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.

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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

(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