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Development of composting technology for biofertiliser production

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CERTIFICA

Que la Tesis Doctoral titulada **“Development of composting technology for biofertiliser production.**”, presentada por **D. André Manuel Simões dos Santos**, ha sido realizada en el Departamento de Conservación de Suelos y Agua y Manejo de Residuos Orgánicos del Centro de Edafología y Biología Aplicada del Segura, CSIC, dentro del proyecto ITN Recovery and Use of Nutrients, Energy and Organic Matter from Animal Waste, ReUseWaste, del Programa People de la UE (Marie Curie Actions) Séptimo Programa Marco FP7/2007-2013/ (REA grant agreement n° 289887).

El presente ejemplar ha sido revisado por el profesor que certifica

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Que la Tesis Doctoral titulada '**Development of composting technology for bio-fertiliser production'** del que es autor el (titulación del alumno) **D. André Manuel Simões dos Santos** ha sido realizada bajo la dirección de los doctores **Dra. Mª Pilar Bernal Calderón** y **Dr. Raul Moral Herrero**, profesores de la UMH, actuando como tutor el Dra. **Concepción Paredes Gil** (UMH). Considero que la tesis es conforme en cuanto a forma y contenido a los requerimientos del Programa de Doctorado ReTos-AAA por tanto, es apta para su exposición y defensa pública.

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Alice: *How long is forever?*
White rabbit: *Sometimes, just a second…*
Alice: *And how long is a second?*
White rabbit: *When you love, an eternity!*

Index

Abstract

The intensification of the pig production systems can lead to an excess of pig slurry produced in areas without enough agricultural land for its direct soil application. Composting has been proved to be a feasible environmentally-friendly management tool, based on nutrient recovery, for the treatment of the pig manure, minimising the environmental problems associated with its accumulation and allowing the safe storage and transportation of the nutrients surplus to areas where nutrients are needed for agriculture.

This thesis focus on the development of the technology to produce high quality biofertilisers by co-composting of the pig slurry with plant residues, as bulking agents, optimising the composting conditions, compost quality, and finally assessing the biofertiliser capacities under agronomic conditions.

The central body of this thesis consists of four international peer-review publications that investigate: 1. the best bulking agent to be used during the co-composting of the solid fraction of pig slurry (SFP) and their implications on GHG mitigation; 2. the influence of the proportion of bulking agent on the composting process and GHG emissions; 3. the organic matter transformations during the composting at different composting scenarios; and 4. the fertiliser efficiency of the composts produced and the potential nitrate leaching risk.

For the first peer-review publication, a self-heating test with several mixtures of SFP and four different bulking agents was run in a laboratory composting reactor. The samples taken from the beginning and the end of the experiment were incubated under aerobic conditions to assess the biodegradability of the mixtures tested and to evaluate their influence on the reduction of the CO_2 emissions, and thus on the promotion of C conservation.

The results indicated that the mixtures elaborated with cotton gin waste and garden prunings had the fastest temperature development, reaching the highest temperatures in the self-heating test, which may indicate a fast composting development. However, the use of maize stalks reduced the CO_2 emissions due to its slow degradability, which could constitute a suitable strategy to promote C conservation during the management of pig slurry by composting.

For the second peer-review publication, the influence of the bulking agent proportion on the composting of the SFP was studied in a composting pilot plant, focussing on the development of the process and on the greenhouse gas emissions. Then, two mixtures of the SFP and cotton gin waste at different proportions were prepared and composted by the Rutgers static pile system in a pilot-scale plant. The results indicated that the pile with the greater proportion of bulking agent led to highest temperatures and a longest thermophilic phase, with greatest aeration demand; but lower organic matter degradation occurred, reducing CH_4 and N_2O emissions with respect to the pile prepared with greater proportion of SFP. The thermal properties of the bulking agent may be responsible for the temperature profile. The OM mineralisation was faster in the pile with higher proportion of SFP, increasing the total-N losses by ammonia emissions. Then, the temperature evolution during the SFP composting process has been shown to rely on the thermal properties of the bulking agent, while the gaseous emissions were very well related to the OM degradation process. Both composts produced were stable, with a good degree of maturity; the compost with the higher proportion of SFP had greater organic matter humification and higher nutrient concentrations.

For the third peer-review publication, different analytical techniques (thermogravimetric analysis, CP MAS NMR and FT-IR spectroscopy) were used to study the organic matter changes during the co-composting of pig slurry with cotton gin waste. Samples from the previous composting experiment at pilot scale and from a field scale composting system, with different proportions of the raw materials and different type of composting system were tested. The results of the thermogravimetric methods showed the degradation of the most labile organic matter during composting; NMR showed during composting a decrease of the carbohydrate molecules and an increase of the aliphatic materials due to a concentration effect. Also, FT-IR spectroscopy was a useful technique to

study the trend of polysaccharides and nitrates as compounds indicative of organic matter transformations during composting.

For the fourth peer-review publication, the fertilising value of compost made from the SFP and cotton gin waste was assessed in a pot trial using ryegrass as a plant test. The potential risk of nitrate-N leaching in the soil after intense rainfall events was also evaluated. The experiment was carried out in a glasshouse using double-layer pots, which allowed the collection of leachates from the pots. The results showed that both composts were able to increase biomass production and soil fertility with respect to the control treatment. The RAE (relative agronomic efficiency) values of compost N reached 47.6 %, indicative of a partial N-mineralisation of the compost organic-N; for compost-P, the RAE reached 56 and 75 % in each compost, and the high solubility of K in the compost gave high RAE values, demonstrating the nutrient fertiliser value of compost prepared from pig slurry. The high Cu and Zn concentrations provided by the composts did not affect negatively the development of the plants, neither provoked great soil accumulation; losses of N by leaching were low, especially at the highest application rate of compost. The use of compost in an agronomic scenario has been suggested for supplying the equilibrated ratio of nutrients required for efficient crop production.

Resumen

La intensificación de los sistemas de producción porcina puede causar un exceso de producción de purines en áreas donde el suelo agrícola disponible para su aplicación directa es limitado o insuficiente. El compostaje ha demostrado ser una herramienta de gestión viable y respetuosa con el medio ambiente para el tratamiento de los purines de cerdo, basada en la recuperación de los nutrientes, y minimizando los problemas ambientales asociados con estos subproductos y permitiendo el almacenamiento y el transporte seguros del excedente de nutrientes a áreas agrícolas donde su aplicación es necesaria.

Esta tesis se centra en el desarrollo de la tecnología de compostaje para el tratamiento de los purines de cerdo con residuos vegetales, como agentes estructurantes, para la producción de fertilizantes orgánicos de calidad mediante la optimización de las condiciones de compostaje y la calidad del compost, para finalmente, evaluar la capacidad fertilizante de los compost en condiciones agronómicas.

La parte central de esta tesis consiste en cuatro publicaciones en revistas internacionales que abordan los siguientes aspectos: 1. Seleccionar el agente estructurante adecuado para el co-compostaje de la fracción sólida del purín de cerdo (SFP) y su implicación en la mitigación de gases de efecto invernadero; 2. Determinar la influencia de la proporción del agente estructurante en el proceso de compostaje y las emisiones de gases de efecto invernadero; 3. Identificar la transformación de materia orgánica (MO) durante el compostaje del purín de cerdo en diferentes escenarios; y 4. Cuantificar la

eficiencia fertilizante de los compost producidos y determinar el riesgo potencial de lixiviación de nitratos.

En la primera publicación, se realizaron ensayos de auto-calentamiento con mezclas de SFP y cuatro agentes estructurantes diferentes, utilizando un reactor de compostaje a nivel de laboratorio. Las muestras tomadas al inicio y al final de dicho experimento se incubaron aeróbicamente para evaluar la biodegradabilidad de las mezclas y su influencia en la reducción de las emisiones de CO_2, y por lo tanto en la conservación de C. Los resultados indicaron que las mezclas elaboradas con residuos de desmotado de algodón y poda de jardín favorecían un rápido incremento de la temperatura, con el desarrollo de valores elevados, lo que podría suponer un mejor desarrollo del proceso de compostaje. Sin embargo, el uso de la caña de maíz redujo las emisiones de CO_2 debido a su lenta descomposición, lo que podría constituir una estrategia adecuada para la conservación del C durante la gestión de los purines mediante compostaje.

En la segunda publicación, la influencia de la proporción del agente estructurante en el compostaje de la SFP se estudió en una planta piloto de compostaje, enfocado hacia el desarrollo del proceso y las emisiones de gases de efecto invernadero. Se prepararon dos mezclas de SFP y de desmotado de algodón a diferentes proporciones, utilizando el sistema de pila estática Rutgers, en una planta a escala piloto. Los resultados indicaron que la pila con la mayor proporción de agente estructurante tuvo las temperaturas más elevadas, con una fase termófila más larga y mayor demanda de aireación; pero la degradación de la materia orgánica fue menor que en la pila con menor proporción de residuo de algodón, reduciendo las emisiones de CH_4 y N_2O. Las propiedades térmicas del agente estructurantes fueron responsables del perfil térmico logrado. La mineralización de la MO fue más rápida en la pila con una mayor proporción de SFP, con pérdidas de N más elevadas asociadas a las emisiones de amoníaco. Por tanto, la evolución de la temperatura durante el compostaje de la fracción sólida del purín de cerdo se asoció a las propiedades térmicas del agente estructurante, mientras que las emisiones gaseosas se relacionaron con el proceso de degradación de la materia orgánica. Ambos compost producidos eran estables, con un buen grado de madurez; el compost con la mayor proporción de fracción sólida de purín logró una materia orgánica con mayor grado de humificación y concentraciones de nutrientes más elevados.

En la tercera publicación, se utilizaron distintas técnicas analíticas (análisis termogravimétrico, CP MAS RMN y espectroscopia FT-IR) para estudiar los cambios de la MO durante el co-compostaje de la fracción sólida de purín con residuo de desmotado de algodón. Se estudiaron muestras de los experimentos anteriores en planta piloto y también de un ensayo a nivel real in granja, utilizando diferentes proporciones de las materias primas y diferentes tipos de sistema de compostaje. Los resultados de los métodos termogravimétricos mostraron la degradación de la MO más lábil durante el compostaje; RMN mostró una disminución de los carbohidratos y un aumento de los compuestos alifáticos durante el compostaje, debido a un efecto de concentración. Además, la espectroscopia FT-IR fue una técnica útil para estudiar la tendencia de los polisacáridos y los nitratos como compuestos indicativos de las transformaciones de la MO durante el compostaje.

En la cuarta publicación, el valor fertilizante del compost producido a partir de la fracción sólida de purín de cerdo y del desmotado de algodón se evaluó en un ensayo en macetas usando césped como planta testigo. También se evaluó el riesgo potencial de lixiviación de nitratos en el suelo después de eventos de lluvia intensos. El experimento se desarrolló en macetas de doble fondo que permiten la recogida de los lixiviados. Los resultados mostraron que ambos compost fueron capaces de aumentar la producción de biomasa y la fertilidad del suelo, con respecto al tratamiento control. Los valores de eficiencia agronómica relativa (EAR) del N del compost alcanzaron el 47%, indicando una mineralización parcial de las formas de N orgánico; la EAR del P del compost alcanzó 56 y 75 % para los compost con mayor y menor proporción de fracción sólida, respectivamente, y la alta solubilidad del K en ambos compost llevó a altos valores de EAR para este nutriente. Las altas concentraciones de Cu y Zn de los compost no afectaron negativamente al desarrollo de las plantas, ni crearon una gran acumulación de metales en el suelo; las pérdidas de N por lixiviación fueron bajas, especialmente con la dosis más alta de compost. Se ha planteado el escenario agronómico para el uso de compost de forma que suministre la proporción de nutrientes adecuada para una eficiente fertilización de los cultivos.

1. Introduction

1.1 Livestock wastes: production, management and treatments.

1.1.1 Livestock production overview in EU.

Livestock can be defined as the domesticated animals rose in an agricultural setting to produce commodities such as food, fibre and labour and their wastes are generally composed by a mixture of faeces, urine, bedding material and water, containing an important fraction of organic matter, nutrients and volatile compounds. According to Steinfeld and Mäki-Hokkonen (1995), livestock production systems are classified in 3 categories: grazing, mixed and industrial systems.

Grazing systems: more than 90% of dry matter fed to animals comes from rangelands, pastures, annual forages and purchased feeds and less than 10% of the total value of production comes from non-livestock farming activities. Annual stocking rates are less than 10 livestock units (LSU) per hectare of agricultural land.

Mixed systems: Mixed farming is probably the most benign agricultural production system, since there are many opportunities for nutrient recycling. In this type of system, more than 10% of the dry matter fed to livestock comes from crop by-products and/or stubble or more than 10% of the value of production comes from non-livestock farming activities. In Europe, 1.5 ha of field per LSU must be available to ensure that there is sufficient cropped area that can recycle the nutrients from manure (Sommer and Christensen, 2013).

Industrial systems: These systems have average stocking rates greater than 10 livestock units per hectare of agricultural land and <10% of the dry matter fed to livestock is produced on the farm. They depend on outside supplies of feed, energy and other inputs and the demand for these inputs can thus have effects on the environment in regions other than those where production occurs.

In Europe, there have been considerable structural changes in the livestock farming, during the last decades – towards intensification – where the number of animal heads increased or remained constant, while the number of farms decreased. Most countries recorded a fall in their respective number of holdings between 2007 and 2010, as the only exceptions were Ireland, Croatia, Malta and Portugal, where the number of holdings was higher (EUROSTAT, 2015). Nowadays, livestock sector represents 48% of the economic income generated annually by agriculture (ATF, 2013). This intensification shows how dynamic this sector is, evolving in response to the rising demands for livestock products from population growth and dietary changes (Delgado, 2005 and Thornton, 2010). In this time, both the global demand for animal products and the amount of crop production used for feed have approximately tripled (330% and 300%, respectively) (FAO, 2015).

According to Figure 1, 98% of EU-28 meat produced in 2013 came from pig, poultry and bovine animals (51, 30 and 17%, respectively) and only 0.02% came from goat and sheep animals. In table 1, the meat production by individual animal per each EU country is shown. Germany and Spain are the main producers of pig meat, producing about one quarter (24.9 % or 5.5 million tonnes) and one sixth (15.6 % or 3.4 million tonnes) of the total meat produced in EU-28, respectively; France, the United Kingdom, Poland, and Germany were the main producers of poultry meat in the EU-28 in 2013, with 11–13 % of the total production; France (19.1 %), Germany (16.8 %) and the United Kingdom (13.5 %) made up roughly half (49.4 %) of total EU-28 beef production in 2013; and the United Kingdom (38.3 %) and Spain (16.8 %) contributed to more than half (55.1 %) of total EU-28 sheep and goat meat production in 2013.

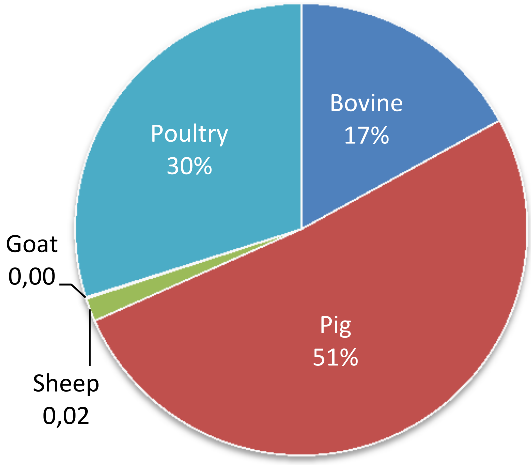

Figure 1 – Livestock meat production in EU-28 in 2013.

The intensification of the livestock production implies an increased pressure on natural resources and on the environment – 80% of all agricultural land is used for grazing or animal feed production and 8% of the global water is used for irrigation of feed crops; and high amounts of wastes are produced, making them a source of air/water/soil pollution (Steinfeld et al., 2006).

