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Effect of lignocellulosic and phenolic compounds on ammonia, nitric oxide and greenhouse gas emissions during composting

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ABSTRACT

Composting is recognised a promising technology for recycling and adding value to agro-food wastes. There are, however, potential environmental risks associated with composting, such as the emission of greenhouse gases (GHGs). The aim of this study was to quantify the emissions of carbon dioxide, methane, nitrous oxide, nitric oxide and ammonia during composting of five agro-food wastes originated from the broccoli, chestnut, olive and grape industries, and to study the relationship between the emissions and the lignin, cellulose, hemicellulose and phenolic contents of the wastes. According to physicochemical indicators monitored during the process, all agro-food residues tested were suitable for composting, with chestnut in the top and broccoli in the bottom of the range. Composting of chestnut and olive led to higher carbon dioxide, methane and nitrous oxide emissions, whereas lower emissions were observed with white grape. A positive correlation was found between phenolics and nitric oxide ($r = 0.63$; $p < 0.01$), but not with the other gases. Lignocellulose showed a positive correlation with nitrous oxide ($r = 0.51$; $p < 0.05$), but not with carbon dioxide and methane. The accumulation of lignin was highest in the chestnut compost, which was associated with lower nitric oxide and ammonia emissions relative to the other waste materials. The results show that wastes with high lignocellulose can be managed using composting with additional benefits on the environment in relation to mitigating nitrogen losses.

1. Introduction

Large amounts of agro-food wastes, generated as a consequence of rapid population growth and subsequent increase in food production and consumption, nowadays pose serious environmental and economic risks (Mirabella et al., 2014). The agro-food sector contributes to the loss of an abundant pool of organic valuable materials that could be used as a substitute for mineral fertilisers and pesticides, thereby promoting a more sustainable agriculture.

Crop residues represent a substantial portion of organic wastes. In southern Europe, grape, olive and chestnut crops are widely cultivated and wineries, chestnut and olive oil mills constitute the dominant agro-industrial activities in the region (Salgado et al., 2014). The winery industry for example, reportedly produces 14.5 Mt of grape byproducts in the region (Pinelo et al., 2006).

Direct soil application of agro-food wastes, especially those rich in bioactive compounds (e.g., polyphenols), is cautiously recommended due to toxic effects on microorganisms and plants (Medina et al., 2015). For these reasons, transformation and stabilisation of these wastes before their application to soil are imperative; composting provides a viable and secure technology option for achieving that goal. Composting can be used to effectively counter the toxicity of wastes while yielding a pathogens-free material. The composting process also reduces the waste volume and weight by about 50% (Senesi, 1989) with a low investment cost compared with other waste treatment technologies (Lim et al., 2016); the reduction in weight ensures a stable final product which can be applied to improve the chemical and physical properties of soils

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(Bustamante et al., 2011), including the performance of plants (Santos et al., 2016).

Composting could lead to secondary pollution involving ammonia (NH_3), nitric oxide (NO) and greenhouse gases (GHG) emissions (Ermolaev et al., 2015), which are known drivers of global warming and stratospheric ozone depletion. Although composting is considered to have a lesser environmental impact compared to other waste treatments (Saer et al., 2013), its advantages can be negated if the composition process is not optimized. Productivity gains following compost application should also be weighed against the amount of gases released during the composting process (Sanchez-Garcia et al., 2015). Quantitative studies on gaseous emissions during the composting process are needed to make such comparisons possible and to develop models; emission models would be useful for environmental assessments involving different conditions such as the waste type, chemical composition, the bulking agents and the processing unit airflow.

The last decade has seen a growing interest in GHG emissions during composting. For example, Sánchez-Monedero et al. (2001) evaluated the effect of olive mill wastes mixed with different agroindustrial by-products on GHG emissions; Cayuela et al. (2012) studied GHG emissions during composting of a lignocellulosic mixture added with different N sources. GHG emissions have also been addressed in composting studies involving varying experimental units and operation schemes: Amlinger et al. (2008) evaluated the influence of turning frequency and different aeration rates on GHG, NH_3 and N_2O emissions; Ermolaev et al. (2015) studied N_2O and CH_4 emissions at different temperatures. These studies collectively demonstrate that the rate of gas production, diffusion and emission from composting piles are highly dependent on the physical characteristics of the starting material, such as its temperature, and its microbial population. There is, however, a lack of information on the relationship between the physical properties of the wastes and GHG emissions during composting. It is reasonable to assume that chemical compounds, such as lignocelluloses and phenolics which are characterised by a low degradation rate, would highly influence the mechanisms involved in GHG emissions during composting.

The objectives of this work were to (i) assess the reuse/recycling potential of broccoli, chestnut, grape and olive wastes as composts, with consequent environmental implications regarding gaseous emissions during the composting process, and (ii) assess the relationship between the mechanisms involved in CO_2, CH_4, N_2O, NO and NH_3 emissions and the lignin, cellulose, hemicellulose and phenolic contents of the wastes. This information would be crucial for disposing and/or valorising agro-food wastes based on sound environmental decision criteria, and through implementation of improved management practices.

2. Materials and methods

2.1. Agro-food wastes and experimental design

The composting experiment was carried out at the Universidade de Trás-os-Montes e Alto Douro (N 41°17′7.28″; W 7°44′36.83″), and lasted ca. 5 months. The compost was produced in 135-L insulated reactors. The air was supplied continuously with a diaphragm pump (KNF, model N010.KN.18, Neuberger GmbH, Freiburg, Germany) from the underside of the reactor, where a perforated plate was positioned between the base and the composting mixture. The photoacoustic and chemiluminescent N oxide analysers used to measure gas concentrations were connected to the reactor with Teflon tubes positioned on the air inlets and outlets. Additional information about the composting system can be found in Santos et al. (2017). Aeration of the composting mixture was at the rate of 20 L h^{-1} kg^{-1} DW (dry weight) during the first 15 d, and 10 L h^{-1} kg^{-1} DW thereafter, using a flowmeter equipped with a needle valve (Aalborg, model P, Orangeburg, USA) operating at 5 L min^{-1}.

Five types of agro-food wastes were used in the composting experiments: (i) broccoli; (ii) chestnut; (iii) white grape marc from *Vitis vinifera* L. var. Moscatel; (iv) red grape marc from *Vitis vinifera* L. var. Alfrocheiro; and (v) olive. Broccoli wastes consisted of rejected flowering inflorescences; chestnut wastes comprised of peels and rejected fruits; grape marc were collected during the grape stripping step of the winemaking process; and olive leaves were obtained from an olive oil extraction plant. Dried wheat straw previously milled (2–4 cm) using a knife mill (Yike, 9FQ-360 straw hammer mill, Zhengzhou, China) was used as structural material. A control treatment was prepared with wheat straw complemented with urea to adjust the carbon-to-nitrogen (C/N) ratio to 40.

