts, the DOM present in the equilibrium solution will be mainly constituted by FA molecules. The comparison (Fig. S8, Supporting Information) revealed similar trends, although the sites are more abundant in the DOM. This difference can be attributed to the low extraction yield for the HS-like fraction and to the presence in the water extracts of non-humified organic matter, small organic acids and cations, which may all contribute to the overestimation of acid sites in the DOM. The mean log K values of the bimodal distributions that characterize the FA fraction are very similar to the values of type 1 and 3 sites in the DOM (Table 4 and Table S6, Supporting Information). In all samples, the most acidic sites in the DOM showed lower log K values than those obtained for the FA fraction. By contrast, the log K values for the weakest sites are lower in the FA fraction than in the DOM. Some of these differences could be attributed to the methodology followed for the potentiometric titrations (Fig. S9, Supporting Information).

The charge curves of the HS-like fractions extracted from the samples collected throughout the composting process revealed clear differences in the FA and HA fractions (Fig. 6). Regarding the FA fraction, a drastic change in the charge curves was observed between UW0 and CUW15. In both samples, the initial charges were similar, but then differed as the pH increased until reaching a value of 6, after which the values increased in parallel. After the first composting cycle, the differences were only observed at low pH values. This indicates that no significant changes in the chemical composition or molecular structure occur in this fraction after the 15-day decomposition phase. By contrast, the HA fraction underwent a gradual increase of charge throughout the pH range as the composting process advanced, along with an increase in the total number of acid sites (Table S6). These changes in the charging behaviour may be attributed to the degradation of molecules with a low degree of humification and to the changes produced in the chemical composition of the HA-like extracts during composting.

A rigorous study of the acid-base properties of HS-like extracts requires determining the intrinsic protonation constants and considering the electrostatic effect of the organic polyelectrolytes. The Donnan model was used in this work, which considers HS to form an electrically neutral gel-like phase (Kinniburgh et al., 1996). The Donnan volume (V_D) is related to the ionic strength through equation (7).

$$V_D = b(1 - \log I) - 1 \tag{7}$$

where b is an empiric parameter characteristic of a particular substance
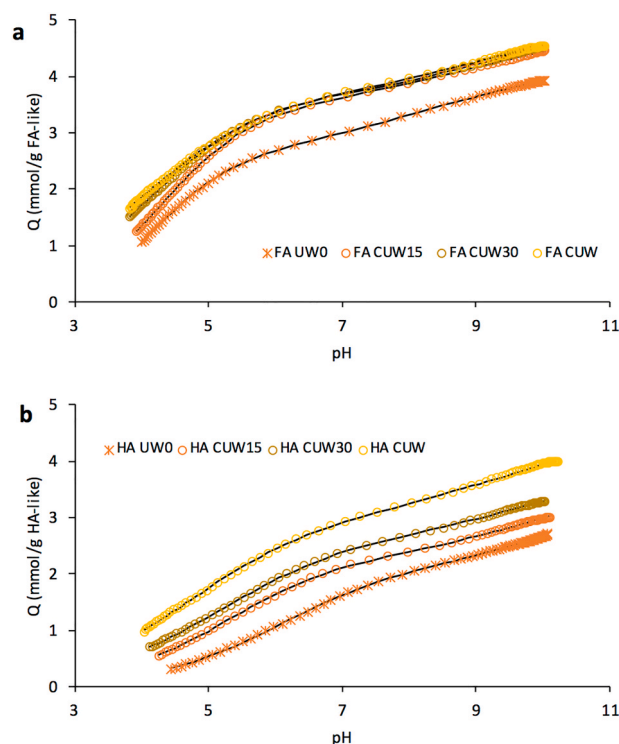
Fig. 6. Charge curves of the a) FA-like and b) HA-like extracted at different stages of the composting process of sample CUW. Symbols represent experimental data from potentiometric titrations and lines represent fits with equation (6).