Table 1: Production of meat in Europe 2013, by type of animal (1000 tonnes of carcass weight). Source: Eurostat 2015.

	Bovine	Pig	Sheep	Goat	Poultry (*)
EU-28	7271.7	21940.1	710.5	47.5	12765
Belgium	249.9	1130.6	2.3	0.1	388.1
Bulgaria	5.7	52.1	-	-	94.7
Czech Republic	64.8	234.3	0.2	-	148.2
Denmark	125.2	1589.4	1.6	-	160.3
Germany	1106	5474	20	-	1456
Estonia	7.6	34.6	0.1	-	-
Ireland	517.6	239.3	57.5	-	-
Greece	50.1	108.6	60.9	24.8	180.5
Spain	580.8	3431.2	118.3	8.9	1342.6
France	1407.9	1938.8	80	6.5	1695
Croatia	47.3	79.8	0.7	-	55.7
Italy	855.3	1625.5	35.3	1.3	1223.5
Cyprus	5.2	48.7	3	2.3	22
Latvia	15.7	26.2	0.2	-	26.7
Lithuania	36.8	67	0.1	-	89.8
Luxembourg	8	10.9	-	-	-
Hungary	22.6	336.7	0.3	-	394.5
Malta	1.1	5.9	0.1	-	4.1
Netherlands	379.1	1307	12.1	1.7	-
Austria	227.2	528.2	7.7	0.8	-
Poland	339	1684.3	0.6	-	1652
Portugal	84.1	345.9	10	0.8	291.7
Romania	29.3	308.4	3.2	-	325.6
Slovenia	32.1	19	0.1	-	57.1
Slovakia	9.5	52.4	0.5	-	-
Finland	80.4	194.5	0.9	-	111.1
Sweden	135.7	234.1	4.9	-	124.8
United Kingdom	847.7	832.9	290.1	0.2	1662.2
Iceland	3.8	6.3	9.8	-	7.8
Serbia	35.5	132.3	0.9	-	55.5

(*): Estimated value for EU-28.

Regarding the environmental implications of livestock production, the intensification of the production systems in EU-27 generates huge amounts of wastes (1400 million tonnes per year; Timmerman et al., 2015) that need to be managed. Table 2 summarise the amount of manure produced by different animal breeds; bovine animals produce higher volume of manure per year than pigs or poultry.

Table 2 – Typical amounts of liquid manure produced by different farm animal breeds excluding water added form various sources (Adapted from Martínez and Burton, 2003).

Animal	Body weight (kg)	Manure produced per animal per year (m^3)	Dry matter content of manure (kg/m^3)
Dairy cow	550	19.4	100
Beef cattle >2 years	500	11.6	100
Beef cattle 1-2 years	400	9.6	100
Beef cattle 0.5-1 year	180	4.8	100
Sow plus litter	200	4.0	60
Pig (dry ration)	35-105	1.6	100
100 Laying hens	220	4.2	300
100 Broilers	220	2.2	600

Livestock wastes can be distinguished in three categories:

Liquid manure (slurry) – Housing system collecting all excreta in liquid form; the animal are kept on sloping solid floors that are regularly swept clear of any excreta. Some dilution can be expected from wash water;

Mixed manure – Housing systems producing solid and liquid manure streams; animals are kept on bedding material, but liquids are drained from the bedding and collected elsewhere;

Solid manure – Housing types producing only solid manure; animals are kept on bedding material which is collected together with all excreta as solid or farm yard manure (FYM).

In Europe, manure application to the soil is regulated by legislation. The Directive on Integrated Pollution Prevention and Control (IPCC Directive) (Directive 0001/2008) purpose to achieve integrated prevention and control of pollution arising from several categories of industrial activities and aims to prevent or minimise emissions to air, water and land, as well as to avoid waste production, in order to achieve a high level of environmental protection as a whole. The IPPC Directive concerns highly polluting industries, e.g. energy, production and processing of metals, minerals, chemicals, waste management and others including agriculture, most particularly intensive pig and poultry farms (EUROSTAT, 2015).

The Nitrates Directive (Directive 0676/1991) is one of the key instruments in the protection of waters against agricultural pressures, in order to reduce the increased nitrate concentration on surface and groundwater, the possible effects on humans, due to the consumption of contaminated water and the deterioration of aquatic ecosystems, caused by the eutrophication of waters. The implementation of the Directive includes the establishment of Code(s) for good agricultural practice at the national level, to be implemented by farmers on a voluntary basis. The Code(s) includes several measures, such as: limiting the time, concentration and conditions of fertiliser's application to the land (in the spring or early autumn; maximum of 210 kg N ha^{-1} yr^{-1}), in order to apply N when the crops needs nutrients and avoid N losses by leaching; requirements for a minimum storage capacity for livestock manure; and a maximum limit of nitrate concentration allowed on water of 50 mgL^{-1}. In the case of Nitrate Vulnerable Zones (NVZ) – areas designated as being at risk from agricultural nitrate pollution – the establishment of Action Programmes by farmers is mandatory. Apart of the measures already described above, other measures such as maximum amount of animal manure to be applied (corresponding to 170 kg N organic ha^{-1} yr^{-1} in NVZ) may also be applied. NVZ increased from 35.5% of EU 15 territory in 1999 up to the 44% in 2003, with further designations thereafter, where United Kingdom, Spain, Italy, Sweden and Belgium had a 32.8, 11, 6, 15 and 24% of the territory designated as NVZ, respectively (COM, 2007; Fig. 2).

However, some countries and regions, developed a centralised control of the residual fluxes, optimising the management and demonstrating that the efficiency of their management models did not affect the nitrate concentration in the surface and groundwater, with the objective to increase the amount of manure allowed to apply to the soil. In table 3 are resumed the countries and regions that are exceptionally allowed to surpass the limiting values of N application to the soil, contemplated in the Nitrates Directive. These exceptions were established after each countries/regions showed consolidated results with respect to the reduction of nitrate leaching, as well fertilisation plans below the economic optimum.

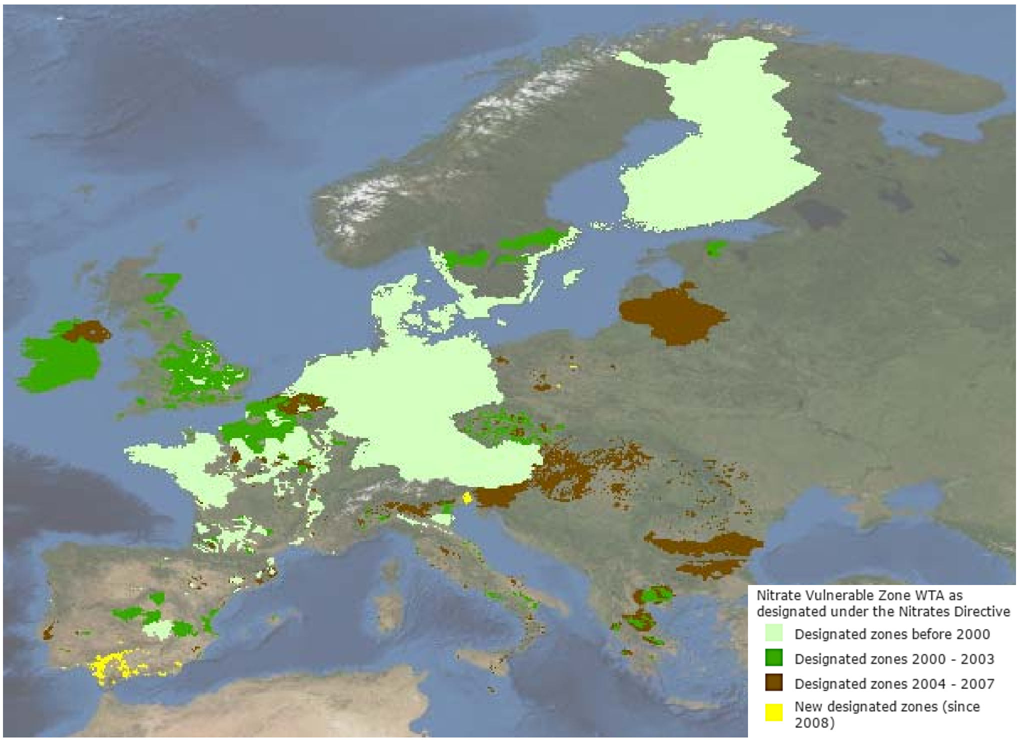

Figure 2 – Nitrate Vulnerable Zones in Europe in 2013 (ArcGIS, 2015).

Table 3 – Exceptions to the Nitrates Directive, referring to the limiting value of manure and fertilisers application to the soil.

Country/Region	**Year (Decision commission)**	**Maximum value based on N (kg N ha^{-1} yr^{-1})**
The Netherland	2010/65/UE	250
Germany	2009/753/CE	230
Ireland	2011/127/UE	250
Flanders (Belgium)	2011/489/UE	250
North Ireland	2011/128/UE	250
Emilia-Romina, Lombardi, Piermont and Veneto (Italy)	2011/721/UE	250
Denmark	2012/659/UE	230
England, Scotland and Wales (UK)	009/431/CE	250
Austria	2006/189/CE	230

1.1.2 Pig sector overview in Spain.

The Spanish pig sector represents 14% of Spanish agricultural production and in terms of economic importance within the Spanish livestock production it ranks first, representing 37% (MAGRAMA, 2015). The intensification of the livestock production systems was well visible in Spain along the years. In 2015, the number of pig farms in Spain was 86,552, 1.2% higher than the previous year and 13% lower than 2007, but with higher efficiency. Pig production in Spain is divided in two systems:

Extensive systems: can be compared to a grazing or mixed system where the animals are kept free-range for part or all of their production cycle (Fig 3a).

Intensive systems: this type of system is similar to the industrial systems explained before. However, its form tends to change from the basic definition due to the welfare rules, allowing the animal to live in better conditions (Fig 3b).

Nowadays in the Spanish pig sector, the 80% of the farms works on intensive production, while 20% as extensive pig production.

Figure 3 – Types of pig production systems: a – Extensive system (Adapted from www.stuff.co.nz/business/farming/agribusiness/66432771/at-home-on-nzs-largest-freefarmed-pig-enterprise); b – Intensive system.

According to the last national data (MAGRAMA, 2015), pig production in Spain accounted for 27 million pigs – 7,682,686 piglets, 6,487,984 weaners, 10,370,484 fatteners, 34,459 boars and 2,407,592 sows – and almost half of the production was concentrated in the north-east (Table 4). The main regions for number of pig are found in Catalonia (7.3 million pigs), Aragón (6.5 million pigs), Castile and León (3.7 million pigs), Andalusia (2.2 million pigs) and Murcia (1.8 million pigs). Within the EU-27, Spain is the second member in terms of pig production, with 18% of the EU census and 17.3% of the production and at international level, Spain is the fourth-largest pig producer (after China, USA and Germany).

Table 4 – Number of pigs per Spanish region (MAGRAMA, 2015).

Region	**Total number of pigs**
Galicia	1,090,123
Aragon	6,466,824
Catalonia	7,340,457
Castile and León	3,687,604
Castile-La Mancha	1,420,003
Valencia	1,080,365
Murcia	1,829,384
Extremadura	1,113,045
Andalusia	2,168,779
Other regions	795,621
Total	**26,992,205**

Even if Murcia is the fifth region in terms of pig production, it is formed by only one province; thus, the province of Murcia is the fourth in terms of number of pigs with a high density of pig farms after Lleida, Huesca and Zaragoza province (MAGRAMA, 2015). Pig production in Murcia is distributed in fattening pigs (56.23%), weaners (20.89%), piglets (15.35%), sows (7.44%) and boars (0.09%). With such high production, great quantities of slurries are produced. The information regarding pig slurry production is scarce and variable; however, a rough estimation can be calculated using the data of the number of pigs in Murcia and the amount of slurry produced per type of pig, given by the Royal Decree 324/2000 (BOE, 2000). The RD 324/2000 establishes basic rules for pig farms planning – maximum productive capacity, minimum location conditions, animal and sanitarian infrastructures and equipment required for an effective and rightful development of piggery production – and establishes a pig slurry production factor per pig, as well the N concentration , taking into account the type of pig (Table 5). In this way, the pig slurry production can be estimated in 4.6 Hm^3 in 2015, equivalent to 217.7 million tonnes of N.

Table 5 – Pig slurry production per type of pig and nitrogen concentration in the slurries before storage (RD 324/2000).

Type of pig	Slurry m^3 per year	Nitrogen kg per pig per year
Sows in closed cycle	17.75	57.6
Sows with suckling piglets (0-6 kg)	5.10	15.0
Sows with piglets (until 20 kg)	6.12	18.0
Sows	2.5	8.5
Piglets (6-20 kg)	0.41	1.19
Fatteners (20-50 kg)	1.8	6.0
Fatteners (50-100 kg)	2.5	8.5
Fatteners (20-100 kg)	2.15	7.25
Weaners	5.11	15.93
Boars	6.12	18.0

There are around 3500 pig farms in Murcia, concentrated mainly in two areas – Guadalentín valley and Campo de Cartagena-Oeste – and the available land for direct application of pig slurries was estimated in 400,211 ha (Europa press, 2015; MANEV, 2012). Taking into account the agricultural production in these areas, 40% of this area is temporary unavailable during the year, since it is dedicated to horticultural crops and the Good Agricultural Practices code only allows slurry application during spring and early autumn. Apart of the high density of pig farms, many farms of the Guadalentín area are located within the limits of the vulnerable zone to nitrates contamination (Figure 4), limiting the amount of slurry application to 170 kg N ha^{-1} yr^{-1} (Royal Decree 261/1996). Considering this limitation, one of the possible options to deal with the surplus of slurries is to transport it to areas where nutrients are scarce – involving an extra cost – or manage the slurries properly and produce a product with added value that creates an economic return to the farmer and at the same time, reduces de volume of the wastes and as well the amount of mineral fertiliser needed.

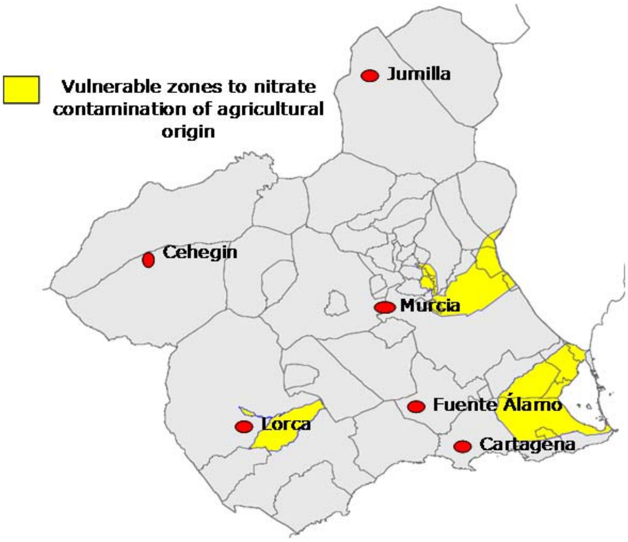

Figure 4 – Vulnerable zones to nitrate pollution from agricultural sources in the Region of Murcia (MANEV, 2012).

1.1.3 Treatment strategies for pig slurry management.

In pig farming, manure management consists of a chain of management stages or technologies. The handling systems differ between animal evolutionary stage, farms, regions and countries (Sommer, 2013) and many treatment technologies can be applied, considering the characteristics of the wastes. Treatment technology includes many processes often comprising a biological and physical step and sometimes the use of chemical additives as well.

Due to the great individuality of farms, pig slurry management cannot be generalised. Each farm needs specific planning to manage effectively the pig slurries produced and no single treatment process can be presented as a universal solution. Solid and liquid manure are important sources of OM, nitrogen (N) and phosphorus (P) for agriculture, but can be also harmful when applied to agricultural land in excessive amounts – leading to pollution of ground water by nitrates, surface water with phosphorous (causing eutrophication), GHG emissions (NH_3, CH_4, NO and N_2O) and soil with heavy metals such as zinc and copper which are used as growth promoters in the feed. In table 6, the great variability of pig slurry characteristics within the farm, depending on the evolutionary stage of the pig can be shown. The pig slurry from each stage should be treated differently, depending on its characteristics.