Twenty-four (24) hours before the composting experiment starts, agro-food raw materials were grinded into pieces of ca. 1 cm in length using a shredder (Viking model GB370S, Langkampfen, Austria) and stored fresh at 4 °C until use.

Four reactors were used per treatment, representing the replicates. Each reactor was filled with 10 kg dry matter (DM) of the waste-straw mixture, in a proportion allowing an initial C/N ratio of ca. 40, as calculated from the elemental contents of the raw materials (Table 1). Treatments consisted of a mixture of the wastes with wheat straw and urea (except for broccoli) and are herein referred to as: “Control”, “Broccoli”, “Chestnut”, “WhiteGrape”, “RedGrape” and “Olive”. Moisture was maintained approximately between 45% and 60% by adding water when necessary. The temperature was measured using TM1 temperature probes (Delta-T Devices, Cambridge, UK) positioned inside the reactors and in the centre of the composting mixture, where the highest temperatures were recorded. The mixture was turned manually once a week during the most biooxidative phase and then every 15 d till the end of the maturation period.

A representative sample of each compost was taken on days 0, 3, 8, 17, 30, 76 and 147, by mixing sub-samples from six different locations in the reactor and at depths between 20 and 80 cm. Each composite sample was disassembled into 3 subsamples, one of which was ground (particle size < 1 mm), frozen and stored for chemical and physical analyses; another subsample was dried at 40 °C for phenolic and lignocellulosic determination; the last subsample was oven dried at 65 °C during 48 h to determine the DM content.

2.2. Measurements of physicochemical properties of the composts

Fresh composts were analysed for their pH, electrical conductivity (EC), and content of organic matter (OM), using standard procedures (CEN, 1999).

Soluble organic nitrogen (ONsol) and soluble organic carbon (OCsol) were determined after extraction of dry samples with 0.01 M $CaCl_2$ (1:10 w/v) in an elemental analyser (Formac, Skalar, Analytical B.V, Breda, Netherlands), followed by chemiluminescence and near infrared (NIR) detection. Total organic N (Nt) and total organic C (Ct) were evaluated by thermoconductivy and NIR detection in a Skalar Primacs SNC-100 and the C/N ratio calculated.

Ammonium N (NH_4^+–N) and nitrate N (NO_3^--N) concentrations were determined in filtered extracts by molecular absorption spectrophotometry with a segmented flow system (SanPlus, Skalar) prior to extraction of samples with 1 M KCl (1:10 v/v) (Houba et al., 1995). Iron (Fe), Zn, Ca, Cu, Mn and Mg were measured by atomic absorption spectroscopy, after nitric-perchloric acid digestion of dry samples. Total P was determined by molecular absorption

Table 1
General characterisation of the initial waste-straw mixtures used for composting.

	pH	EC ($dS\ m^{-1}$) (water 1:5)	OCsol ($g\ C\ kg^{-1}$ of DM)	OM ($g\ C\ kg^{-1}$ of DM)	ONsol ($g\ N\ kg^{-1}$ of DM)	Nt ($g\ N\ kg^{-1}$of DM)	NH_4^+–N ($mg\ N\ kg^{-1}$ of DM)	NO_3^--N ($mg\ N\ kg^{-1}$ of DM)
Control	8.11 ± 0.48 a	1.79 ± 0.07 bc	8.89 ± 1.84 cd	938.0 ± 24.0 a	4.84 ± 2.00 a	13.8 ± 0.5 a	693.4 ± 167.9 ab	0.18 ± 0.06 c
Broccoli	8.04 ± 0.24 a	2.18 ± 0.27 ab	6.99 ± 1.03 cd	927.1 ± 19.6 a	4.06 ± 0.28 a	19.8 ± 3.2 a	1075.5 ± 156.4 a	7.18 ± 2.77 a
Chestnut	7.69 ± 0.55 a	1.26 ± 0.21 d	6.06 ± 1.40 d	959.0 ± 4.7 a	4.21 ± 0.92 a	15.0 ± 2.2 a	686.0 ± 295.1 ab	0.44 ± 0.10 bc
WhiteGrape	5.18 ± 0.39 c	2.55 ± 0.22 a	19.65 ± 3.67 a	946.6 ± 4.8 a	5.69 ± 1.25 a	15.0 ± 2.2 a	378.4 ± 151.7 b	4.88 ± 1.03 ab
RedGrape	4.51 ± 0.34 c	2.47 ± 0.28 a	18.51 ± 5.29 ab	943.8 ± 5.6 a	4.97 ± 0.74 a	16.1 ± 1.1 a	222.2 ± 63.3 b	5.24 ± 1.14 a
Olive	6.24 ± 0.63 b	1.61 ± 0.16 cd	12.70 ± 1.20 bc	948.2 ± 6.8 a	4.21 ± 1.02 a	16.6 ± 2.8 a	280.0 ± 127.1 b	0.20 ± 0.09 c

EC = electrical conductivity; OCsol = soluble organic carbon; OM = organic matter; ONsol = soluble organic nitrogen; Nt = total nitrogen.
Values within a column, with the same letter are not significantly different ($p < 0.05$). Values are expressed as mean ± SD (standard deviation) of four replicates.

spectrophotometry with the Skalar segmented flow system.

Phytochemical analyses consisted of the extraction and quantification of total phenolics and gallic acid. Total phenolics were extracted using the Folin-Ciocalteu reagent, and detected by spectrophotometry, as described by Javanmardi et al. (2003). A calibration curve with different gallic acid concentrations (Sigma-Aldrich, Taufkirchen, Germany) was constructed and all data quantified as mg gallic acid equivalent (GAE) g^{-1} DM. Gallic acid was determined by high performance liquid chromatography as reported by Santos et al. (2017).

The lignocellulosic fractions were determined in the raw materials, waste-straw mixtures and final composts. Neutral-detergent fiber (NDF), acid-detergent fiber (ADF) and acid-detergent lignin (ADL) were determined by the sequential method of Van Soest et al. (1991). Hemicellulose and cellulose were calculated as the difference between NDF and ADF, and between ADF and ADL. All analyses were done in four replicates.