and describes V_D variation with the ionic strength. The optimization of b allows for calculating the electrostatic potential in the Donnan phase and the intrinsic protonation parameters (Table 5). These parameters can be compared to the intrinsic parameters specifically obtained for other compost derived HS-like (Table S7, Supporting Information). The average values obtained for the parameter b, 0.62 for FA-like and 0.45 for HA-like, are higher for the FA-like fraction, similarly to the values reported by Plaza et al. (2005) for the HS extracted from compost derived from olive mill wastewater. An exception to this trend has been reported by Fernández et al. (2007) and by van Zomeren et al. (2009), who found very similar values for this parameter in the fulvic and humic fractions extracted from compost (Table S7, Supporting Information). Analysis of the results obtained for the HS-like fractions extracted at different stages of the composting process indicates that b decreases throughout the maturation process. The same variation was reported by Plaza et al. (2005). The higher b values observed for the HS-like in the first stages of composting suggest a high contribution of small molecular weight particles. This situation reverses as HS-like condensation occurs during the composting process.

The average content of total acid sites, M_T, obtained for all the samples, 5.58 and 4.00 mmol/g for FA-like and for HA-like, respectively, was small compared to the literature data (Table S7, Supporting Information). However, when the abundance of carboxylic and phenolic groups is expressed as a percentage of the total content of acid groups, the results are almost identical to the percentages reported by Plaza et al. (2005), with carboxylic groups representing approximately 65% of the total acid sites in both FA and HA fractions. Campitelli et al. (2012) and Li et al. (2011) obtained a similar ratio of carboxylic and phenolic groups for HA extracts from compost and vermicompost, although the method used to quantify the acid sites was different. Compared to other HS-like derived from compost (Fernández et al., 2007; van Zomeren et al., 2009), our samples have lower percentage of carboxylic groups. The distribution of acid groups, between carboxylic and phenolic type,

Table 5
Intrinsic acid-base parameters of the HS-like extracted from the compost. Errors associated to the fitting are also shown.

	b	log K_1	M_1 (mmol/g_{SH})	m_1	log K_2	M_2 (mmol/g_{SH})	m_2	R^2	RMSE	M_T (mmol/g_{SH})
FA CLW	0.57	2.72 ± 0.02	3.02 ± 0.02	0.44 ± 0.02	8.31 ± 0.02	1.56 ± 0.02	0.43 ± 0.02	0.9997	0.0154	4.58
FA CUW	0.63	2.93 ± 0.01	3.49 ± 0.08	0.60 ± 0.01	7.76 ± 0.16	1.62 ± 0.23	0.34 ± 0.05	0.9998	0.0142	5.11
FA CDDW	0.66	2.76 ± 0.01	3.46 ± 0.07	0.54 ± 0.01	7.58 ± 0.08	1.51 ± 0.16	0.30 ± 0.03	0.9999	0.0073	4.96
FA CSS	0.65	3.38 ± 0.04	4.77 ± 0.16	0.45 ± 0.01	8.07 ± 0.17	2.81 ± 0.49	0.39 ± 0.06	0.9998	0.0260	7.57
FACVA	0.60	3.31 ± 0.01	3.01 ± 0.15	0.88 ± 0.03	7.42 ± 0.14	2.61 ± 0.39	0.32 ± 0.05	0.9996	0.0270	5.63
FA CVDW	0.63	2.63 ± 0.01	3.89 ± 0.04	0.54 ± 0.01	8.03 ± 0.06	1.72 ± 0.11	0.40 ± 0.03	0.9997	0.0190	5.61
Average FA[a]	0.62 ± 0.03	2.96 ± 0.32	3.61 ± 0.60	0.58 ± 0.15	7.86 ± 0.53	1.97 ± 0.53	0.36 ± 0.05			5.58 ± 0.97
HA CLW	0.47	3.64 ± 0.02	2.64 ± 0.03	0.39 ± 0.01	8.43 ± 0.10	1.31 ± 0.13	0.57 ± 0.05	0.9999	0.0070	3.95
HA CUW	0.46	3.41 ± 0.04	2.80 ± 0.19	0.60 ± 0.03	7.88 ± 0.22	1.94 ± 0.48	0.33 ± 0.08	0.9994	0.0272	4.74
HA CDDW	0.48	3.15 ± 0.04	2.93 ± 0.11	0.47 ± 0.01	7.96 ± 0.22	1.49 ± 0.31	0.36 ± 0.07	0.9998	0.0132	4.42
HA CSS	0.43	3.78 ± 0.07	2.60 ± 0.07	0.30 ± 0.01	8.46 ± 0.21	1.11 ± 0.24	0.55 ± 0.09	0.9999	0.0081	3.70
HACVA	0.45	3.46 ± 0.03	2.47 ± 0.03	0.44 ± 0.01	8.37 ± 0.11	1.09 ± 0.13	0.57 ± 0.06	0.9998	0.0124	3.56
HA CVDW	0.44	3.47 ± 0.02	2.43 ± 0.04	0.60 ± 0.01	8.15 ± 0.19	1.32 ± 0.20	0.50 ± 0.07	0.9998	0.0138	3.75
Average HA[a]	0.46 ± 0.02	3.49 ± 0.21	2.62 ± 0.19	0.47 ± 0.11	8.21 ± 0.25	1.38 ± 0.29	0.48 ± 0.10			4.00 ± 0.44
FA CUW15	0.74	3.53 ± 0.01	3.38 ± 0.09	0.87 ± 0.02	8.00 ± 0.27	1.62 ± 0.33	0.35 ± 0.08	0.9995	0.0260	5.00
FA CUW30	0.68	3.15 ± 0.01	3.45 ± 0.03	0.71 ± 0.01	7.96 ± 0.07	1.69 ± 0.09	0.34 ± 0.02	1.0000	0.0060	5.14
HA CUW15	0.50	4.15 ± 0.02	2.15 ± 0.08	0.69 ± 0.02	8.14 ± 0.21	1.42 ± 0.28	0.41 ± 0.08	0.9998	0.0132	3.57
HA CUW30	0.48	3.93 ± 0.03	2.50 ± 0.09	0.59 ± 0.01	8.12 ± 0.28	1.37 ± 0.34	0.41 ± 0.09	0.9998	0.0133	3.88