Table 6 – Physico-chemical characteristics of pig slurry depending on the evolutionary stage of the pig (adapted from Sánchez and González, 2005).

Parameter	Gestating	Fattening pigs	Closed Cycle
EC (dS m^{-1})	1.24	1.33	1.86
DM (g kg^{-1})	21.4	36.1	42.5
OM (g kg^{-1})	14.4	27.0	31.8
NH_4^+-N (g kg^{-1})	1.5	1.7	2.4
Inorganic-N (g kg^{-1})	2.1	2.5	3.3
TN (g kg^{-1})	2.6	3.1	4.1
P (g kg^{-1})	0.69	0.77	0.99
C/N	2.8	4.6	3.9
K (g kg^{-1})	0.86	0.75	1.37
Mg (g kg^{-1})	0.17	0.23	0.28
Ca (g kg^{-1})	0.80	1.21	1.41
Na (g kg^{-1})	0.21	0.23	0.26
Zn (mg kg^{-1})	19.7	24.9	30.6
Cu (mg kg^{-1})	8.9	13.3	18.6
Al (mg kg^{-1})	18.9	36.9	56.3

EC: electrical conductivity; DM. dry matter, OM: organic matter; NH_4^+-N: ammonium nitrogen; TN: total nitrogen; P: phosphorous; C/N. carbon to nitrogen ratio; K: potassium; Mg: magnesium; Ca: calcium; Na: Sodium; Zn: zinc; Cu: copper; Al: aluminium.

The direct soil application of pig slurry to agricultural land is the easiest and cheap option for recycling the organic matter and nutrients within the soil-plant system, reducing the use of synthetic fertilisers in agriculture. However, some characteristics of the pig slurry – high EC, heavy metals concentration, faecal microorganisms, as well pathogens – may limit the direct land application in agriculture (Christensen et al., 2013; Bernal et al., 1992, 1993). Then, different treatment technologies are nowadays available for managing the slurries, either through depuration system with nutrient and OM removal or by technologies for recycling the organic matter, macronutrients (N, P, K, Ca and Na) and micronutrients (Cu, Zn, Fe, Al and Mg) present in the pig slurries, by concentrating them into products with enhanced characteristics, beneficial for plant growth.

According to the IPCC (2006), there are many different treatment technologies available to manage the surplus of pig slurries produced. The technics include from direct land application, storage of the solid and/or liquid fraction, to anaerobic and aerobic treatments. In table 7 some of the possible manure managing systems that can be applied are summarised.

Table 7 – Definitions of manure management systems according to IPCC (2006).

System		Definition
Pasture/Range/Paddock		The manure from pasture and range grazing animals is allowed to lie as deposited, and is not managed.
Daily spread		Manure is routinely removed from a confinement facility and is applied to cropland or pasture within 24 hours of excretion.
Solid storage		The storage of manure, typically for a period of several months, in unconfined piles or stacks. Manure is able to be stacked due to the presence of a sufficient amount of bedding material or loss of moisture by evaporation.
Dry lot		Paved or unpaved open confinement area without any vegetative cover where the accumulated manure can be removed periodically.
Liquid/slurry storage		Manure is stored as excreted or with some minimal addition of water in either tanks or earthen ponds outside the animal housing, usually for periods less than one year.
Uncovered anaerobic lagoon		A type of liquid storage system designed and operated to combine waste stabilization and storage. Lagoon supernatant is usually used to remove manure from the associated confinement facilities to the lagoon. Anaerobic lagoons are designed with varying lengths of storage (up to a year or greater), depending on the climate region, the volatile solids loading rate, and other operational factors. The water from the lagoon may be recycled as flush water or used to irrigate and fertilise fields.
Pit storage below animal confinements		Collection and storage of manure usually with little or no added water typically below a slatted floor in an enclosed animal confinement facility, usually for periods less than one year.
Anaerobic digester		Animal excreta with or without straw are collected and anaerobically digested in a large digester or covered lagoon. Digesters are designed and operated for waste stabilisation by the microbial reduction of complex organic compounds to CO_2 and CH_4, which is captured and flared or used as a fuel.
Cattle and swine deep bedding		The dung and urine are excreted on fields. The sun dried dung cakes are burned for fuel.
Composting [a]	In vessel	In an enclosed channel, with forced aeration and continuous mixing.
	Static pile	In piles with forced aeration but no mixing.
	Intensive windrow	In windrows with regular turning for mixing and aeration.
	Passive windrow	In windrows with infrequent turning for mixing and aeration.
Poultry manure with litter		Similar to cattle and pig deep bedding except that usually it is not combined with a dry lot or pasture.
Poultry manure without litter		May be similar to open pits in enclosed animal confinement facilities or may be designed and operated to dry the manure as it accumulates. The latter is known as a high-rise manure management system and is a form of passive windrow composting when designed and operated properly.
Aerobic treatment		The bio-oxidation of manure collected as a liquid with either forced or natural aeration. Natural aeration is limited to aerobic and facultative ponds and wetland systems and is due primarily to photosynthesis. Hence, these systems typically become anoxic during periods without sunlight.

[a] Composting is the biological oxidation of a solid waste including manure usually with bedding or another organic carbon source typically at thermophilic temperatures produced by microbial heat production.

Ultimately, the objective of pig slurry management is to:

- Reduction of the volume of wastes generated;
- Recycling of the nutrients for agricultural use;
- Production of a stable and improved product;
- Reduction of mineral fertilisers use;
- Improvement of soil physico-chemical and biological characteristics;
- Reduction of malodours and elimination of pathogens;

However, an inadequate pig slurry management can lead to several environmental problems:

In the soil:

- Superficial crust, increasing the superficial runoff;
- Possible anaerobic sites;
- Phytotoxicity;
- N leaching;
- Heavy metals and pharmaceutical contamination;
- Bioaccumulation of heavy metals (Cu and Zn);
- Salinization;

In the atmosphere:

- Malodours;
- Biological contamination by pathogens dispersion;
- GHG and ammonia emissions;

In water:

- Surface and groundwater contamination causing: eutrophication (excess of P and N); turbidity, hindering photosynthetic processes; and anaerobic conditions;
- Deterioration of water quality for consume;

The solid-liquid separation systems can be considered a pre-treatment for animal slurry management, obtaining a solid fraction (where solids and nutrients are concentrated) and a liquid fraction for individual management. Solid-liquid separation of animal slurries and other agricultural products can be an integral part of a livestock operation ranging from improved facility performance to enhanced nutrient management. It is an alternative manure treatment method, considering that improves manure handling properties and produce the solids for energy generation and compost production (Bicudo, 2009). The separation of phases allows reducing the initial size of the lagoon or storage pond, which lowers construction costs; increasing handling flexibility for ultimate disposal and use of animal waste; for lagoons, extending the time between solids cleanout, which makes treatment more efficient and controls odour; and reducing the slurry transport cost by concentrating the nutrients in the solid fraction which can be easily exported to other agricultural areas and obtaining an economical benefit from the solids (Sorensen et al., 2003; MANEV, 2012).

The separation of phases of slurries into a nutrient- and DM-rich solid fraction and an N-rich liquid fraction can be done by different separation systems; for instance, mechanical screen separators, sedimentation, centrifugation, biological treatments and reverse osmosis. The costs of separation depends on the sophistication and efficiency of the technique, being sedimentation, mechanical screen separation and centrifugation simple techniques that are cost effective, while biological treatments, evaporation, ultrafiltration and reverse osmosis are more complex and expensive techniques (Burton, 1997). However, a combination of separation technics can be used, depending on the required separation efficiency. Figure 5 illustrates the solid-liquid separation of pig slurry by centrifugation and posterior combination of chemical and mechanical treatment (precipitation with hydrated lime in a sedimentation tank) to recover the maximum of P in the sludge, to be used afterwards as fertiliser. The separated products obtained are a P-rich solid fraction and a N-rich liquid fraction, due to the forms that nutrients are mostly found in the slurries – most of P is undissolved and bound to particles or colloids (Masse et al. 2005) while N is in a soluble form (NH_4^+-N) – and can be applied directly to the soil or stored for later application/treatment. Also, Riaño and García-Gonzáles (2014) combined different separation methods on raw pig slurry – mechanical separation with screw-press, coagulation and flocculation techniques and sedimentation – removing about of 71 % of total solids, 91 % of total chemical oxygen demand, 97 % of total Kjeldahl nitrogen and 89 % of total P.

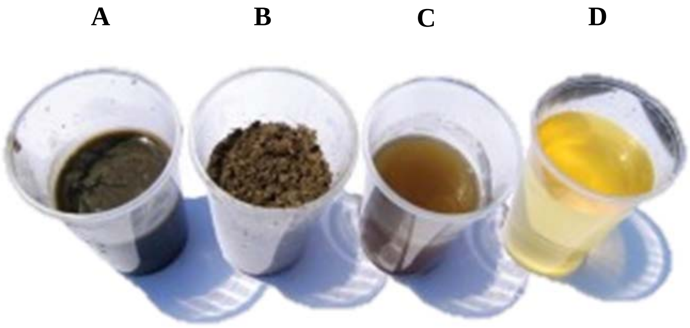

Figure 5 – **A:** Raw slurry before separation; **B** and **C:** solids and liquid from centrifuge separation; **D:** liquids after chemical treatment of the liquid fraction (source: Emerson, 2015).

The storage of livestock manures is an important step in the manure management chain, being a common action in EU and also can be considered part of the treatment process, because it enhances the timeliness and convenience of disposal. Nutrients, such as N and P, dry matter and biological oxygen demand (BOD) can be reduced during storage and in multiple store units connected in series, BOD and pathogens can be reduced (Burton and Turner, 2003). Pig manure can be stored as a solid or semi-solid, as slurry or as liquid and each one requires different operating measures to deal with it. Most of the storage facilities for slurries and liquids are concrete isolated tanks but opened lagoons and lined ponds are commonly observed in Mediterranean countries (figure 6A). The high temperatures and low rainfall, characteristic of these regions, favour the evaporation of the water, concentrating the livestock manure in the sludge at the bottom of the pond, which can be removed when dry. Solid manure can be piled up on concrete isolated tanks or floors (figure 6B) and if not covered, a leachate collection system should be installed. Considering the nature of the semi-solids, some leaching may occur due to gravity when pilled, requiring an isolated tank or box for its confinement.

During storage, most of the nutrients losses observed are due to NH_3 volatilisation to the atmosphere. Nitrogen volatilization is usually quite significant in lagoons due to the large surface area. Also, when storage time is increased, biological activity converts the organic nitrogen to into ammonia, promoting N-losses by volatilisation. However, some N_2O losses can occur if anaerobic conditions prevail. P and K are not lost during storage, unless the storage facilities are not well isolated (Bicudo, 2009).

According to the last survey from EUROSTAT, 32 % of agricultural holdings in the EU-28 with livestock had storage facilities for manure in 2010, equivalent to 2.2 million holdings. A relatively low proportion of livestock holdings had manure storage facilities in Cyprus, Bulgaria, Portugal, Greece, Lithuania and Romania (no more than 15 %), while 15 of the EU Member States reported that more than half of their livestock farms had manure storage facilities – this share rising to above 90 % in Austria and Slovakia.

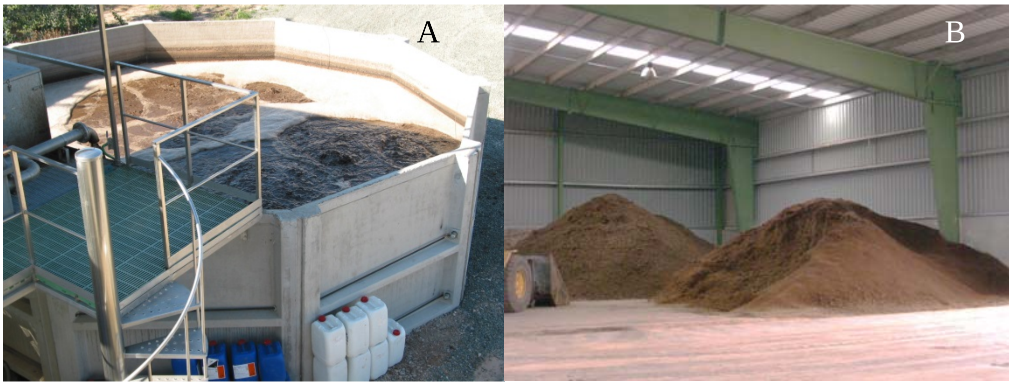

Figure 6 – Pig waste storage facilities: A – slurry storage; B – solid fraction storage.

Other management technologies are quite popular in Europe. The stabilisation of manure is important prior its use in agriculture. The most common methods for stabilising pig wastes are anaerobic digestion and composting. The stabilisation process reduces the organic matter and water contents, unpleasant odours, concentrations of pathogenic microorganisms, and weed seeds (Prasad et al., 2014).

Anaerobic digestion is a biological process operated in the absence of O_2, where microorganisms break down the organic compounds into CH_4 and CO_2 (biogas). The biogas produced can be directly flamed and converted into CO_2 or be treated in a combined heat and power plant (CHP), producing electricity and heat, or can be upgraded to bio-methane. The CO_2 released in this process is not considered a GHG, since it does not have an anthropogenic origin. The digestate remaining in the reactor is a nutrient-rich, stable and odour and pathogen-free product, with great agricultural properties (Fig. 7).

In 2010, Germany, Italy and Austria were the countries with higher anaerobic digestion installations for livestock manure treatment. In Germany and Austria, most of the facilities found were farm size installations, with a totality of 3,800 and 307, capable to treat 15,395 and 1,564 tonnes of livestock manure per year, respectively. Italy and the Netherlands had most of the small/medium size installations found in EU-27, 289 and 100, capable to treat 35,000 and 13,750 tonnes of livestock manure per year, respectively. The higher number of large scale installations were also found in the Netherlands and Italy, 30 and 24, capable to treat 75,000 and 75,343 tonnes of livestock manure per year, respectively (Foged et al., 2011). The vast majority of installed digestion capacity is single-phase (97%) and continuous processes (the reactor is fed continuously) dominate over batch (the reactor is fed only at the beginning of the process) (76% and 24% respectively).

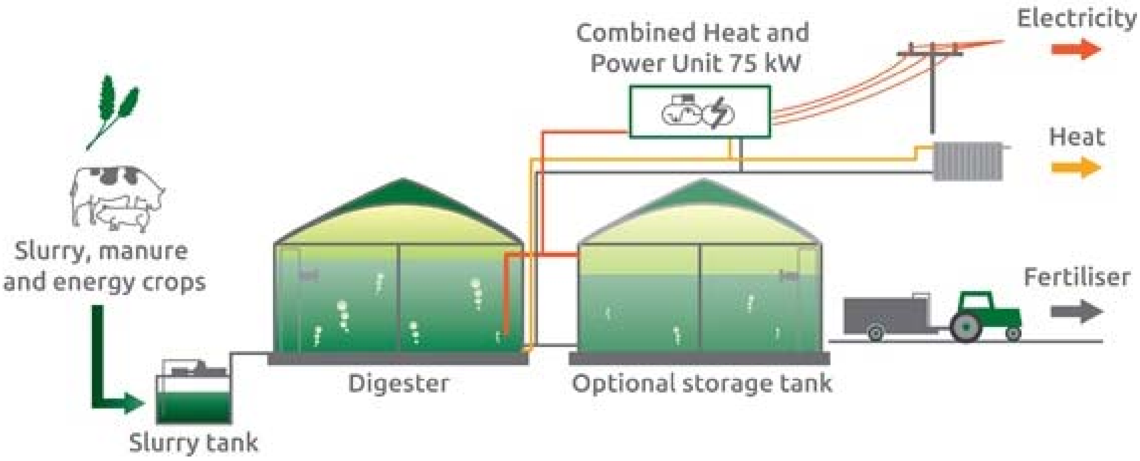

Figure 7 – An overview of the anaerobic technology (Adapted from www.rawad.co.uk/farmers/technology).