2.3. Measurements of gas emissions

Emissions of CO_2, CH_4 and N_2O were measured using a 1412 Photoacoustic Field Gas Monitor (Innova AirTech Instruments, Ballerup, Denmark), with internal filters for water vapour, and particulate and optical filters for CO_2 (UA0982), CH_4 (UA0969) and N_2O (UA0985). The CO_2, CH_4 and N_2O detection limits specified for the analyser were 1.5, 0.4 and 0.03 ppm, respectively. Emissions of NO and NH_3 were performed with a chemiluminescent N oxide analyser (SIR MODEL S-5012, Madrid, Spain) with a detection limit of 0.5 ppb. Emission rates at the different events were determined after discounting the concentration of each gas in the inlet air to the outlet air in INNOVA and SIR data.

All gases were sampled once a day during the first 8 d of composting, every two days for the following three weeks and then on days 31, 36, 42, 49, 59. Ammonia (NH_3) and NO were measured on days 66, 73, 80, 87, 94, 104, 110, 117, 125, 130; and CO_2, N_2O and CH_4 on days 80, 104, 117 and 147. To minimise the influence of ambient air on the gas concentrations, measurements were always done before homogenisation or collection of the composts.

To get the cumulative CO_2, CH_4 and CO_2 emissions, daily fluxes from contiguous measurements were averaged and multiplied by the interval between sampling periods. In order to evaluate the effect of the different treatments on total GHG emissions, the measured emissions were converted into CO_2-equivalents according to the IPCC GWP factors of 28 and 265 times as much as CO_2 for CH_4 and N_2O, respectively (IPCC, 2013).

2.4. Statistical analyses

The results are presented as mean ± standard deviation (SD) and all analytical determinations were made in quadruplicate. To evaluate the effects of each treatment (factor) at different sampling times (d) on physicochemical parameters, lignocellulosic composition and gas emissions, data were analysed by a two-way repeated measures analysis of variance. Differences between means were determined by the Tukey's honestly significant difference test at a significance level of 0.05. The relationship between total phenolic compounds, lignocellulosic compounds, and gaseous emissions were assessed by calculating Pearson's correlation r values. The referred statistical analyses were performed using the Statistix 10.0 software (Analytical Software, Tallahassee, USA). Prior to these tests, normality and homogeneity of the data were checked using Shapiro-Wilk and Levene tests.

3. Results and discussion

3.1. Evolution of physicochemical parameters during composting

3.1.1. Temperature

With regard to temperature variations with composting time, significant differences ($p < 0.05$) between treatments were observed. The highest temperature (54 °C) was reached with Broccoli – at a faster rate than with the other treatments –, and was maintained for five consecutive days. Broccoli also resulted in the longer thermophilic phase and this may be explained by a greater content of easily degradable organic compounds in broccoli wastes, as compared to the other materials (Table 1). This pattern of temperature change during composting has also been observed with garden leaves (Kalamdhad et al., 2009), and horticultural wastes (Gavilanes-Terán et al., 2016).

The slowest increase in temperature was observed with Control, Chestnut, and Olive, probably because the wastes contained an organic matter more resistant to microbial degradation (Table 1). At the end of the composting process, the average temperature for all treatments had returned to or near ambient values (ca. 13 °C), an indication of the slowdown of microbial activities.

3.1.2. Physicochemical parameters

The physicochemical characteristics of the waste-straw mixtures at different times are displayed in Fig. 1. With the exception of WhiteGrape, the pH of the mixtures remained constant after 3 days, which could be attributed to lower microbial activities and the stabilisation of the composts. At the end of composting, final pH values ranged from 8.99 (WhiteGrape) to 9.26 (Chestnut) (Fig. 1a). Although such high pH values might stimulate NH_3 losses (Lasaridi and Stentiford, 1998), taking into consideration other indices used to assess the performance of the composting process such as microbial degradations or agronomic tests, it is reasonable to say that all composts were safe for soil application, as attested by the production of lettuce plants fertilised with the same materials in a pot experiment (Santos et al., 2016).

A strong increase in electrical conductivity (EC) values was observed during the first days of composting, corresponding to the

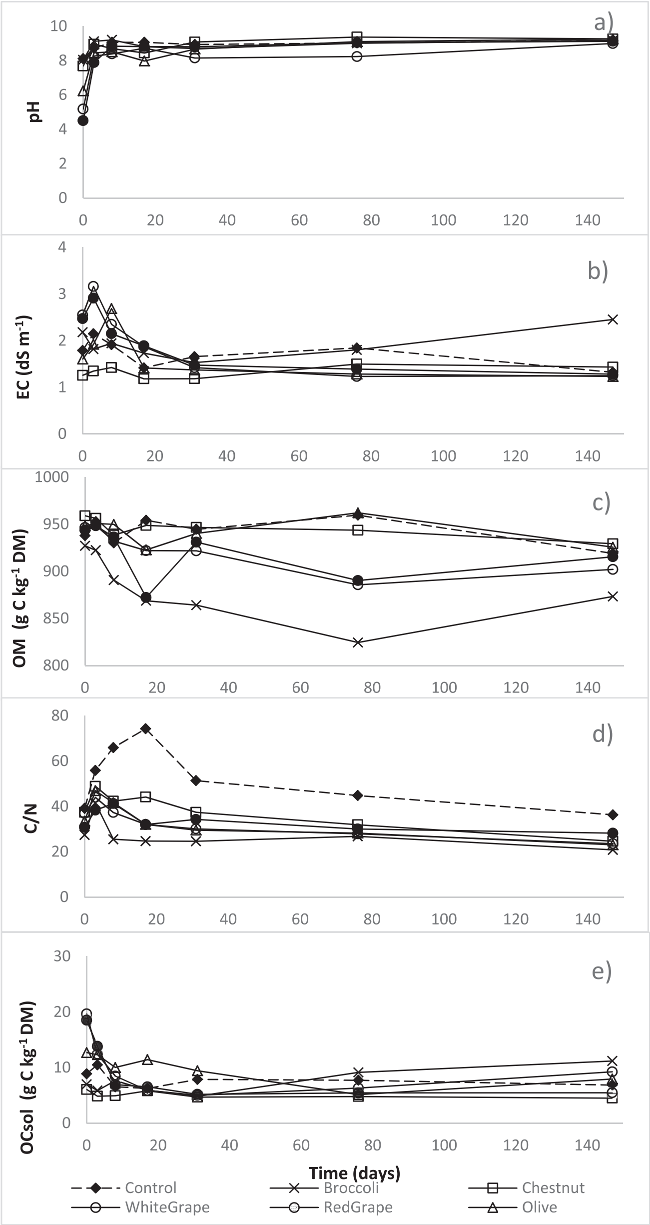

Fig. 1. Evolution of main physicochemical characteristics of the waste-straw mixtures during composting. a) pH; b) Electrical conductivity; c) Organic matter; d) C/N ratio; e) Organic soluble Nitrogen.

thermophilic phase; and then a decrease as the composting process progressed, indicating accrued benefits in terms of final-product quality (Fig. 1b). The only exception was with Broccoli, for which an opposite trend was observed. Final EC values were in the range of 1.23 dS m^{-1} for Olive and 2.45 dS m^{-1} for Broccoli, which were all below the maximum EC value of 3 dSmm^{-1} recommended for compost application to soil (Solano et al., 2001).