[a] Calculated average value for the model parameters of HS-like extracts.

in HS-like extracted during the maturation process is not very different. An increase in the total content of acid groups, as opposed to the DOM, was observed during the composting process, which agrees with the behaviour displayed by the charge curves of the HS-like extracts (Fig. 6). As previously reported by Plaza et al. (2005), a loss of aliphatic structures and carbohydrates, along with an increase in acid functional groups and groups containing N and S occur during the composting process. This increase in the site abundance was more evident in the HA-like extracts, from 3.57 to 4.74 mmol/g, than in the FA-like extracts, from 5.00 to 5.11 mmol/g, agreeing with the separation observed between the charge curves with the composting time (Fig. 6).

Average values for log K of carboxylic and phenolic groups were 2.96 and 7.86 for FA-like, and 3.49 and 8.21 for HA-like, respectively. These are comparable to the values specifically obtained with the NICA-Donnan model for HS-like extracted from compost found in the literature (Table S7, Supporting Information). On the other hand, the log K values calculated with the Henderson-Hasselbalch equation for other compost HA were almost 2 log units higher (Campitelli et al., 2012). When compared with the generic values obtained for aquatic and terrestrial HS (Milne et al., 2001), the values obtained are rather similar, indicating that the nature of the acid sites present in the HS molecules is related. As the composting process advances, log K experienced a shift toward a more acidic character (Table 5). The same trend was described by Plaza et al. (2005), although the decrease in their log K values for the HA-like was more pronounced. This result indicates that, in general, the HS-like become more acidic during the composting process possibly due to the oxidation reactions in the lignin or to the microbial degradation of carbohydrates (Sánchez-Monedero et al., 2002).

3.3. Testing the compost as soil amendment

The physico-chemical characteristics of the Haplic Cambisol and the variations in these after amendment with compost of different feedstock (except compost CVDW, which was not applied due to limited sample availability) are shown in Table 6. Soil Ch2 showed an acidic character, characteristic of mine soils developed in areas rich in mineral sulphides. The carbon content was lower than 1% and the values of available phosphorus (Olsen P) and CEC were relatively low, reflecting the low productivity of the soil (Hazelton and Murphy, 2007).