Composting is a biological treatment in which aerobic thermophilic and mesophilic microorganisms degrade labile OM producing fully-mineralised materials (carbon dioxide (CO_2), water (H_2O), ammonium (NH_4^+)) and also stabilised OM (partially humified) (Chefetz et al., 1996), where a large amount of heat is produced by microorganisms during digestion of the organic matter (Vanotti et al., 2006).

Composting of animal manures has been traditionally carried out by the farmers after manure collection for better handling, transport and management (Bernal et al., 2009). The composts produced can be used in agriculture, being rich in nutrients beneficial for plant growth.

Considering that exists several treatment technologies available to treat the solid fraction of livestock manure, the last inventory of manure processing activities in Europe reported the composting technology as the mostly chosen by farmers. In 2010, farm, small/medium and large size compost installations represented 94, 60 and 11 % of the installations where compost technology was used to treat the solid fraction of livestock manure, accounting with 1,180, 101 and 7 installations in EU-27, capable to treat 2,730, 15,776 and 63,837 tonnes of livestock manure per year, respectively. Most of the farm size installations were located in the United Kingdom and Greece, being Spain and Belgium the countries were most of the small/medium and large size installations were found (Foged et al., 2011; Fig. 8a, b,c).

Figure 8 – Composting installations: a – farm size; b – small/medium size; c – large size.

1.2 Composting process for manure management.

1.2.1 Definitions and conditions.

Composting of organic wastes is a biooxidative process involving the mineralisation and partial humification of the organic matter, leading to a stabilised final product, free of phytotoxicity and pathogens and with certain humic properties that will not be harmful for plants, when applied to the soil (Zucconi and de Bertoldi, 1987;). During the composting process, microorganisms transform organic matter into CO_2, biomass, thermoenergy (heat) and humus-like end-product (Tuomela et al., 2000). Composting has the potential to stabilise the organic N fraction of manure and increase its fertiliser value (Bernal et al., 2009). This process, recycles wastes, reduces their volume, removes unpleasant odours and pathogens and produces a high value biofertiliser for plants.

During the composting, several factors can affect the development of the process: C/N ratio, moisture content, oxygen concentration, particle size, pH and temperature.

The adequate C/N ratio for composting is in the range 25-30, since microorganisms require 25-30 parts of C per unit of N (Bishop and Godfrey, 1983). High C/N ratios implies an excess of degradable substrate (C forms) for microorganisms, increasing the time of composting. However, a low C/N ratio, implies an excess of N per degradable C and inorganic N is produced in excess, promoting ammonia volatilisation or by leaching of the composting mass. Low C/ ratios are usually found in the composting of pig slurry. The addition of bulking agents can correct the low C/N ratios verified during the composting of pig slurry, providing degradable organic-C.

The optimum water content for composting varies with the waste to be composted, but generally the mixture should be at 50-60% (Gajalakshmi and Abbasi, 2008). The moisture content should not saturate the pores, allowing the circulation of O_2 and the gases resulting from the OM degradation. When the moisture content exceeds 60%, O_2 movement is inhibited and the process tends to become anaerobic (Das and Keener, 1997). During composting, the high temperatures observed, promotes water evaporate. In order to control temperature and maintain the decomposition rate by the microbial activity, rewetting may be applied.

For materials with high moisture content, the selection of a bulking agent with low-moisture bulking materials, such as sawdust or straw, should be preferred to reduce the potential excess of moisture and provide adequate porosity in the compost heap (Imbeah, 1998). Cotton gin waste also seemed to be effective in controlling the excessive moisture of high moisture materials such as olive mill waste and sewage sludge, providing a good structure to the pile (Paredes et al., 1996; Sánchez-Monedero et al., 2001).

Aeration is essential in aerobic processes, providing mass flow for oxygen replenishment and moisture and carbon dioxide removal and serving as a heat transfer fluid for temperature management through energy redistribution and heat removal (Richard et al., 2004). The optimum O_2 concentration is between 15 and 20% (Miller, 1992). Airflow values too high, promotes the decrease in temperature of the pile, producing compost with a low degree of degradation and airflow values too low promotes the anaerobic process due to the lack of oxygen or the increase in temperature of the pile with the possibility of combustion. Both scenarios can stop microbiological activity. Controlled aeration should maintain temperatures below 60-65ºC, which ensures that enough O_2 is supplied (Finstein et al., 1985).

Particle size and distribution are critical parameters for balancing the surface area for growth of microorganisms and the maintenance of adequate porosity for aeration. Compost with large particles does not decompose adequately due to the difficult accessibility for the microorganisms, and during decomposition, particles may coat the surface with an impenetrable humified layer (Bernal et al., 1993). However, compaction can occur when particles are too small, reducing the porosity (Haug, 1993). Optimum particle size of 10 mm is found for agitated systems and forced aeration, but for large heaps and natural aeration, 50 mm size may be adequate (Gajalakshimi and Abbasi, 2008). These factors are material-specific: particle size and distribution, shape, packing and moisture content control the porosity of the composting mass.

Porosity refers to the volume of material voids that can be filled by water and/or air. It is one of the key factors in the composting process, because it is related, directly or indirectly, with most of the other factors, being inversely related to bulk density and directly related with aeration. Aeration and porosity/density can be regulated in an industrial scenario by frequent pile turning. It is important to investigate the effect of pile settlement on porosity, if we want to produce compost with high fertilizer properties.

Pile settlement is observed since the moment that the pile is built, until the end of the composting process. This occurs when excessive external force is applied to a composting pile or when the pile itself becomes so large that the overburden compresses the material at the base (Keshav and Keener 1997), where primary settlement is originated in the first few days by the dissipation of gas and leachates from the porous matrix, and secondary settlement caused by the particles reorientation and biodegradation (Wall and Zeiss, 1995; Gourc et al., 2010).

According to Van Ginkel, J.T. et al. (1999), there is a valid relationship between bulk density and height and between airfilled volume fraction and height for composting animal manure with a vegetal waste. A few studies have described pile height reductions from 15% to 30% (Trémier et al., 2009; Van Lier et al., 1994; Yue et al., 2008) and it can also be observed a gradient of compaction from the top to the bottom of the compost pile, decreasing the porosity, turning in a decrease of oxygen in the mass, which is related to the possible presence of anaerobic microsites. Fukumoto et al. (2003) also observed a direct relationship between the size of the pile with the GHG emissions during the composting of pig manure with sawdust, concluding that when the volume of the pile is reduced, lower CH_4 and N_2O emissions were observed, considering that the compaction effect is reduced and the possible anaerobic microsites are scarce. Keshav and Keener (1997) observed a direct relationship between the moisture content of the samples with compaction, where samples with high moisture content seem to compact more.

Porosity greater than 50% causes the pile to remain at a low temperature, because energy lost exceeds heat produced. Too low porosity leads also to anaerobic conditions and odour generation. The percentage air-filled pore space of composting piles should be in the range of 35-50%.

Usually pH is not a key factor for composting in case of pig slurry, due to the neutral-basic pH values of the this (Moral et al., 2005; Yagüe et al., 2012). However, is the factor that regulates N-losses by ammonia volatilisation, which can be particularly high at pH > 7.5. In this case, high pH values during composting can be regulated by adding elemental sulphur (Mari et al., 2005). A pH of 6.7-9.0 supports good microbial activity during composting, but optimum values are between 5.5 and 8.0 (de Bertoldi et al., 1983; Miller, 1992).The pH increases during the bio-oxidative phase of composting, due to the degradation of OM of acidic character. However, during maturation it tends to decrease, owing to the nitrification of the NH_3-N, which is an acidifying process.

Optimum temperatures for composting are considered in a range of 40-65ºC (de Bertoldi et al., 1983), temperatures above 55ºC are required for minimum of two weeks, to a correct sanitation of the compost. Microbial activity starts to decline rapidly when temperature reach values higher than 63ºC, as the optimum for various thermophiles is surpassed. The range of 52-60ºC is the most favourable for decomposition (Miller, 1992). The regulation of the temperature is required for controlled composting and can be achieved through several strategies (Miller, 1992): control the size and shape of the composting mass; improve cooling and favourable temperature redistribution by turning operations, which means heat removal through evaporation cooling; and achieve superior temperature control in systems that actively remove heat through temperature feedback-controlled ventilation (Rutgers strategy; Finstein et al., 1985).

Although it is difficult to generalise for all type of substrates and management conditions, optimum ranges for the condition parameters are recommended for composting of solid manure in table 8.

Table 8 - Recommended conditions for composting of solid manure (Rynk, 1992).

Condition	***Reasonable Range***	***Preferred Range***
C/N ratio	20 – 40	25 – 30
Moisture content (%)	45 – 65	50 – 60
Oxygen concentration (%)	>5	>5
Particle size (diameter in cm)	0.5 – 5.0	0.5 – 2.5
pH	5.5 – 8.0	5.5 – 8.0
Temperature (ºC)	43 – 66	54 – 60

During the composting process, the evolution of temperature indicates the different steps of the process (Bernal et al., 2009). The energy produced by the microorganisms during degradation of the organic matter, throught the microbial metabolism, is released as heat increasing the temperature of the composting mass (Tuomela et al., 2000). In general, the composting process is constituted by different phases (Fig. 9):

- Mesophilic phase, lasting 1-3 days, mesophilic organisms (optimum growth temperature range = 20-45 °C) multiply rapidly on the readily available sugars and amino acids. They generate heat by their own metabolism and raise the temperature to a point where their own activities become suppressed;
- Thermophilic phase, where thermophilic microorganisms, such as bacteria, fungi and actinomycetes (optimum growth temperature range = 50-70 °C or more) degrade more complex compounds like fats, cellulose, hemicellulose and some lignin. During this phase the maximum degradation of the OM occurs together with the destruction of pathogens, due to the high temperatures achieved (65 °C or higher).
- Cooling phase, in which the microbial activity is decreasing due to the consumption of the degradable organic compounds, the temperature is reduced to mesophilic values and a re-colonisation by mesophilic microorganisms takes place, with the degradation of the remaining soluble organic matter (sugars, cellulose and hemicellulose); These three steps constitute the biooxidative phase of composting
- Curing or maturity phase, characterised by temperatures near to the external values, due to the reduction of the microbial activity and re-heading does not occur. Humification of the organic matter takes place so the material becomes dark brown to black in colour. The particles reduce in size and become consistent and soil-like in texture.

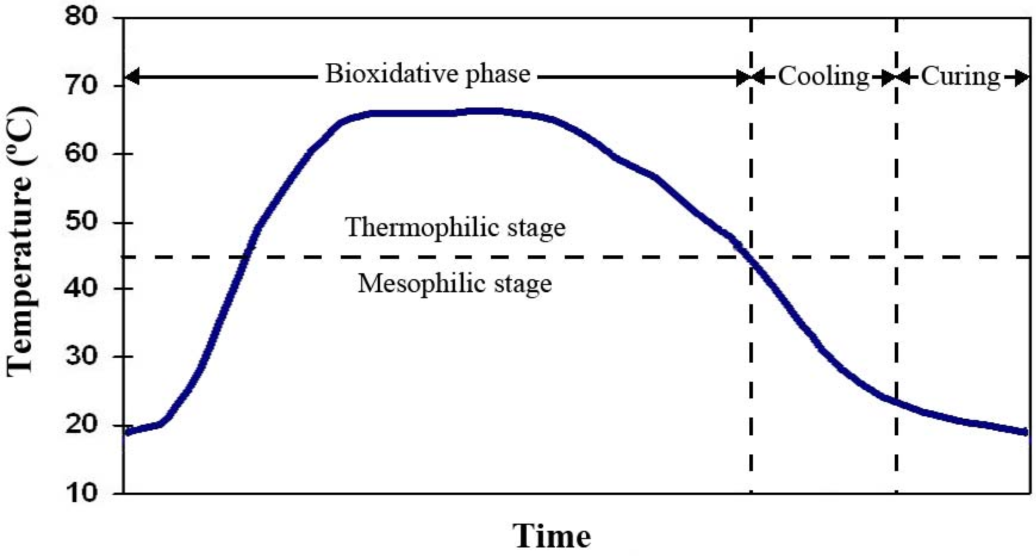

Figure 9 – Pattern of temperature during composting (Adapted from www.recycledorganics.com).

1.2.2 Composting systems.

Composting systems can be divided in open or in-vessel systems. Open systems includes the windrow and static pile (with induced or forced aeration) composting. The opens systems consist basically in piling up the materials under natural or forced ventilation, favouring the biooxidation of the mixtures. These systems are cost effective and low technology is required. In other hand, in the in-vessel systems, the composting process occurs inside enclosed reactors. These systems provides better control of the composting conditions of the process, requiring less space to operate, reducing the composting time and avoiding the odour emissions. For these reasons, in-vessel systems are more expensive than open systems, making the turned windrow (Fig. 10a) and the aerated static pile composting systems (Fig. 10b) preferable by farmers.

Turned windrow composting: Organic waste is formed into rows of long piles called “windrows” and aerated by mechanical turning the pile periodically The ideal pile height, which is between 1 and 3 m, allows for a pile large enough to generate sufficient heat and maintain temperatures, yet small enough to allow oxygen to flow to the windrow's core. The ideal pile width is between 3 and 4 m. Composting piles can have 20 m long or more, depending on the available space. Windrow composting often requires large tracts of land, sturdy equipment, a continual supply of labour to maintain and operate the facility, and patience to experiment with various materials mixtures and turning frequencies.

Passive windrow composting: To aerate the pile, layers of loosely piled bulking agents (wood chips, cereal straw, garden pruning, etc.) are added so that air can pass from the bottom to the top of the pile (passive aeration).

Aerated static pile composting: In aerated static pile composting, organic waste is mixed together in one large pile instead of rows. The piles are placed over a network of pipes that deliver air into or draw air out of the pile. Air blowers might be activated by a timer or a temperature sensors, inducing forced aeration (Rutgers system, Finstein et al.,1985). Other static system introduce the air in the composting mass from the surface through suction (Bestville system). The piles are usually turned once or twice during the process, to mix the materials. These methods typically requires equipment such as blowers, pipes, sensors, and fans, which might involve significant costs and technical assistance. Having a controlled supply of air enables construction of large piles, which require less land than the windrow method. Actively aerated windrows will compost more quickly. Although no turning of the material is required in either system, occasional turning is still recommended to redistribute moisture and expose fresh material to microbial activity.

Figure 10 – a: Windrow composting pile system (Adapted from www.caerphilly.gov.uk/hovwp/en/organic_project.html); B: aerated static pile composting system (Adapted from www.compostsystems.com/).

In-vessel systems: are essentially closed reactors which can incorporate process gas treatment. They can be categorised broadly into five types: containers, silos, agitated bays (bed), tunnels and enclosed halls. Oxygen supply and temperature control occur through mechanical agitation and/or forced aeration. Tunnel composting units are large-scale rectangular vessels employing forced-aeration systems. Although some systems operate on a continuous flow using moving floors, typically they are used to process material in single batches. The rotating drum is a continuous processing system, in which the material is mixed, aerated and moved along the length of the drum by means of specially designed baffles and tines situated in its walls. Some systems use forced aeration rather than passive air flow. In agitated bays and beds, the material is fed into a large, enclosed building where it is placed either in long, concrete-walled bays or in extended beds. The material is turned with specialised machinery.

1.2.3 Composting of pig slurry.

Composting is a feasible technique to treat pig manure because it does not requires a sophisticate technology and it is not difficult to manage and control, as anaerobic digestion, pyrolysis or gasification, only requires space and the control of certain factors, like C/N ratio, moisture content, O_2 concentration, particle size, pH and temperature. These parameters are able to affect negatively the development of the composting process if not controlled properly.