The C/N ratio for all the mixtures (ca. 40) first increased, and then decreased with composting time to a final ratio ranged from 20.9 with Broccoli to 36.3 with Control (Fig. 1d). The final C/N ratios exceeded the threshold limit of 20 recommended by Golueke (1981). The C/N ratio should be considered only as a relative indicator of compost maturation here since the bioavailability of organic C matters more than the total organic C content in high lignocellulosic materials (Sánchez-Monedero et al., 2001), such as those used in the present study.

The OM content decreased with composting time, and hence with mass reduction (Fig. 1c). The highest OM content was observed with Chestnut, and it decreased with composting time from 959.0 g C kg^{-1} DM to 929.4 g C kg^{-1} DM. The lowest OM content was observed with Broccoli, and it decreased from 927.1 g C kg^{-1} to 873.4 g C kg^{-1}, with significant differences ($p < 0.05$) as compared to all other treatments (Fig. 1c).

The same behaviour observed with OM was seen with OCsol, though with opposite directions of change. At the end of composting, the lowest OCsol content (4.50 g C kg^{-1} DM) was observed with Chestnut, and the highest (11.18 g C kg^{-1} DM) with Broccoli (Fig. 1e). Differences ($p < 0.05$) between treatments could be explained by different turnover rates of labile and stable fractions of organic compounds. After 36 days, degradation of easily degradable compounds had already occurred in Control, Chestnut, and RedGrape. These treatments also exhibited stable OCsol contents until the end of the experiment (Fig. 1e), indicating that equilibrium between microbial degradation of complex organic structures like cellulose and hemicellulose and production of soluble compounds (Serramiá et al., 2010) had been reached.

As a result of DM loss, the contents of all elements in the different materials increased during composting (Supplementary Figure S1). Substantial amounts of mineral nutrients were present in all treatments, which for a fertilisation point of view, is an important quality for a final compost. Higher P, Mg, Fe and Zn contents were obtained with Broccoli, as compared with all other treatments ($p < 0.05$). Broccoli compost was also found to be a rich source of Ca (12.29 g kg^{-1} DM), which is essential for plant nutrition. Previous studies have shown that micronutrients and heavy metals are present in significant amounts in vegetable wastes, and concurring with the results of this study, are increased during composting (Gavilanes-Terán et al., 2016).

3.1.3. Nitrogen contents

Fig. 2 shows the time course of total nitrogen (Nt), soluble organic nitrogen (ONsol) ammonium (NH_4^+) and nitrate (NO_3^-) changes during composting.

Total nitrogen decreased at the beginning of composting and slightly increased as the process progressed, probably as a result of a concentration effect caused by weight loss associated with OM mineralisation (Senesi, 1989). At the end of the process, highest Nt (24.12 g N kg^{-1} DM) and ONsol (3.03 g N kg^{-1} DM) contents were obtained with Broccoli, and were significantly different ($p < 0.05$) from the contents obtained with the other treatments (Fig. 2a and b). Although the initial mixture of Broccoli was rich in Nt and ONsol, its initial content of OCsol was lower when compared with most of the other treatments (Table 1).

According to the data shown in Fig. 2c, NH_4^+ contents were initially increased as a consequence of ammonifying activities. The highest NH_4^+ content was observed on day 3 (1453.9 mg N kg^{-1} DM for Control), coinciding with a peak in soluble N contents. A significant decrease was observed with all treatments, mostly due to volatilisation of NH_3 and/or immobilisation or nitrification processes as seen in Fig. 3. A slightly different trend of change was observed with Broccoli, with an initial decrease of NH_4^+ contents by day 3, followed by a sharp increase peaking at day 17, and a progressive decrease (Fig. 2c). By the end of composting, NH_4^+ content was significantly lower ($p < 0.05$) with Broccoli than with the other treatments. The largest decrease in NH_4^+ contents observed with Broccoli (Fig. 2c) as compared to its initial richness in NH_4^+ (Table 1) was probably related to higher Nt and ONsol contents. The final NH_4^+ contents in most piles were below the maximum recommended value for a mature compost, i.e., 400 mg kg^{-1}.

As observed for NH_4^+, NO_3^- contents for all treatments increased shapely within the first days of composting (Fig. 2d). The highest

NO_3^- content was observed in the initial broccoli mixture (Table 1), which also led to significant N_2O emissions (see Table 3). In previous studies using pig manure with straw (Szanto et al., 2007) and olive mill wastes with different agro-industrial by-products (Sánchez-Monedero et al., 2010), a correlation was found between N_2O emissions and NO_3^- contents during periods of intense nitrification.