Application of compost led to an improvement of different soil quality indicators, particularly pH, available phosphorus and CEC. This effect increased with the amount of compost in the amendment. The pH of the compost samples ranged between 6.16 and 9.76, and application of the amendment therefore had a positive effect on the soil. Sample CSS was the only compost that did not increase the soil pH above 7, although this compost, together with compost CUW, supplied the greatest amounts of organic matter. Application of amendments containing 10% of CUW or CSS increased the carbon content from 0.66% to 3.28% and 3.47%, respectively. Also, application of sample CSS produced the greatest increase in total P on the amended soil, but the relative concentration of available P forms is lower than with the other compost. Thus, application of composts CDDW and CLW produced an increase in the concentration of Olsen P from 4.6 mg/kg to 206.6 and 365 mg/kg, respectively. Both samples contain more than 10% of the total P as available P forms (Table 1), which may favour plant productivity. Finally, compost CLW also generated the greatest increase in the CEC relative to the control, from 1.27 to 37.3 cmol (+)/kg. The concentration of exchangeable cations in the amended soil increased significantly with the content of compost, irrespective of the feedstock (Table S8, Supporting Information).

Seed germination was favoured by increasing the content of compost in the amended soil, as reflected by the increase in GI, although the intensity of the increase depended on the compost used (Table 6). Thus, the GI values were highest in samples amended with CLW and CDDW. Application of both composts generated the highest increase in the concentration of available P and exchangeable cations, and yielded the

Table 6

Variation of the soil properties and the parameters obtained in the germination assays following the application of compost as a soil amendment..

	pH	%C	%N	P-total (mg/kg)	P-Olsen (mg/kg)	CEC (cmol₊/kg)	Root length (cm)	NRE	RSG (%)	RRG (%)	GI (%)
Ch2 (Control)	4.53	0.66	n.d.	258.0	4.6	1.27	4.32	0.0	100.0	100.0	100.0
Ch2 + 2%CLW	7.13	0.96	0.05	509.8	53.6	12.3	6.39	0.48	100.0	147.7	147.7
Ch2 +5%CLW	7.77	1.59	0.09	640.4	105.7	27.1	6.62*	0.53*	109.4	153.1*	167.5*
Ch2 + 10%CLW	8.19*	1.90	0.13	846.6	365.0*	37.3*	6.56	0.52	103.8	151.8	157.5
Ch2 + 2%CUW	6.63	1.06	0.02	347.4	3.8	4.4	5.75	0.34	113.2	134.1	151.8
Ch2 +5%CUW	7.59	1.38	0.06	429.5	9.9	13.2	5.80	0.47	105.7	147.4	155.8
Ch2 + 10%CUW	7.77	3.28	0.32	603.5	22.0	20.0	6.37	0.33	107.5	133.0	143.0
Ch2 + 2%CSS	5.34	1.29	n.d.	704.5	28.1	2.8	3.97	−0.08	103.8	91.9	95.4
Ch2 +5%CSS	5.98	2.59	0.53	1338.2	42.5	6.7	5.01	0.16	103.8	115.8	120.2
Ch2 + 10%CSS	6.15	3.47*	0.39*	1956.2*	101.6	10.8	5.08	0.17	113.2*	117.5	133.0
Ch2 + 2%CVA	6.63	0.98	n.d.	478.8	29.6	6.2	5.97	0.38	100.0	138.0	138.0
Ch2 +5%CVA	7.59	1.36	0.06	733.6	39.9	11.5	6.24	0.44	107.5	144.4	155.3
Ch2 + 10%CVA	7.77	2.04	0.16	1128.3	78.4	23.4	6.47	0.50	100.0	149.6	149.6
Ch2 + 2%CDDW	7.21	0.93	0.06	534.7	48.1	12.1	6.55	0.52	103.8	151.5	157.2
Ch2 +5%CDDW	7.49	1.56	0.48	760.1	69.2	16.1	6.14	0.42	111.3	141.9	158.0
Ch2 + 10%CDDW	7.79	2.29	0.27	1002.4	206.6	22.3	6.26	0.45	110.4	144.7	159.7

n.d. – non detected *Indicates the case with the higher increase in the corresponding parameter after the amendment application. CEC: cation exchange capacity. NRE: normalized residual elongation index. RSG: relative seed germination index. RRG: relative radicle growth index. GI: germination index.