Since pig slurry is a semi-liquid material with low dry matter content, a solid-liquid separation is required to reduce its moisture, and for obtaining a solid material for composting. Such solid fraction of pig slurry is rich in N with respect to TOC, giving a low C/N ratio for composting. Then, a second condition for it composting is to be mixed with a bulking agent (mostly vegetal, with high concentration of TOC), to improve C/N ratio, able to absorb the excess of moisture from the solid pig slurry, and give support and develop the composting matrix (Chang and Chen, 2010) and to prevent odour formation or combustible gases production, derived from possible anaerobic conditions. When plant wastes are used as bulking agent, the process is called co-composting, in this way the recycling of those residues is also promoted.

In order to choose the adequate bulking agent o use during composting, several criteria are taken into account: the availability of the materials, their efficiency during the composting process and the possibility of testing new materials. Cereal straw (Szanto et al. 2007, Zhu et al. 2004, McCarthey et al., 2011, Hsu et al. 2001), sawdust (Lo et al. 1993, Fukumoto et al. 2009, Tiquia and Tam 1998, Huang et al. 2004, McCarthey et al. 2011) and cotton gin (Vanotti et al. 2006) are the materials mostly used as bulking agent for the co-composting of the solid fraction of pig slurry. Also, maize stalks and barley straw are materials commonly used in the composting of animal manures (Bernal et al., 2009), while cotton gin is a material that shows good properties for the co-composting of materials with high moisture content (Paredes et al., 1996; Sánchez-Monedero et al., 2001) and garden pruning is a green waste now in study (Estevez-Schwarz et al., 2012).

The use of lignocellulosic materials is frequent during the composting of N-rich wastes, because they can retain the excess of moisture, provide structural support and provide the source of C for a balanced C/N ratio for composting. Being rich in lignin – recalcitrant materials – the C source is slowly consumed by microorganisms, maintaining then the C/N ratio and preventing N-losses (Doublet et al., 2012; Paredes et al., 1996a).

The use of composting technology for manure management presents some advantages and disadvantages:

Composting advantages:

- Compost is a marketable product. Gardeners, landscapers, farmers, and others are willing to purchase quality compost. Price depends on the local market, quality of compost, and the raw materials used;
- Pathogens and weed seeds are destroyed in a properly managed windrow if the temperature remains above 40°C for a minimum of two weeks;
- The mass and volume of the manure is reduced when composted primarily due to moisture content reduction, making it easier to handle than manure and increases the distance of land application of the nutrients;
- Composting allows recycling the nutrients from manures as they are concentrated in the compost. When compost is added to the soil, it provides organic matter, reduces potential for soil erosion, and reduces fertiliser requirements;

- Compost is a stable product which is free from offensive odours;
- Compost can be stored without odour or fly problems and is a product which can be applied to the land when it is convenient for the farmer;

Composting converts NH_4-N to NO_3-N which is directly plant available. But organic-N is also formed which is less susceptible to leaching and will slowly be converted into available-N.

Composting Disadvantages:

- Composting requires a time commitment to properly manage the windrows to produce quality compost;
- Specialised windrow turners may be required, but they can come at with a high price tag;
- The composting site and storage for finished product can use a considerable area of land;
- Requirement for a bulking agent to obtain quality compost. Also have the necessity of pre-treatments or conditioners;
- Some additional fertiliser may be needed to meet crop requirements.

1.2.4 Agronomical and quality parameters of compost.

The maturity and quality assessment in composts is an important factor that affects the efficient use of composting products in agriculture.

Prior to its use, composting products have to meet some legislative requirements to be consider able to be used as fertilising product, ensuring a sufficient level of sanitisation (JRC, 2014; BOE, 2013). Such requirements regards parameters such: the temperature achieved during the process, presence of pathogens and weed seeds and concentration of heavy-metals and organic pollutants at the final product.

Temperature should be higher than 65 °C or more for at least 5 days; 60 °C or more for at least 7 days; 55 °C or more for at least 14 days; E. coli should be lower than 1000 CFU g^{-1} of fresh mass and there is a maximum of 2 weed seeds per litre of compost; heavy metals concentration should be lower than the values resumed in table 9 (lower than class C for Spain).

The proposed end-of-waste criteria for compost include: minimum organic matter content – 15% on dry matter weight with mineral components (e.g. sand, soil); Limited content of macroscopic impurities – 0.5% on dry matter weight for glass, metal and plastics > 2 mm; Limited content of organic pollutants (mg kg^{-1} dry weight) – PCB7 < 0.2; PAH16 < 6; PFC < 0.1; and PCDD/F < 30 (ng I-TEQ kg^{-1} dry weight).

Table 9 - Limits for potentially-toxic elements in compost I EU-27 and in Spain (mg/kg DM).

Trace elements	**EU (JRC, 2014)**	**Spain (BOE, 2013)**		
		Class A	Class B	Class C
Cd	1.5	0.7	2	3
Cr	100	70	250	300
Cr (VI)	n.d.	n.d.	n.d.	n.d.
Cu	200	70	300	400
Hg	1	0.4	1.5	2.5
Ni	50	25	90	100
Pb	120	45	150	200
Zn	600	200	500	1000

n.d.: Not detectable.

The quality of compost is based on the concentrations of heavy metals and organic pollutants, with impurities (> 2 mm) limited to < 0.5 % and gravel and stones (> 5 mm) to < 5 %, all normalised to an OM content of 30 %.

The most limiting heavy-metal elements, regarding pig slurry composting are copper and zinc, due to the great application of those elements during feed, to enhance pig development and disease control.

Spanish legislation, concerning fertiliser products (BOE, 2013) is a little bit harsher when it comes to regulating the characteristics of fertilisers made from organic wastes, in particular for heavy metals concentration. However, the limits for moisture content to values lower than 40 %; the total organic matter should be higher than 35 %; C/N ratio have to be lower than 20; concerning particle size, 90 % of the product should be < 25 mm and Salmonella spp. should be absent in 25 g and *Escherichia coli* < 1000 MPN per g. Heavy metal limits are established for three quality products, A, B and C (Table 9); Cr (IV) should be absent for all classes. Products of class C cannot be applied to agricultural soils at application rates greater than 5 t (DM)/ha/year.

However, the parameters mentioned above are not sufficient to assess compost quality. According to Bernal et al. (2009), compost quality should also be based in other to two criteria: maturity and stability. Stability refers to a specific stage or decomposition or state of OM during composting, which is related to the types of organic compounds remaining and the resultant biological activity in the material (California Compost Quality Council, 2001); and maturity is the degree or level of completeness of composting and implies improved qualities resulting from ‘ageing’ or ‘curing’ of a product.

Despite all the available parameters to establish the maturity and stability of composts, no single parameter can be universally applied to all the composts due to wide variations in composition of raw materials used. Hence, maturity should be assessed by using at least two parameters that can be: physical, chemical and biological. Also, the limiting values used as reference (Table 10) should be seen as reference values, considering that some of them are defined for composts made from wastes different then livestock manure.

Physical: Temperature, colour, odour, particle size distribution, moisture and air content; physical parameters are frequently used but they give only general information regarding maturity of compost.

Chemical: C/N ratio in solid and water extract, ions, pH, EC, and OM in water extract, cation exchange capacity, ammonia-N content, lignin and other organic compounds, humification indices and humic-like substances characterisation by elemental and functional group analyses, molecular weight distribution, E_4/E_6 ratio, pyrolysis GC-MS, spectroscopic analyses (NMR and FTIR, Fluorescence, etc.), etc.; chemical parameters are widely used to assess the compost maturity, since are more reliable than the physical parameters.

Biological: respiration (O_2 uptake/consumption; CO_2 production; self-heating test; biodegradable constituents), phytopathogenic supresivity, activity and biomass of microorganisms, germination and plant growth tests; these parameters are also widely used to assess compost maturity, being comparatively more reliable than the other parameters.

Table 10 – Limit values of some maturity parameters (Adapted from Bernal et al., 2009)

Parameters	Limits
GI	> 50 %
NH_4^+-N	< 0.4 g kg^{-1}
NH_4^+-N/NO_3^--N	< 0.16
C/N	< 12
C_w	< 10 g kg^{-1}
C_{ex}	< 60 g kg^{-1}
C_{FA}	< 12.5 g kg^{-1}
CEC	> 67 meq 100 g^{-1} OM
HR	> 7 %
HI	≥ 3.5 %
PHA	≥ 50 %
PI	≥ 1 %

GI: germination index; C_w: water-soluble C; C_{ex}: extractable C; C_{FA}: fulvic acids C; CEC: cation exchange capacity; HR: humification rate; HI: humification index; PHA; percentage of humic acids; PI: polymerisation index.

Self-heating tests are commonly used to assess compost maturity rate (Brinton et al. 1995), based on stability, relating the temperature increase of the material with the degree of maturity of the material – composts that present a quick temperature increase are considered immature. Also, respiration tests based on CO_2-C production or oxygen (O_2) consumption are common procedures for determining compost stability (Barrena-Gómez et al. 2006). Adani et al. (2006) correlated the dynamic respiration index with temperature and airflow rate for determining biological stability of compost. These tests can also be used as a tool to determine the biodegradability of the material, according to Qiu et al. (2005) temperature and CO_2 concentrations are directly related with microbial activity.

1.2.4.1 Case studies of the use of compost as organic fertiliser.

Composting has been practised in rural areas for centuries. Farmers traditionally put agricultural and some animal waste on their fields to improve crop yields and remove the wastes from farm. Previously, composts were defined as products with great concentration of nutrients, organic matter and humic substances and great potential to be commercialised as organic fertilisers, beneficial for a correct plant growth. In this sense, compost applicability varies with its quality (Fig 11).

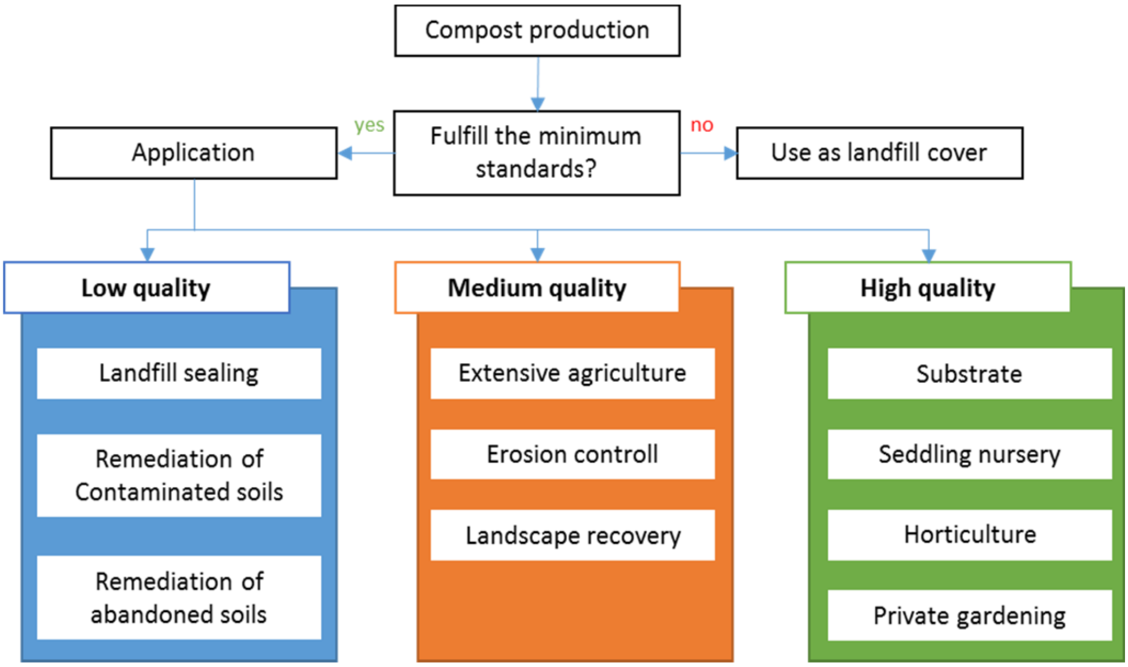

Figure 11 – Possible compost applications (Adapted from www.ucp.cat).

Mulching consists in unincorporated surface application of composts or composted materials to the soil. Compost is applied as a blanket on the top of soil surface to depths typically ranging from 1.25 - 10 cm, depending on budgets and site-specific conditions. They may be vegetated (Fig. 12a) or without vegetation (Fig 12b).

Vegetated compost blankets, when applied at a uniform depth, can give close to 100 percent cover (Faucette, 2004). Due to their fertility and water-holding properties, compost blankets should be more successful than wood mulches on steep hill slopes for vegetation establishment (Faucette et al., 2007). Compost blankets absorb the energy of rainfall which could have dislocated soil particles. They also help to absorb substantial amounts of moisture to reduce flow velocities which reduces scouring and improves water infiltration. Glanville et al. (2003) reported that when compost is applied as 5 and 10 cm blankets, there was no significant difference observed between the two different depths with respect to soil erosion rates when rainfall was simulated to achieve an intensity of 95 mm hr^{-1}. The 5 cm layer performed as well as the 10 cm blanket with respect to erosion control, water quality, and vegetation benefits.

Figure 12 – Compost application to the soil: a – with vegetation (Adapted from www.biocycle.net/2014/09/18/10-trends-in-the-compost-marketplace); b – without vegetation.

When incorporated into the soil as a soil amendment, compost improves it structure, increasing its water holding capacity and humic properties, allows the nutrients recycling from manure, providing essential macro- and micro-nutrients for plant nutrition (Martinez et al., 2003; Moreno et al., 1996; Huag,1993). Organic-N that did not degrade during the composting process may readily mineralise after compost incorporation in soil, being available for plant growth.

The use of compost as organic fertiliser also helps to develop a superior environment for revegetation/vegetation establishment. It helps to increase plant productivity (Guerrero et al., 2001) by increasing soil organic matter content and fertility (Butler and Muir, 2006). Compost applied into the topsoil helps improve soil structure, water penetration and tilt, and reduce the soil bulk density (Cogger, 2005; Pengcheng et al., 2008). In some cases compost applied as a soil amendment can also serve as a disease suppressant (De Cuester and Holtink, 1999; Graham, 1998) by increasing the activity of soil's beneficial organisms (Zibilske, 1998).

In a long-term agricultural experiment performed by Badeba et al. (2014) where compost, mineral fertiliser and a combination of both were used as amendments to the soil, to assess the implications on the crop yield and improvement of soil quality, the authors concluded the addition of either compost alone, or in combination with mineral fertiliser, improves soil and maize productivity in a long-term on-farm experiment more than with a sole fertiliser or unfertilised control.

During the last years, the use of compost as substrate or component of substrate for seedling production has been on focus. In Mediterranean countries is a common practice, considering the severe climate conditions. The use of compost as growing media allows the energy cost reduction needed for photosynthesis and helps to maintain the control of climate condition in the greenhouse (Agulló, 2012).

In a horticultural perspective, substrate is all the solid materials different from soil, natural or synthetic, mineral or organic, that once put in a container, in a pure form or mixed with other materials, allows the anchoring of the root system, acting as a support for the plant. Substrates can be involved, or not, in the process of plant nutrition. Most of the substrates used in seedling nursery have limited origins and high transport costs associated. Peat is an organic material, resulting from an accumulation of partially decayed vegetation or organic matter. Peatland ecosystems are considered as a natural C sink, being almost one third of the soil C existent in the world found in this ecosystem. In this sense, there is a need to find a substitute for peat use, in order to avoid C release to the atmosphere and consequent climatic changes.

In Mediterranean countries, the horticultural sector has achieved a high relative importance, especially Spain, being one of the greatest horticultural producers, where curiously the natural resources for growing media are negligible. In this scenario, composting is a routine, efficient and sustainable treatment to obtain stabilized organic resources that can be used in extensive and intensive agriculture for amendment and background fertilising purposes. However, in soilless cultivation conditions, the growing media must accomplish specific high standards of quality, environmental and safety issues, and moreover specific conditions depending on the type of cultivation requirements (seedling-propagation-growing; Agulló, 2011).