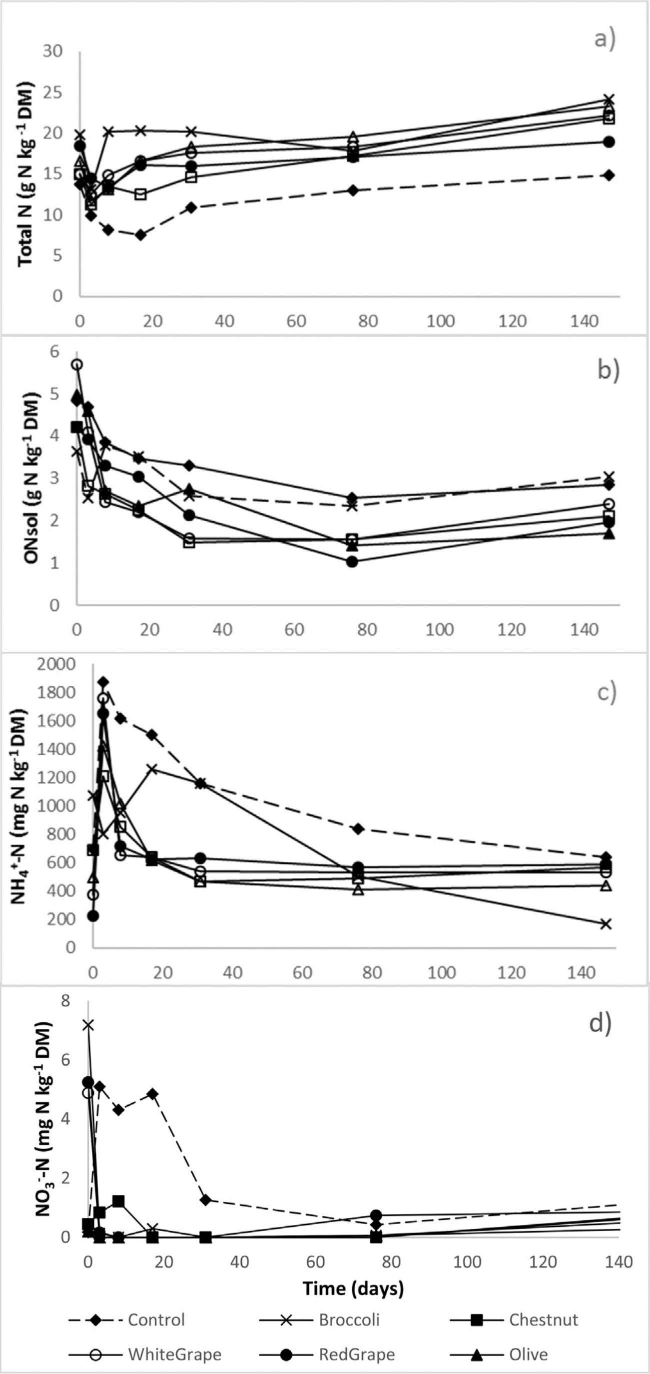

Fig. 2. Evolution of the contents of N forms in different waste-straw mixtures during composting. a) total Nitrogen, b) Organic soluble Nitrogen; c) NH_4^+–N; d) NO_3^--N.

3.2. Evolution of phenolic and lignocellulosic contents during composting

The contents of phenolics, hemicellulose, cellulose and lignin in the raw materials, waste-straw mixtures and final composts are presented in Table 2. Statistical analyses showed that time interacted with all the treatments to affect both the total phenolics and lignocelluloses.

The initial straw (3.75 mg g^{-1} DM) and broccoli (6.61 mg g^{-1} of DM) had the lowest contents of total phenolics, while olive (25.12 mg g^{-1} DM) and white grape (30.04. mg g^{-1} DM) had the highest contents. For all treatments, a significant decrease ($p < 0.05$) in phenolics occurred throughout the composting process, with final values ranging from 0.15 mg g^{-1} DM with Olive to 1.18 mg g^{-1} DM with Control (Table 2), indicating progressive degradation. It is possible that as soon as these phenolics were degraded and released, they were incorporated into biosynthetic pathways leading to the formation of humic substances (Stevenson, 1994).

The HPLC method used in this study for the separation of individual phenolics allowed the identification of the two tannins, namely gallic acid (in all treatments) and ellagic acid (in only the raw chestnut and initial chestnut-straw mixture). An increase in gallic acid contents occurred during composting (Table 2), reflecting a cumulative effect of straw added to wastes, but also the degradation of polyphenols into simple phenolics. Gallic acid exhibits a strong thermal stability and is metabolised only at temperatures above 60 °C (Volf et al., 2014). The maximum temperature reached during composting was 54 °C, which reasonably explains the presence of gallic acid in the composts at the end of the process.

Although beneficial at low levels, excess levels of water-soluble phenolics in composts may have adverse environmental impacts, mostly in inhibiting seed germination (Morthup et al., 1998) and limiting nitrogen immobilisation in soil (Bustamante et al., 2007).

Raw straw used as Control and raw chestnut had significantly higher ($p < 0.05$) contents of hemicellulose than the other materials, 386.3 and 358.4 g kg^{-1} DM, respectively (Table 2). These contents remained relatively unchanged after mixing with the co-substrate, but were significantly reduced ($p < 0.05$) by about 85% by the end of composting. In the case of RedGrape, WhiteGrape, Olive and Broccoli, hemicellulose contents measured at the end of composting were also much lower than those registered early in the process. Chestnut and straw, however, underwent the most intense degradation.

A more pronounced degradation of hemicellulose was observed than of cellulose, indicating that hemicellulose was the first cellulosic fraction used by microorganisms as C and energy source, as also reported by Serramiá et al. (2010). Hemicellulose is a smaller branched carbohydrate compared to cellulose, which is made of very long unbranched fibrils held together by hydrogen bonding that prevents easy access by microorganisms and enzymes (Komilis and Ham, 2003).

The straw had the highest content of cellulose (413.0 g kg^{-1} DM), while the raw Broccoli, Chestnut and Olive had the lowest contents (112.3, 143.3 and 150.1 g kg^{-1} DM), with WhiteGrape and RedGrape in the middle range (ca. 200 g kg^{-1} DM) (Table 2). By the end of composting, significantly higher ($p < 0.05$) reductions in cellulose contents were recorded with Olive (72%) and Broccoli (76%). The lowest reduction in cellulose content was observed for Chestnut (29%), which also exhibited the highest reduction in hemicellulose content (Table 2).

As for lignin, its “relative proportion” increased as a consequence of the intense degradation of the holocellulose fraction (cellulose + hemicellulose). Olive, RedGrape and WhiteGrape were the wastes that contained more lignin (Table 2). These treatments took longer to react to temperature changes. Lignin acts as a protective factor for the cellulosic and hemicellulosic fractions and the

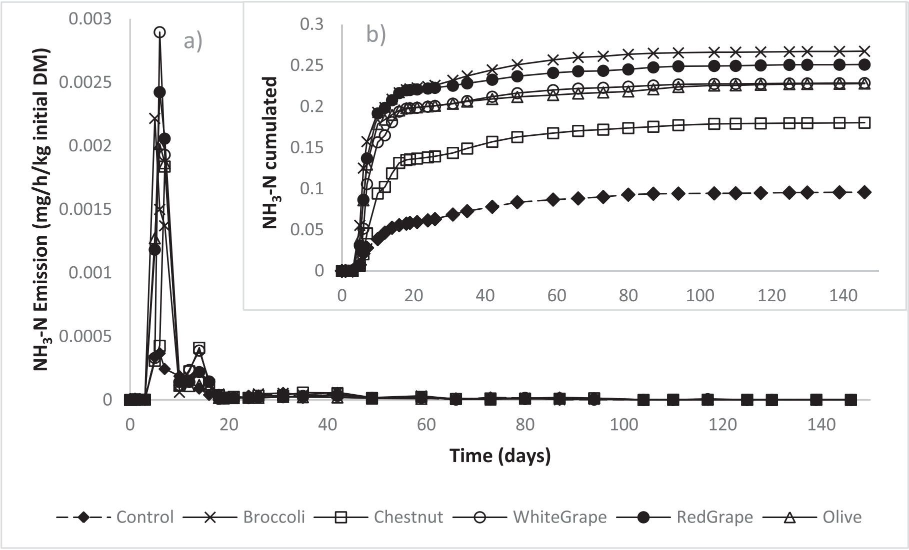

Fig. 3. Evolution of instantaneous and accumulated NH_3 emissions during composting: (a) instantaneous ammonia emissions, (b) accumulated NH_3 emissions.