optimal pH for plant growth. On the other hand, the smallest increase in GI occurred with compost CSS. Although this compost yielded the greatest increase in C, N and total P in the soil, it did not generate such a large increase in pH as the other compost. Compost CSS was produced from sewage sludge, and therefore the concentration of species that are potentially toxic to *Lollium perenne* may be significant. When the germination tests were conducted with the water extracts from the compost, similar tendencies were observed. Samples CLW and CDDW showed the GI values above 100%, while sample CSS yielded the lowest GI, ~60% (Fig. S10, Supporting Information). The low GI for sample CSS cofirms the existence of phytotoxic effects and the lack of maturity of this compost (Cesaro et al., 2019). The other compost, on the other hand, could be considered free of phytotoxic substances. Other factors that inhibit seed germination include high salinity and excess of ammonium (Hoekstra et al., 2002). The concentration of ammonium in the solutions used in the germination assay was not determined, although it reached values higher than 150 mg/L in the original CSS sample (Table 2). The lower positive effect of CSS on the amended soil was also reflected in the values of the NRE index (related to root growth), which reached a maximum value of 0.17 in the soil amended with 10% of compost. Root growth is a more sensitive parameter, although it is more difficult to quantify than seed germination. For the other samples, the values of NRE ranged between 0.33 and 0.53, and application of compost CLW had the most positive effect.

The effects of the application of compost on shoot and root growth are shown in Fig. S11 (Supporting Information). No clear trend was observed in the growth of the aerial part of the seedlings in relation to the different amendments, nor in the different compost percentages in each. However, the effect on root growth decreased in the order CLW > CVA > CUW > CDDW > CSS. A good correlation between the NRE index and the %N in the compost was observed (Fig. S12, Supporting Information), although the variables were inversely related, so that as the N content increased, the root growth decreased. The correlations between total P and K, were lower (R^2, 0.28–0.60). The increase in K led to an increase in the NRE index, whereas the opposite effect was observed in the case of total P. Therefore, a compost with a well-balanced NPK index (Fig. S13, Supporting Information) is needed in order to obtain a positive effect on the root growth. Thus, sample CSS (NPK, 3.6-4.8-0.5) with high N and low K content produced a smaller increase, while the opposite was found for sample CLW (NPK, 1.8-31-3.6).

4. Conclusions

Compost and vermicompost samples were studied to evaluate both the effect of the composting process and the effect of the feedstock

material. The evolution of the organic matter stabilization was also monitored during composting. A decrease of the C/N ratio led to a CEC increase as the composting process progressed, whereas a linear increase of CEC as a function of C/N ratio was observed when mature compost samples from different feedstock were analysed. In both cases the correlation can be interpreted as an increase in the degree of maturity. The concentration of DOC in water extracts can be used to quantify the content of HS-like compounds in the compost, which is especially relevant since the extraction procedure for humic substances is time-consuming.

The potentiometric study of the acid-base properties of HS-like fractions extracted from compost revealed an increase in the total amount of acidic sites during the maturation of the compost, thus enhancing the possibility of interaction and removal of heavy metals from soils. Also, considering the interaction between the soil fractions and the compost, it may be useful to study the acid-base behaviour of the DOM in the equilibrium solution, since these are the processes that are more likely to take place in the environment. The worms that participate in the vermicomposting process seem to perform a more efficient degradation of the original aliphatic materials, as it can be deduced by the higher abundance of acidic groups compared to traditionally composed samples.

The use of the compost as amendment improve the quality of unproductive mine soils. Depending on the feedstock material, different parameters were improved, i.e. urban waste compost generated a greater increase in the organic carbon, while domestic waste compost and livestock manure compost increase the concentration of bioavailable nutrients in the soil. Seed germination was favoured after the application of these compost samples, indicating that the nutrient content of the selected compost must be balanced to optimize soil fertility and plant growth.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.113702.

Credit author statement

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