Some research work on organic materials has been done for partially or completely substitute peat as a substrate. Several organic materials have been referred to be used as substrate after composted, considering that they present similar physico-chemical characteristics as the ones found for peat. Even if the use of compost as peat substitute may be an attractive economic and environmental solution, it may present some limitations: high EC, undesirable physical properties and possible toxicity related with high heavy metals concentration (Sánchez-Monedero et al., 2004; Spiers and Fietje, 2000; Herrera et al., 2008). However, these limitations can be minimised by mixing the composts with peat.

Luo et al. (2015) conducted a study on the feasibility of using litter compost from a pig-on-litter system in the nursery and growth of vegetables to replace part of peat in substrates containing peat, vermiculite and perlite. The author found that litter compost from a pig-on-litter system could be used as a nutrient source to replace up to 40% of peat without negative effect on tomato seedlings, when also vermiculite and perlite were added in the substrate; and for the Chinese cabbage the peat addition could be cut down to 20% without apparently affecting the plant growth in the substrates with 30% of compost, when also vermiculite and perlite were added in the substrates.

1.2.5. Environmental implications.

Environmental implications can outcome during the composting process and/or after compost application to the soil, regarding GHG emissions and loss of N.

Although ammonia is not considered a GHG, its emissions during composting are usually studied, since it is involved in the formation of acid rain and from the point of view of the nitrogen conservation in the end-product because of the potential use of compost in agriculture as organic fertiliser. Also, CO_2 emissions coming from biological process are not considered to contribute to global warming since this carbon has a biogenic origin, i.e., this carbon has been previously fixed biologically (Sánchez et al., 2015).

CH_4 and N_2O emissions during composting are related with the poor control conditions of the process, allowing anaerobic conditions to occur. N_2O is released during denitrification of nitrite and nitrate. However emissions from of these gases are considered low if the process has good aeration. Their importance is related with contribution to global warming since they have a warming potential 25 (CH_4) and 298 (N_2O) times higher than that of CO_2 (IPCC 2007). The composting technology can be seen as useful tool in the management of pig slurry, being able to reduce GHG emissions, even considering the emissions associated due to the characteristics of the composting process. According to Brown et al. (2008), the emissions during composting are minimal compared to the benefits associated to the reduction of CH_4 emissions when manure is stored under anaerobic conditions, allowing to reduce 99% of CH_4 emissions and 75% of N_2O emissions with the separation of pig slurry into solid and liquid portions and later treatment of the solids by aerated composting (Vanotti et al., 2008). Pardo et al. (2015) referred the addition or substitution of certain bulking agents as a method to reduce CH_4 and N_2O emissions during composting, indicating that a reduction of 53 and 71 % can be achieved, respectively. Even if composting promotes some NH_3 emissions, they indicated that covering or compaction could be used in order to reduce those emissions by 61 and 54 %, respectively.

The use of compost as amendment was referred as a mitigation strategy for GHG emissions. Ho et al., (2015) found that the addition of compost to the soil contributed to increased methane uptake and was able to offset approximately 16% of net emitted carbon dioxide. By increasing the nutrient concentration, new methanotrophs appear in the soil, oxidising methane over a wide range of concentrations, from atmospheric levels to very high concentrations. The use of compost in agriculture has a positive effect in GHG emissions since its application as an organic amendment provokes that carbon stays bound to soil (Sánchez et al., 2015), considering that composts are constitute by an important lignocellulosic part, being slowly released to the soil, allowing C conservation in the soil and reducing CO_2 emissions. Applying compost to agricultural soils could thus reduce the impact of carbon dioxide and methane emission.

During the composting process, N losses may occur through NH_3 volatilisation, denitrification, nitrification and nitrate leaching. N-rich materials, such as manures, have great concentration of ammonia, being lost when high temperatures are found (beginning of the process). Ammonia loss during turnings can occur, by exposing the active material to the atmosphere, representing a minor loss. Considering that the nitrate concentration at the beginning of the process is low, NO_3^--N losses by denitrification or leaching are also low, however, at the end of the process, nitrate concentration is high, increasing the potential risk of leaching (Pardo et al., 2015). Nitrate-N leaching should not occur, unless poor composting installations are established.

However, after compost application to the soil, some of the mineralised N may be leached or lost by volatilisation (Fig.13; Cambardella et al., 2003). Composts from livestock manures are rich in ammonium-N and nitrate-N. Ammonium is readily absorbed in the soil and leaching of ammonium is usually very low in most soils, but it can be leached by macropore flow occurring shortly after application (Parkes et al., 1997). Organic-N in the composts tends to be mineralised after compost incorporation in the soil. The application of composts rich in NH_4^+-N may promote some losses by ammonia volatilisation, if not incorporated in the soil, considering that it is not immediately nitrified into nitrate.

Under anaerobic conditions, N_2O may be formed by denitrification and lost to the atmosphere. Contrarily to ammonium, nitrate is not absorbed and stays in solution and is therefore more vulnerable to leaching. Nitrate-N leaching in compost amended soils is the main mechanism of N loss. Leaching is usually affected by:

- Type of soil, since sandy soils do not retain as well the water as clay soils;
- Climatic conditions and irrigation – water is the transport mechanism of nitrate and when water is abundant, promotes nitrate-N leaching to deeper zones and ultimately to the groundwater;
- Amount of N applied by amendments – excessive amount of organic or mineral fertilisers promotes the N leaching through the soils.

However, composts are less vulnerable to nitrate leaching during the first year of application. Long-term compost application increases the nitrate leaching risk, considering that organic-N is mineralised along the years, providing inorganic-N, increasing the nitrate concentration in the soils (Sorensen and Jensen, 2013).

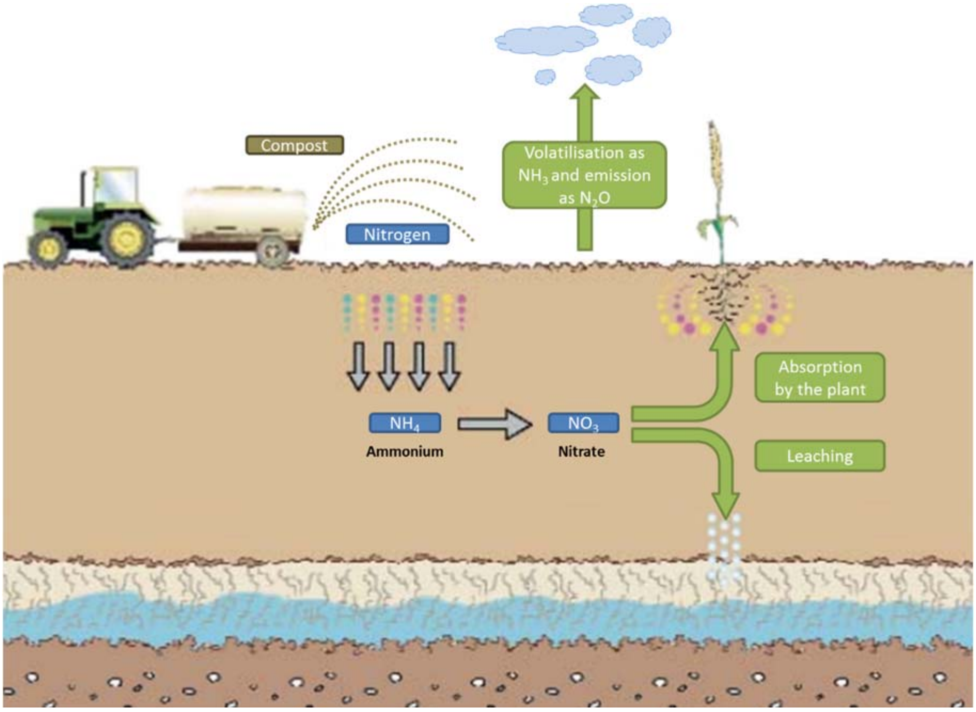

Figure 13 – Pathway of N after soil application.

1.2.6 Advanced techniques for compost analysis.

The understanding of OM transformation throughout the composting process and proper evaluation of compost stability and maturity are essential for successful utilisation of composts. Apart of the classical physico-chemical analysis commonly used for the effect, advance techniques can be useful characterisation tools for studying the transformation of OM during the composting process, as well evaluating the stability and maturity of the composts produced. These are some of the useful techniques:

Fourier transform infrared spectroscopy (FT-IR):

In this technique, energy absorption is due to the vibrational and rotation movements of the different groups and bonds of molecules and vibrational resonance can be classified in two groups:

- Stretching – the distance between bonds changes by enlargement and stretching;
- Bending – atoms disposition changes in relation with the bond axis;

The infrared spectrum is obtained by irradiating the sample with wavelength between 4000 and 400 cm^{-1}. The infrared radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The data is registered as an interferogram (a plot of the intensity at each individual frequency) and decoded by mathematical technique – Fourier transform – in a spectrum (a plot of the transmittance at each wavelength; Fig. 14).

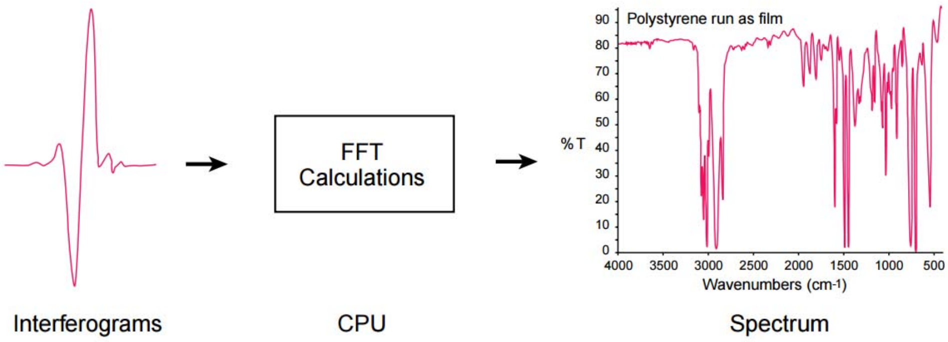

Figure 14 – Decoding of interferograms by Fourier transform (Adapted from Thermo Nicolet Corporation, 2001).

The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) of every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis. A characteristic behaviour in compost samples is a reduction of 1560 cm^{-1} peak which probably due to relatively rapid biodegradation of the amino chain. The aromatic region and the 1800 cm^{-1} peaks became sharpen during composting, indicating the humification of the organic matter. Peaks in the aliphatic region at 2930 and 2850 cm^{-1} decreased, while the 1450 cm^{-1} peak increased (Chefetz et al., 1996).

As shown in Fig. 15, the peaks represent certain molecules, according to the range of wavelength. The analysis of the sample at time 0 and at time 63 (mature compost) allows to observe that the easily degradable organic matter constituents such as short aliphatic chains, polysaccharides and alcohols are chemically or biologically oxidised, leading to increased aromatic structures of high stability, considering that the area of the peaks for these compounds is lower at time 63, with the higher peaks, indicating the formation of more stable compounds from the polymerisation of aromatic compounds.

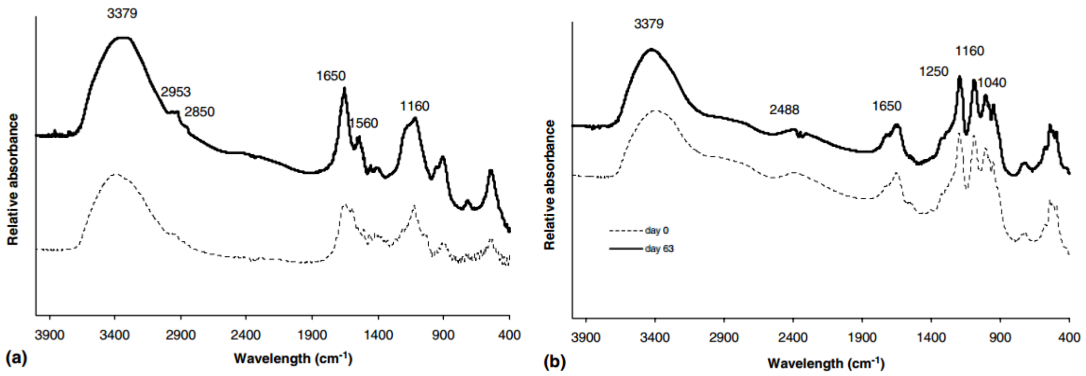

Figure 15 – FTIR spectrum of (a) humic acids and (b) fulvic acids at day 0 and day 63 (Adapted from Huang et al., 2006).

FTIR technology presents some advantages, such as:

- It is a non-destructive technique;
- It provides a precise measurement method without external calibration;
- It can increase speed, collecting a scan every second;
- It can increase sensitivity – one second scans can be co-added together to ratio out random noise;
- It has greater optical throughput;

Nuclear magnetic resonance spectroscopy (NMR):

Nuclear magnetic resonance (NMR) spectroscopy is a technique that detects the chemical environment of atomic nuclei by the absorption of radio-frequency electromagnetic radiation when in the presence of a high magnetic field. NMR is used in chemistry and related fields for high-resolution molecular structure determination and the study of molecular dynamics. The mostly studied nuclei are ^{13}C and ^{1}H.

The nuclei charge of ^{13}C and ^{1}H when spin, creates a magnetic field along its axis. If these nucleus are under an external magnetic field influence of intensity B_0, it will perform a precession movement around the axis of this field. If "I" is the quantic number of spin, it will determine the number of possible orientations of the nuclei in the external magnetic field, accordingly 2I+1. For both ^{13}C and ^{1}H, the "I" value is ½, which allows two different orientations, one parallel and other antiparallel to the field B_0 ($I = + ½$ and $I = - ½$).

The NMR spectroscopy considers that between the two orientations exists a different population that changes when perturbation occurs. This perturbation is achieved when the samples are submitted under an electromagnetic radiation for a short period of time, where its associated magnetic field, B_1, interacts with the nucleus by absorbing energy when the frequency of this radiation resonate with the one from the precession. When returns to equilibrium, a signal is obtained. The detected signal is called free induction decay of simply FID. Fourier transformation is than performed on the recorded FID to get the NMR frequency spectrum (Fig. 16).

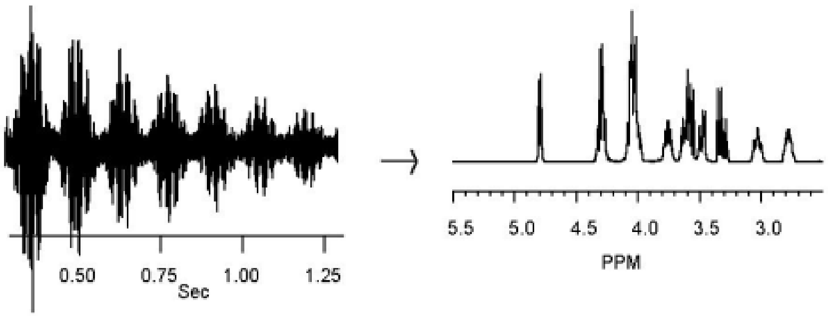

Figure 16 – Free induction decay (on the left); NMR frequency spectra (on the right) after Fourier transformation (Adapted from Rangus, M., 2007).

High resolution of the solid-state NMR spectra can be achieved by spinning the sample around an axis inclined at 54.74° also referred to as a magic-angle spinning (MAS). In this sense, the anisotropic part – the electron distribution of molecules with abnormally high electron density – of the interaction vanishes and only the isotropic contribution remains. Cross polarisation (CP) allows obtaining higher resolution ^{13}C spectra by polarisation from abundant spins, such as ^{1}H, is transferred to dilute spins, such as ^{13}C, by matching the precession frequencies of the abundant and rare spin types in the rotating reference frame. Cross polarization requires that nuclei are dipolar coupled and is usually combined with the magic-angle spinning. In this case it is referred as CP-MAS ^{13}C NMR.