Table 2
Evolution of the contents of total phenolics, gallic acid, lignocellulosic compounds (normalised to a constant ash content) and related ratio in the raw materials, initial straw-waste mixtures and final composts.

	Total phenolics ($mg\ g^{-1}$ DM)	Gallic acid ($\mu g\ g^{-1}$ DM)	Hemicellulose ($g\ kg^{-1}$DM)	Cellulose ($g\ kg^{-1}$DM)	Lignin ($g\ kg^{-1}$DM)	Lignocellulose ($g\ kg^{-1}$DM)	Lignin/holocellulose ratio
Raw materials							
Straw	3.75 ± 0.69 e	26.16 ± 0.93 a	386.3 ± 12.7 a	413.0 ± 5.33 a	48.60 ± 1.50 b	847.9 ± 15.7 a	0.06 ± 0.00 c
Broccoli	6.61 ± 0.02 d	4.19 ± 0.03 c	32.03 ± 4.50 d	112.3 ± 17.8 c	43.40 ± 15.8 b	187.8 ± 2.31 d	0.31 ± 0.15 bc
Chestnut	14.99 ± 0.47 c	17.66 ± 0.67 b	358.4 ± 28.1 a	143.3 ± 12.0 c	167.2 ± 22.8 a	668.9 ± 16.3 b	0.33 ± 0.06 bc
White Grape	30.04 ± 0.73 a	11.53 ± 1.41 bc	69.38 ± 6.44 bc	208.0 ± 8.42 b	187.7 ± 15.5 a	465.0 ± 10.4 c	0.68 ± 0.08 ab
Red Grape	24.50 ± 0.61 b	14.37 ± 2.01 b	51.31 ± 8.09 cd	202.6 ± 2.65 b	197.3 ± 3.67 a	451.2 ± 9.60 c	0.78 ± 0.03 ab
Olive	25.12 ± 0.63 b	12.75 ± 2.06 b	97.81 ± 1.31 b	150.1 ± 4.79 c	225.8 ± 1.54 a	473.8 ± 4.09 c	0.91 ± 0.01 a
Initial straw-wastes mixtures							
Control	3.75 ± 0.69 d	26.16 ± 0.93 a	386.3 ± 12.7 a	413.0 ± 5.33 a	48.60 ± 1.50 b	847.9 ± 15.7 a	0.06 ± 0.00 a
Broccoli	4.29 ± 0.19 d	20.62 ± 1.27 a	280.0 ± 10.2 b	322.8 ± 5.05 b	47.04 ± 5.16 b	649.9 ± 11.7 d	0.08 ± 0.01 a
Chestnut	8.25 ± 0.59 c	23.66 ± 0.89 a	375.2 ± 16.4 a	305.1 ± 6.29 b	96.03 ± 9.64 ab	776.3 ± 2.96 b	0.14 ± 0.02 a
WhiteGrape	13.74 ± 0.61 a	21.32 ± 1.62 a	265.9 ± 9.88 b	335.1 ± 6.11 b	101.5 ± 6.50 ab	702.4 ± 11.9 c	0.17 ± 0.01 a
RedGrape	11.78 ± 0.37 b	22.35 ± 0.83 a	252.3 ± 4.53 b	328.9 ± 2.20 b	108.1 ± 2.29 ab	689.3 ± 5.87 cd	0.19 ± 0.00 a
Olive	12.30 ± 0.61 b	21.49 ± 0.88 a	270.9 ± 8.13 b	307.9 ± 3.06 b	119.5 ± 0. 32 a	698.3 ± 7.81 c	0.21 ± 0.00 a
Final composts							
Control	1.18 ± 0.08 a	22.64 ± 0.92 a	55.65 ± 6.98 b	240.4 ± 3.73 a	248.1 ± 2.08 cd	544.2 ± 5.66 b	0.84 ± 0.01 b
Broccoli	1.17 ± 0.32 a	23.45 ± 0.81 a	115.5 ± 8.39 a	75.80 ± 3.99 c	205.9 ± 37.1 d	397.2 ± 33.4 d	1.16 ± 0.52 ab
Chestnut	1.07 ± 0.10 a	25.96 ± 1.87 a	58.95 ± 15.9 b	215.1 ± 17.5 ab	379.7 ± 18.4 a	653.8 ± 12.8 a	1.40 ± 0.23 a
WhiteGrape	1.02 ± 0.35 a	30.41 ± 6.58 a	108.9 ± 21.7 a	184.6 ± 46.9 b	352.0 ± 37.1 a	645.4 ± 32.3 a	1.27 ± 0.42 ab
RedGrape	0.74 ± 0.06 a	28.82 ± 2.73 a	131.4 ± 31.2 a	182.2 ± 2.95 b	324.5 ± 49.9 ab	638.1 ± 71.0 a	1.06 ± 0.38 ab
Olive	0.15 ± 0.00 a	30.02 ± 9.36 a	10.88 ± 4.12 a	86.00 ± 43.6 c	285.9 ± 40.3 bc	480.6 ± 139 c	1.58 ± 0.61 a

Values within a column, for the same day, with the same letter are not significantly different ($p < 0.05$). Values are expressed as mean ± SD (standard deviation) of four replicates.

biodegradation of lignin usually occurs tardily and at a very low rate (Malherbe and Cloete, 2002). At the end of the composting process, Chestnut, WhiteGrape and RedGrape were the treatments with highest lignin contents (Table 2).

The lignin/holocellulose ratio has been proposed as an index to monitor the biodegradability of the OM (Francou et al., 2008), and can be useful to understand a compost resistance to degradation after soil application. The lowest lignin/holocellulose ratio was with the Control, and increased from an initial value of 0.06 to a final value of 0.84, which was significantly lower ($p < 0.05$) than the final highest value obtained with Olive i.e., 1.58 (Table 2). The increase of this ratio for all treatments indicates stabilisation of the OM.