Solid state cross polarization with magic-angle spinning (CP-MAS ^{13}C NMR) spectroscopy is a useful analytical tool for its capacity to selectively identify different types of C moieties and to compare difference in concentration of main functional groups (Adani et al., 2006) (Fig. 17). It allowed to investigate samples without any need of extraction and fractionation and thus to collect direct information on the structural characteristic of whole organic matter during the composting process (Conte et al., 2004 and Albrecht et al., 2008). One of the advantages when applied to compost samples is that the presence of impurities with paramagnetic character is low and the OM content is high. CP-MAS ^{13}C NMR can be also used to study the composition and degradation of humic substances (Conte et al., 2004; Cook, 2004) and also to evaluate the quality and maturity degree of composts.

The typical behaviour observed in a spectrum from samples referred to the composting process is a reduction of the 30 ppm peak; appearance of the 55 ppm peak as shoulder in the mature compost and an increase of the aromatic region peak (130 and 150 ppm peaks); total aliphatic C (0-112 ppm), polysaccharide (60-112 ppm) and alkyl groups (0-50 ppm) decreased in the raw material when compared with the matured compost. Also aromatic components, including aromatic and phenolic carbons, carboxyl C and C = O carbonyl C was higher in the mature compost than in the raw materials (Kogel-Knabner et al., 1991; Chefetz et al., 1996).

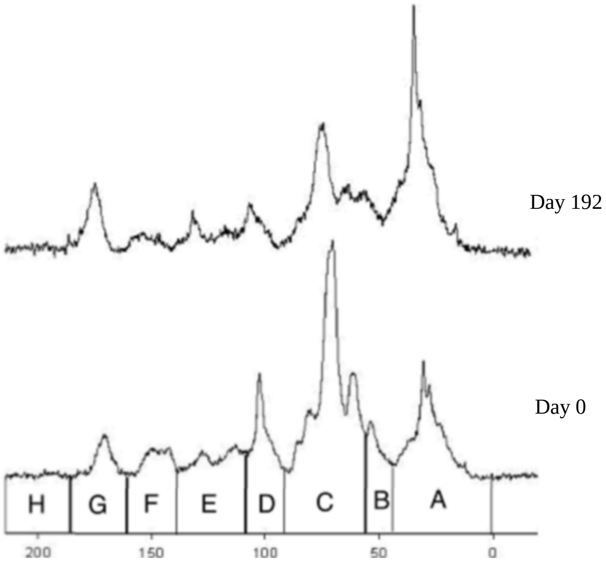

Figure 17 – CP-MAS ^{13}C NMR spectrum from compost produced with vegetal wastes and cow manure at day 0 and day 192 (mature compost). Regions based on chemical displacement (ppm): (A) aliphatic C, 0-47 ppm; (B) methoxyl C, 47- 60 ppm; (C) alkyl-O C, 60-95 ppm; (D) di-O-alkyl C, 95-110 ppm; (E) aromatics C (without bonded O), 110-140 ppm; (F) phenolic C (aromatic-C with bonded O), 140-165 ppm; (G) carboxyl C, 165-190 ppm; (H) carbonyl C, 195-215 ppm (adapted from Moreno and Moral, 2008).

Thermal analysis (TG, DTG and DTA):

Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) are based on a programmed heating of the sample in controlled atmosphere which provide qualitative and quantitative information regarding the humic matter content of the composts. These methods appear promising since they serve to integrate the information obtained from the chemical parameters associated with humification. Thermogravimetry is a technique in which the weight change (increase or decrease) is measured during the incremental heating of the sample. The combined analysis of TG, DTG and DTA supplies information about the stability of the organic compounds in the sample.

The first decrease observed around 100 ºC in TG traces is associated with moisture removal from the samples and the second, more intense, is related with the removal of hemicellulosic and cellulosic materials (Fig. 18a). The first derivative of the TG trace (DTG) on time permits a better resolution of the steps by which the reactions take place, clearly identifying the temperatures at which mass loss is at a maximum, as well as superimposed transformations appear more clearly shown as DTG peaks. It also indicates the rate of mass loss of the samples in function of the temperatures achieved (Fig 18b). A first exothermic peak is normally observed between 180-410 ^{0}C, referring to cellulosic materials, while more complex molecules (lignin and humified material) are associated with the second exothermic peak observed between 410-600 ^{0}C (Baffi et al., 2007).

Particularly, in DTA the difference between the temperature of the sample and a reference material (usually a thermally-inert substance such as calcined kaolinite or alumina) is measured as a function of the applied temperature. Depending on the reactions that occur at the various temperatures, the resulting graph is a curve showing endothermic and exothermic peaks, whose positions are determined by both the structure and the chemical composition of the test substance, while the peak areas are related to the energy involved in the reactions which occur (Fig. 18c). As observed in DTG curves, the first exothermic peak is normally observed between 180-410 ^{0}C, referring to cellulosic materials, while more complex molecules (lignin and humified material) are associated with the second exothermic peak observed between 410-600 ^{0}C (Baffi et al., 2007). A decrease in the first peak, in comparison to the mature samples, can be observed, corresponding to the degradation of carbohydrates, while an increase in the second peak is normally observed and corresponds to an increase in more stable compounds. This increase can be linked to a concentration effect or to the synthesis of more stable molecules during the maturation phase of the composting process. The use of thermogravimetric curves can be a useful tools for the analysis of the OM changes during the composting process, as well to assess the maturity degree of the composts.

One of the advantages of using these analytical methods lies on the simplicity of the samples preparation, requiring only a basic pretreatment of drying and milling.

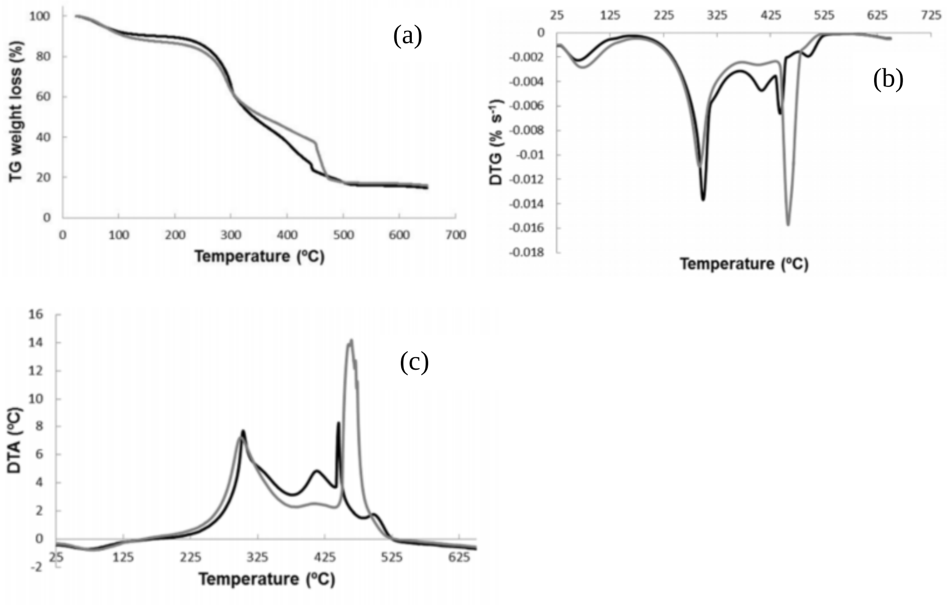

Figure 18 – TG curves (a), DTG curves (b) and DTA curves (c) of compost produced with cattle manure and exhausted grape marc; Black line corresponds to the samples at the initial phase of the composting process and the grey line corresponds to the mature composts (Adapted from Torres-Climent et al., 2015).

1.3 References

Adani, F., Ricca, G., Tambone, F., Genevini, P. 2006. Isolation of the stable fraction (the core) of humic acid. Chemosphere, 65: 1300-1307.

Agulló, E., Bustamante, M.A., Suárez-Estrella, F, Moreno, J., Pasqual, J.A., Ros, M., Paredes, C., Moral, R., 2011. Use of functional biosolidsderived composts as growing media for the production of lavender (*Lavandula dentata*) and rosemary (*Rosmarinus officinalis*). International Symposium on Growing Media, Composting and Substrate Analysis, Barcelona. P. 145.

Agulló, E. 2012. Compost vitivinícolas en agricultura: Uso como enmienda orgánica en cultivos extensivos y como ingrediente en medios de cultivo sin suelo. Ph.D. thesis. Universidad Miguel Hernández de Elche.

Albrecht R., Verrecchia, E., Pfeifer, H.R. 2015. The use of solid-phase fluorescence spectroscopy in the characterization of organic matter transformations. Talanta, 134: 453–459.

ArcGIS, 2015: www.arcgis.com/home/webmap/viewer.html?webmap=55d53aa 0382a425d905 99f4de650cf6c.

ATF, 2015: Animal Task Force – Report and innovation for a sustainable livestock sector in Europe. (http://www.animaltaskforce.eu/Portals/0/ATF/horizon2020/ATF%20white%20paper%20Research%20priorities%20for%20a%20sustainable%20livestock%20sector%20in%20Europe.pdf).

Badeba, W., Kurltun, E., Lemenih, M., Tolera, M. 2014. Long-term addition of compost and NP fertilizer increases crop yield and improves soil quality in experiments on smallholder farms. Agriculture, Ecosystems and Environmt, 195: 193-201.

Baffi, C., Dell'Abate, M.T., Nassisi, A., Silva, S., Benedetti, A., Genevini, P.G., Adani, F., 2007. Determination of biological stability in compost: A comparison of methodologies. Soil Biology and Biochemistry, 39: 1284-1293.

Barrena-Gómez, R., Lima, F.V., Ferrer, A.S. 2006. The use of respiration indices in the composting process: a review. Waste Management and Research, 24: 37–47.

Bernal M.P., Roig A., Madrid R., Navarro A.F. 1992. Salinity risks on calcareous soils following pig slurry applications, Soil Use Manage, 8: 125–130.

Bernal M.P., Roig A., García D. 1993. Nutrient balances in calcareous soils after application of different rates of pig slurry. Soil Use Manage, 9: 9–14.

Bernal, M.P., Alburquerque, J.A., Moral, R. 2009. Composting of animal manures and chemical criteria for compost maturity assessment. A review. Bioresource Technology, 100: 5444-5453.

Bicudo, J.R. 2009. Animal solid manure: Storage, handling and disposal in agricultural mechanization and automation. IN: P. McNulty and P.M. Grace, eds. Encyclopedia of Life Support Systems. EOLSS Publishers, Oxford, U.K.

Bishop, P.L., Godfrey, C. 1983. Nitrogen transformation during sewage composting. Biocycle, 24: 34-39.

BOE, 1996. Real Decreto 261/1996, de 16 de febrero, sobre protección de las aguas contra la contaminación producida por los nitratos procedentes de fuentes agrarias. Boletín Oficial del Estado A- A-1996-5618.

BOE, 2000. Real Decreto 324/2000, de 3 de marzo, por el que se establecen normas básicas de ordenación de las explotaciones porcinas. Boletín Oficial del Estado A-2000-4447.

BOE, 2013. Real Decreto 506/2013, de 28 de junio, sobre productos fertilizantes. Boletín Oficial del Estado 164: 51119-51207.

Brinton, W.F., Evans, E., Droffner, M.L., Brinton, R.B. 1995. A standardized Dewar test for evaluation of compost self-heating. BioCycle, 36: 1-16.

Burton, C.H. 1997. Manure Management – Treatment Strategies for Sustainable AgricultureSilsoe Research Institute, Silsoe, UK.

Burton, H. and Turner, C. 2003. Manure management, treatment strategies for sustainable agriculture (second ed.). Silsoe Research Institute, Lister and Durling Printers, Flitwick, Bedford, United Kingdom.

Butler, T.J., Muir, J.P. 2006. Dairy manure compost improves soil and increases tall wheat grass yield. Agronomy Journal, 98: 1090-1096.

Cambardella, C.A., Richard, T.L., Russel, A. 2003. Compost mineralization in soil as function of composting process conditions. European Journal of Soil Biology, 39: 117-127.

Chang, J.I., Chen, Y.J. 2010 Effects of bulking agents on food waste composting. Bioresource Technology, 101: 5917–5924.

Chefetz, B., P.G. Hatcher, Y. Hadar and Y. Chen, 1996. Chemical and biological characterization of organic matter during composting of municipal solid waste. Journal of Environmental Quallity, 25: 776-785.

Christensen, M.L., Christensen, K.V., Sommer, S.G. 2013. Solid-liquid separation of animal slurry in *Animal manure recycling: treatment and management* (eds. Sommer, S.G., Christensen, M.L., Schmidt, T. and Jensen, L.S.) Wiley publishing, West Sussex, 1-4.

Cogger, C.G. 2005. Potential compost benefits for restoration of soils disturbed by urban development. Compost Science and Utilization, 13: 243-251.

COM (Commission of the European communities), 2007. Report from the commission to the council and the European parliament.

Conte, P., Spaccini, R., Piccolo, A. 2004. Distribution of a C-13-labelled hydrophobic tracer over humic fractions of different size and composition. Fresenius Environmental Bulletin, 13: 238-243.

Cook, R.L. 2004. Coupling NMR to NOM. Analytical and Bioanalytical Chemistry, 378: 1484-1503.

Das, K., Keener, H.M. 1997. Moisture effect on compaction and permeability in composts. Journal of Environmental Engineering, 123: 275-281.

De Ceuster, T., Hoitink. H. 1999. Prospects for composts and biocontrol agents as substitutes for methyl bromide in biological control of plant diseases. Compost Science and Utilization, 7: 6-15.

Delgado, C.L., 2005. Rising demand for meat and milk in developing countries: implications for grasslands-based livestock production M.G. DA (Ed.), Grassland: A global resource, Wageningen Academic Publishers, Wageningen (The Netherlands), pp. 29–39.

Doublet, J., Francou, C., Poitrenaud, M., Houot, S. 2012. Influence of bulking agents on organic matter evolution during sewage sludge composting; consequences on compost organic matter stability and N availability. Bioresource Technology, 102: 1298–1307.

EC (2001). Working document: Biological treatment of biowaste, 2nd draft. European Commission, Directorate General Environment.

Emerson, D. 2015. New technologies capture phosphorus and ammonia. BioCycle 56: 8, 51.

Estévez-Schwarz, I., Seoane, S., Núñez, A., López-Mosquera, M.E. 2012. Production and characterization of a compost made from garden and other types of waste. Polish Journal of Environmental Studies, 21: 43-52.

Europa press: www.europapress.es/murcia/noticia-murcia-tercera-region-espana-produccion-ganado-porcino-20151104092729.html

European Bioplastics, 2015. Anaerobic digestion: Fact sheet. (en.european-bioplastics.org/wp-content/uploads/2011/04/fs/FactSheet_Anaerobic_ Digestion .pdf.)

EUROSTAT (2015). epp.eurostat.ec.europa.eu/statistics_explained/ index.php/ Statistical_themes.

Faucette, L.B. 2004. Environmental benefits and impacts if compost systems and industry standard BMPs used for erosion control in construction activities. Ph.D. Dissertation, Institute of Ecology, University of Georgia.

Faucette, L.B., J. Governo, C.F. Jordan, B.G. Lockaby, H.F. Carino, R. Governo. 2007. Erosion control and stormwater quality from straw with PAM, mulch, and compost blankets of varying particle sizes,‖ Journal of Soil and Water Conservation, 62: 404-413.

Finstein, M.S., Miller, F.C., MacGregor, S.T., Psarianos, K.M. 1985. The Rutgers strategy for composting: process design and control. EPA Project Summary, EPA 600/S2-85/059, Cincinnati, Ohio.

Foged, Lyngsø, H., Flotats, X., Blasi, A.B., Palatsi, J., Magri, A., Schelde, K.M. 2011. Inventory of manure processing activities in Europe. Technical Report No. I concerning “Manure Processing Activities in Europe” to the European Commission, Directorate-General Environment. 138 pp.