All the composts obtained were found suitable for agricultural use though the Broccoli had lowest OM, C/N, lignin, NH_4^+, NO_3^-, and cellulose contents compared to the other composts.

3.3. *Evolution of gaseous emissions during composting*

3.3.1. *Carbon dioxide*

Throughout composting, CO_2 fluxes were significantly ($p < 0.05$) affected, regardless of the type of waste. Composting with Olive led to the maximum average emission of 125.6 g CO_2—C kg^{-1} initial DM on day 9, while the lowest emission (34.6 g CO_2—C kg^{-1} initial DM) was observed on day 16 on the WhiteGrape (Supplementary Figure S1a. Major CO_2 fluxes were detected during the first 13 days of composting. After this initial period, a decrease in emissions occurred, with values equalising among the treatments towards the end of the experiment and leading to the accumulated CO_2—C emissions time pattern shown in Supplementary Figure S1a). Only Olive led to emission values over 100 g CO_2—C kg^{-1} initial DM. The final accumulated CO_2—C flux emissions (mg CO_2—C kg^{-1} initial

DM) are presented in Table 3. The highest emissions were observed with Olive and Chestnut, and the lowest emission with WhiteGrape. No significant correlation ($p < 0.05$) was found between final cumulative CO_2 emissions and the total phenolic and lignocellulosic contents of the initial waste-straw mixtures.

3.3.2. *Methane*

The production of CH_4 occurs in anaerobic micro-sites particles of compost materials, when degradation of fresh and easily available organic materials exhausts the oxygen (Epstein, 1997).

CH_4 emissions were highest in the early phase of the composting process, mostly during the first 13 days, when microbial activities were intense and the demand for aeration high. These fluxes pattern are responsible for the accumulated CH_4–C emissions presented in Supplementary Figure S1b. Statistical analyses indicated that CH_4 emissions differed ($p < 0.05$) among time, but not among waste types. Composting with Olive caused low CH_4 emissions during the first days of the process, with an average value of - 0.70 g CH_4–C kg^{-1} initial DM, whereas the lowest values were obtained with WhiteGrape and RedGrape. A sharp decrease of CH_4 emissions occurred as composting progressed, leading to negligible emissions towards the end of the experiment (Supplementary Figure S1b).

Accumulated CH_4 emissions (Table 3) correlated negatively with CO_2 emissions (r = - 0.756; $p < 0.001$), but not with the total phenolic and lignocellulosic contents of the initial waste-straw mixtures.

3.3.3. *Nitrous oxide*

N_2O is formed through nitrification and/or denitrification, under both aerobic and anaerobic conditions (Williams et al., 1998). Results showed that N_2O emissions were affected ($p < 0.05$) by all treatments and time. N_2O emission rates were high in the first 10 days of composting, with a peak in emissions on day 7 recorded for Olive (0.80 g N_2O–N kg^{-1} initial DM). The accumulated N_2O–N emissions during the composting process are illustrated in Supplementary Figure S1c. Table 3 shows the final accumulated emissions values, which ranged from 0.08 g N_2O–N kg^{-1} initial DM (WhiteGrape) to 0.91 g N_2O–N kg^{-1} initial DM (Olive and Chestnut). Accumulated N_2O emissions in RedGrape, Broccoli and WhiteGrape treatments were 2.62, 3.78, and 8.50 times lowers than in the Control. A significant correlation was found between cumulative N_2O emissions and the hemicellulose (r = 0.522; $p < 0.01$) and lignocellulose ($r = 0.506$; $p < 0.05$) contents of the initial waste-straw mixtures, but not with the total phenolic content.

3.3.4. *Ammonia*

The waste type, the time, and their interaction significantly affected ammonia emissions (Fig. 3). Highest emissions occurred during the first 10 days of composting, corresponding to the most bioactive period of the process, with peak values of 0.003 (WhiteGrape) and 0.02 g NH_3–N kg^{-1} initial DM (RedGrape) on day 6 (Fig. 3a). The straw treatment (Control) emitted less NH_3 when compared with all the other treatments. After day 18, the emissions progressively decreased to null values, with no significantly differences ($p < 0.05$) between treatments.

The lowest cumulative NH_3 emissions were calculated for Control and Chestnut, and were significantly different ($p < 0.05$) from those calculated for the other treatments (Fig. 3b). As a carbon-rich material, straw contains a substantial amount of degradable carbon, which stimulates immobilisation of ammonium on microbial biomass (Sommer et al., 2006), with subsequent increase in the C/N ratio (Table 1). The use of straw as bulking agent could improve compost porosity and increase oxygen concentrations (Chowdhury et al., 2015). Sánchez-Monedero et al. (2001) reported that the use of wastes with high lignocellulose contents led a reduction of about 25% of N losses during the composting process. In agreement with the results of the present study, treatments with higher C/N ratios and lignocellulose contents (Control and Chestnut) led to lower cumulative NH_3 emissions. Broccoli with the lowest C/N ratio (Table 1) and lignocellulose content (Table 2) led to higher emissions. Cumulative NH_3 emissions were highly and negatively correlated with lignocellulose (r = - 0.873; $p < 0.001$), and positively correlated with the total phenolic contents ($r = 0.462$; $p < 0.05$) of the initial waste-straw mixtures.

3.3.5. *Nitric oxide*

Nitric oxide (NO) is a precursor of tropospheric ozone, a greenhouse gas formed by photochemical reaction and which plays key roles in atmospheric chemistry (Williams et al., 1998). Few reports have measured NO emissions during composting trials. In the present study, time and waste type significantly ($p < 0.05$) affected NO emissions. In concordance with ammonia data, NO was emitted primarily during the first 10 days of composting (Fig. 4a) with the highest peak values being recorded on day 6 for RedGrape (0.17 g NO–N kg^{-1} initial DM) and WhiteGrape (0.16 g NO–N kg^{-1} initial DM). After day 14, emissions started to decrease and remained close to zero until the end of the composting process. As with NH_3, the lowest cumulative NO emissions were calculated for Control and Chestnut (ca. 8.7 g NO–N kg^{-1} initial DM at the end of composting); but the highest for Olive (15.8 g NO–N kg^{-1} initial DM) rather than Broccoli (Fig. 4b). Cumulative NO emissions correlated negatively with lignocellulose (r = - 0.633; $p < 0.001$) and hemicellulose (r = - 0.779; $p < 0.001$) and positively with lignin ($r = 0.523$; $p < 0.01$) and total phenolics ($r = 0.626$; $p < 0.01$).

3.3.6. *Greenhouse gas emissions*

Emissions of N_2O, CO_2, and CH_4 throughout the composting process were summed to get total GHG emissions, after their conversion into CO_2-equivalents. The different treatments significantly

Table 3
Final accumulated GHG emissions (CO_2, N_2O and CH_4) expressed as CO_2 equivalents.

	Accumulated emissions (g kg^{-1} Initial DM)			GHG emissions (g CO_2 eq. kg^{-1} initial DM)	Contribution (%)			GHG emissions without CO_2 (g CO_2 eq. kg^{-1} initial DM)
	CO_2	CH_4	N_2O		CO_2	CH_4	N_2O	
Control	255.6 ± 35.5 ab	−0.79 ± 0.5 a	0.68 ± 0.1 a	450.2 ± 63.0 ab	56.80 ± 1.2 a	- 3.68 ± 2.2 a	46.88 ± 1.8 a	194.6 ± 28.4 a
Broccoli	144.2 ± 60.9 bc	−0.50 ± 0.6 a	0.18 ± 0.1 b	189.1 ± 81.1 bc	72.43 ± 13.1 a	−4.78 ± 3.4 a	32.36 ± 9.8 bc	44.9 ± 33.4 b
Chestnut	354.5 ± 34.3 a	−0.79 ± 0.5 a	0.90 ± 0.2 a	616.4 ± 74.7 a	57.65 ± 2.0 a	−2.78 ± 1.3 a	44.93 ± 3.2 ab	261.9 ± 42.1 a
WhiteGrape	58.0 ± 9.3 c	−0.10 ± 0.0 a	0.08 ± 0.0 b	79.9 ± 10.6 c	72.58 ± 5.3 a	−2.58 ± 0.4 a	30.00 ± 5.3 c	21.8 ± 5.0 b
RedGrape	150.0 ± 72.2 bc	−0.57 ± 0.8 a	0.26 ± 0.1 b	220.0 ± 59.9 bc	64.77 ± 12.6 a	−4.03 ± 4.1 a	39.26 ± 9.7 abc	70.1 ± 26.3 b
Olive	420.8 ± 117.2 a	−0.97 ± 0.5 a	0.91 ± 0.4 a	683.0 ± 94.4 a	62.15 ± 3.0 a	−2.85 ± 0.9 a	40.70 ± 3.7 abc	262.2 ± 99.5 a

Values within a column, with the same letter are not significantly different ($p < 0.05$). Values are expressed as mean ± SD (standard deviation) of four replicates.

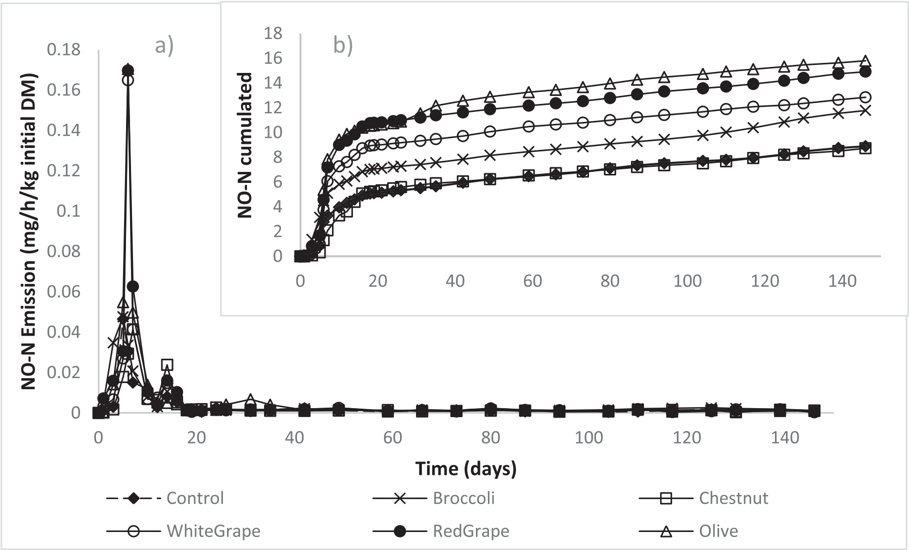

Fig. 4. Evolution of instantaneous and accumulated NO emissions during composting: (a) instantaneous ammonia emissions, (b) accumulated NO emissions.

($p < 0.0001$) affected total GHG emissions, with values ranging from 79.9 (WhiteGrape) to 683.0 g CO_2-eq. kg^{-1} initial DM (Olive) (Table 3). When CO_2 emissions were excluded from total GHG calculations, total GHG (without CO_2) emissions ranged from 21.8 to 262.2 g CO_2-eq. kg^{-1} DM (Table 3). Of all the agro-food waste materials used in the experiment, it was clear that white grape's marc could effectively be transformed and reused as organic fertiliser, with the lowest negative environmental impacts.

4. Conclusions

The findings presented in this study provide information on physicochemical changes and gaseous emissions (GHG, NH_3 and NO) during composting of agro-food wastes.

Carbon dioxide, CH_4, N_2O, NH_3 and NO were quantified over five months of composting using mixture containing broccoli, olive, chestnut, and white or red grape wastes. Significant variations were observed over time and between the different wastes. White grape exhibited the lowest GHG emissions, with 58.0 CO_2, -0.10 CH_4, and 0.08 N_2O g kg^{-1} initial DM, which corresponded to GHG emissions of 79.9 g CO_2 eq. kg^{-1} initial DM. Broccoli contributed as much to the global warming potential as red grape (189.1 and 220.0 g CO_2 eq. kg^{-1} initial DM), and chestnut and olive contributed thrice as much as the formers (616.4 and 683.0 g CO_2 eq. kg^{-1} initial DM). A higher content of hemicelluloses in the wastes seemed to entail a higher emission of N_2O. The lowest NH_3 and NO emissions were registered during the intense degradation of chestnut and olive residues. Composting with chestnut lowered the emissions of NH_3 and NO up to levels similar to those found in wheat straw ($<$ 0.01 g NH_3–N, 8.7 g NO–N kg^{-1} initial DM). These changes were closely associated with the lignocellulosic composition of the wastes, a finding with significant implications for the choice of composting materials. These results suggest the potential use of wastes rich in lignocelluloses in composting for the purpose of reducing N losses by NH_3 and NO emissions. Although composting raised the pH and EC of the final composts, the increase in nutrient contents and lignin/holocellulose ratios indicates that a safe compost could be obtained under optimized conditions with negligible environmental impacts. These results can be helpful to investigators, producers and agro-industry companies in adopting best practices for valorisation of wastes, and in implementing mitigation strategies for GHG, NO and NH_3 emissions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jclepro.2017.10.050.

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