Food and Agriculture Organization of the United Nations, FAO (2015). FAOSTAT database. Accessed at (2015) http://faostat.fao.org.

Fukumoto, Y., Osada, T., Hanajima, D., Haga, K. 2003. Patterns and quantities of NH3, N2O and CH4 emissions during swine manure composting witout forced aeration – effect of compost pile scale. Bioresource Technology, 89: 109-114.

Fukumoto, Y., Inubushi, K. 2009. Effect of nitrite accumulation on nitrous oxide emission and total nitrogen loss during swine manure composting. Soil Science Plant Nutrition, 55: 428-434.

Gajalakshmi, S., Abbasi, S.A. 2008. Solid waste management by composting: State of the art. Critical Reviews in Environmental Science Technology, 38: 311-400.

Glanville, T.D., Persyn, R.A., Richard, T.L. 2003. Final Report, Impacts of compost blankets on erosion control, revegetation, and water quality at highway construction sites in Iowa, Ames, Iowa, Iowa State University of Science and Technology.

Graham, J.H. 1998. Composted municipal wastes increase, growth, yield and disease tolerance of citrus, pp189-192. In, Composting in the Southeast, 1998 Conference proceedings September, 1998, 9 - 11. University of Georgia, Athens, Georgia.

Gourc, J., Staub, M.J., Conte, M. 2010. Decoupling MSW settlement into mechanical and biochemical processes – Modelling and validation on large-scale setups. Waste Management, 30: 1556–1568.

Guerrero, C., Gomez, I., Moral, R., Mataix-Solera, J., Mataix-Beneyto, J., Hernandez, T. 2001. Reclamation of a burned forest soil with municipal waste compost, macronutrient dynamic and improved vegetation cover recovery. Bioresource Technology, 76: 221-227.

Herrera, F., Castillo, J.E., Chica, A.F., López Bellido, L. 2008. Use of municipal solid waste compost (MSWC) as a growing medium in the nursery production of tomato plants. Bioresource Technology, 99: 287-296.

Ho, A., Reim, A., Kim, S., Meima-Franke, M., Termorshuizen, A., de Boer, W., van der Putten, W. & Bodelier, P. 2015. Unexpected stimulation of soil methane uptake as emergent property of agricultural soils following bio-based residue application. Global Change Biology. DOI: 10.1111/gcb.12974.

Hsu, J., Lo, S. 2001. Effect of composting on characterization and leaching of copper and manganese, and zinc from swine manure. Environmental Pollution, 114: 119-127.

Huag, R.T. 1993. The Practical Handbook of Compost Engineering. Lewis Publishers, Boca Raton, FL.

Huang, G.F., Wong, J.W.C, Wu, Q.T., Nagar, B.B. 2004. Effect of C/N on composting of pig manure with sawdust. Waste Management, 24: 805–813.

Huang, G.F., Wu, Q.T., Wong, J.W.C., Nagar, B.B. 2006. Transformation of organic matter during co-composting of pig manure with sawdust. Bioresource Technology, 97: 1834-1842.

Imbeah, M, 1998. Composting piggery waste: a review. Bioresource Technology, 63: 197-203.

IPCC, 2006: 2006 IPCC Guidelines for National Greenhouse Gas Inventories – Agriculture, Forestry and Other Land Use. (http://www.ipcc-nggip.iges.or.jp/public/2006gl/vol4.html).

IPCC, 2007. IPCC Fourth Assessment Report: Climate Change 2007. Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge.

JRC, 2014. Technical report for End-of-waste criteria on Biodegradable waste subject to biological treatment (compost & digestate) – Technical proposals, Seville, Spain (doi:10.2791/6295)

Keshav, D. and keener, H.M. 1997. Moisture effect on compaction and permeability in composts. Journal of Environmental Engineering, 123: 275-281.

Kogel-Knabner, I., P.G. Hatcher and W. Zech, 1991. Chemical structured studies of forest soil humic acids: Aromatic carbon fraction. Soil Science Society of America Journal, 55: 241-247.

Lo, K.V., Lau, A.K., Liao, P.H. 1993. Composting of separated solid swine wastes. Journal of Agricultural Engineering Research, 54: 307-317.

Luo, J., Fan, R.Q., Wang, T., Gao, Y., Liu, L.Z., Yan, S.H., Zhang, Z.H. 2015. Evaluation of spent pig litter compost as a peat substitute in soilless growth media. Biological Agriculture and Horticulture. DOI: 10.1080/01448765. 2015.1005669.

MAGRAMA – Estadísticas ganaderas y de calidad y evaluación ambiental del Ministerio de Agricultura, Alimentación y Medio Ambiente. (www.magrama.gob.es) Consulted in December 2015.

MANEV (2012). Evaluation of manure management and treatment technology for environmental protection and sustainable livestock farming in Europe.

Deliverable: A database of pig slurry production in the Region of Murcia. CEBAS-CSIC.

Mari, I., Ehaliotis, C., Kotsou, M., Chatzipavlidis, I., Georgakakis, D. 2005. Use of sulfur to control pH in composts derived from olive processing by-products. Compost Science Utilization, 13: 281-287.

Martínez, J.,Burton, C. 2003. Manure management and treatment: an overview of the European situation. Public communication in the International Conference of Animal Hygiene. Mexico. 12 pp.

Martínez, F., Cuevas, G., Calvo, R., Walter. I. 2003. Biowaste effects on soil and native plants in a semiarid ecosystem. Journal of Environmental Quality, 32: 472-479.

Masse, L., D. I. Masse, V. Beaudette, and M. Muir 2005. Size distribution and composition of particles in raw and anaerobically digested swine manure. Transactions of the Asae. 48:5: 1943-1949.

McCarthy, G., Lawlor, P.G., Coffey, L., Nolan, T., Gutierrez, M., Gardiner, G.E. 2011. An assessment of pathogen removal during composting of the separated solid fraction of pig manure. Bioresource Technology, 102: 9059–9067.

Miller, F.C. 1992. Composting as a process based on the control of ecologically selective factors. In: Metting, F.B. Jr. (Ed.). Soil Microbial Ecology. Applications in Agricultural and Environmental Management. Marcel Dekker, Inc., New York, 515-544.

Moral, R., Pérez-Murcia, M.D., Pérez-Espinosa, A., Moreno-Caselles, J., Paredes, C. 2005. Estimation of nutrient values of pig slurries in Southeast Spain easily determined properties. Waste Management, 25: 719-725.

Moreno, J.L., Garcia, C., Hernandez, T., Pascual J.A. 1996. Transference of heavy metals from a calcareous soil amended with sewage-sludge compost to barley plants. Bioresource Technology, 55: 251-258.

Moreno, J. and Moral, R. (eds). COMPOSTAJE. Ediciones MUNDI-PRENSA (Madrid, Barcelona, México), pp: 243-283. ISBN: 978-84-8476-346-8.

Pardo, G, Moral, R., Aguilera, E, del Prado, A. 2015. Gaseous emissions from management of solid waste: systematic review. Global Change Biology, 21: 1313-1327.

Parkes, M.E., Campbell, J., Vinten, A.J.A. 1997. Practice to avoid contamination in drainflow and runoff from slurry spreading in spring. Soil Use Management, 13: 36-42.

Pengcheng, G., Xinbao, T., Yana, T., Yingxu, C. 2008. Application of sewage sludge compost on highway embankments. Waste Management, 28: 1630-1636

Prasad, R., Huchmuth, G., Wilkie, A.C. 2014. Anaerobic Digesters for Manure Management at Livestock Operations. (http://edis.ifas.ufl.edu/ss615).

Qiu, S., McComb, A.J., Bell, R.W., Davis, J.A. 2003. Response of soil microbial activity to temperature, moisture, and litter leaching on a wetland transect during seasonal refilling. Wetland Ecology Management, 13: 43–54.

Rangus, M. 2007. NMR spectroscopy in solids: A comparison to NMR spectroscopy in liquids. Seminar.

Riaño, B., García-Gonzáles, M.C. 2014. On-farm treatment of swine manure based on solid-liquid separation and biological nitrification-denitrification of the liquid fraction. Journal of Environmental management, 132: 87-93.

Richard, T. L., Veeken, A. H. M., de Wilde, V. and Hamelers, H. V. M. 2004. Air-Filled Porosity and Permeability Relationships during Solid-State Fermentation, 20: 1372-1381.

Rynk, R. (editor) 1992. On-Farm Composting Handbook. NRAS-54. Northeast Regional Agricultural Engineering Service. 152 Riley-Robb Hall, Cooperative Extension, Ithaca, NY. 14853-5701

Sánchez, M., González, J.L. 2005. The fertilizer value of pig slurry. I. Values depending on the type of operation. Bioresource Technology, 96: 1117-1123.

Sánchez, A., Artola, A., Font, X., Gea, T., Barrena, R., Gabriel, D., Sánchez-Monedero, M.A., Roig, A. Cayuela, M.L., Mondini, C. 2015. Greenhouse gas emissions from organic waste composting: Emissions and measurement. E. Lichtfouse et al. (eds.), CO_2 Sequestration, Biofuels and Depollution, Environmental Chemistry for a Sustainable World 5, DOI 10.1007/978-3-319-11906-9_2.

Sánchez, A, Gabarell, X., Artola, A., Barrena, R., Colón, J., Font, X., Komilis, D. 2015. Resource Recovery to Approach Zero Municipal Waste.

Taherzadeh, M., Richards, T. (eds.): chapter 5; CRC press., ISBN: 978-1-4822-4036-8.

Sánchez-Monedero, M.A., Roig, A., Cegarra, J., Bernal, M.P., Noguera, P., Abad, M. 2004. Composts as media constituents for vegetable transplant production. Compost Science and Utilization, 12: 161-168.

Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M. 2007. Climate Change 2007: The physical science basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L., editors. Cambridge, United Kingdom and New York, NY, USA: Cambridge University Press pp. 996.

Sommer, S.G. 2013. Animal manure – From waste to raw materials and goods in *Animal manure recycling: treatment and management* (eds. Sommer, S.G., Christensen, M.L., Schmidt, T. and Jensen, L.S.) Wiley publishing, West Sussex, 1-4.

Sommer, S.G., Christensen, M.L. 2013. Animal production and animal manure management in *Animal manure recycling: treatment and management* (eds. Sommer, S.G., Christensen, M.L., Schmidt, T. and Jensen, L.S.) Wiley publishing, West Sussex, 5-23.

Sorensen, C.A., Jacobsen, B.H., Sommer, S.G. 2003. An assessment tool applied to manure management systems using innovative technologies. Biosystems Engineering, 86: 315-325.

Sorensen, P, Jensen, L.S. 2013. Nutrient leaching and runoff from land application of animal manure and measures for reduction in *Animal manure recycling: treatment and management* (eds. Sommer, S.G., Christensen, M.L., Schmidt, T. and Jensen, L.S.) Wiley publishing, West Sussex, 5-23.

Spiers, T.M., Fietje, G. 2000. Green waste compost as a component in soilless growing media. Compost Science and Utilization, 8 : 19–23.

Steinfeld, H., Mäki-Hokkonen, J. 1995. A classification of livestock production systems. World Animal Review 84/85, pp. 83-94

Steinfeld H, Gerber P, Wassenaar T, Castel V, Rosales M, de Haan C. 2006. Livestock's Long Shadow: Environmental Issues and

Options. Rome: Food and Agriculture Organization of the United Nations. http://www.fao.org/ docrep/010/a0701e/a0701e00.HTM.

Steinfeld, H., Mooney, H.A., Schneider, F., Neville, L.E. 2010. Livestock in a Changing Landscape. Drivers, Consequences, and Responses. Volume 1. Washington D.C., USA: Island Press. pp. 396.

Szanto, G.L., Hamelers, H.V.M., Rulkens, W.H., Veeken, A.H.M. 2006. NH_3, N_2O and CH_4 emissions during passively aerated composting of straw-rich pig manure. Bioresource Technology, 98: 2659–2670.

Thermo Nicolet Corporation. 2001. Introduction to Fourier transform induced spectroscopy. (http://mmrc.caltech.edu/FTIR/FTIRintro.pdf).

Thornton, P.K., 2010. Thornton Livestock production: recent trends, future prospects Philosophical Transactions of the Royal Society B, 365: 2853–2867.

Timmerman, M., Schuman, E., van Eekert, M., van Rien, J. 2015. Optimizating the performance of a reactor by reducing the retention time and addition of glycerin for anaerobically digesting manure. Environmental Technology, 36: 1223-1236.

Tiquia, S.M., Tam, N.F.Y. 1998. Elimination of phytotoxicity during co-composting of spent pig-manure sawdust litter and pig sludge. Bioresource Technology, 65: 43-49.

Torres-Climent, A., Gomis, P., Martín-Mata, J., Bustamante, M.A., Marhuenda-Egea, F.C., Pérez-Murcia, M.D., Pérez-Espinosa, A., Paredes, C., Moral R. 2015. Chemical, Thermal and Spectroscopic Methods to Assess Biodegradation of Winery-Distillery Wastes during Composting. Public Library of Science 10(9): e0138925. doi:10.1371/journal.pone.0138925.

Trémier, A., Teglia, C., Barrington, S. 2009. Effect of initial physical characteristics on sludge compost performance. Bioresource Technology, 100: 3751–3758.

Van Ginkel, J.T. Raats, P.A.C., Van Haneghem, I.A. 1999. Bulk density and porosity distributions in a compost pile. Netherlands Journal of Agricultural Science, 47, 105-121.

Van Lier, J.J.C., Van Ginkel, J.T., Straatsma, G., Gerrits, J.P.G., Van Griensven, L.J.L.D. 1994. Composting of mushroom substrate in a fermentation tunnel: compost parameters and a mathematical model. Netherlands Journal of Agricultural Science, 42: 271–292.

Vanotti, M., Millner, P., Szogi, A., Campbell, C., Fetterman, L. 2006. Aerobic Composting of Swine Manure Solids Mixed with Cotton Gin Waste. Paper number 064061 2006 ASAE Annual Meeting. (doi: 10.13031/2013.21112).

Vanotti, M., Szogi, A., Vives, C. 2008. Greenhouse gas emission reduction and environmental quality improvement from implementation of aerobic waste treatment systems in swine farms. Waste Management, 28: 759–766.

Wall, D.K., Zeiss, C. 1995. Municipal landfill biodegradation and settlement. Journal of Environmental Engineering, 121: 214–223.

Yagüe, M.R., Bosch-Serra, A.D., Boixadera, J. 2012. Measurement and estimation of the fertilizer value of pig slurry by physicochemical models: Usefulness and constraints. Biosystems Engineering, 3: 206-216.

Yue, B., Chen, T., Gao, D., Zheng, G., Liu, B., Lee, D. 2008. Pile settlement and volume reduction measurement during forced-aeration static composting. Bioresource Technology, 99: 7450–7457.

Zhu, N., Deng, C., Xiong, Y., Qian, H. 2004. Performance characteristics of three aeration systems in the swine manure composting. Bioresource Technology, 95: 319–326.

Zibilske, L.M. 1998. Composting organic wastes,‖ In: Principles and applications of soil microbiology. D.M. Sylvia, Fuhrman, J.J., Hartel, P.G., Zuberer D.A. (eds.) Prentice Hall. Inc. Upper Saddle River, New Jersey, pp 482-497.

Zucconi, F., de Bertoldi, M., 1987. Compost specifications for the production and characterization of compost from municipal solid waste. In: de Bertoldi, M., Ferranti, M.P., L'Hermite, P., Zucconi, F. (Eds.), Compost: Production, Quality and Use. Elsevier, Barking, pp. 30–50.

2. Objectives

The study of key waste fluxes, its management and the optimization of the overall waste chains are one of the most important goals for achieve circular and green economy targets in the UE in terms of agronomic and environmental issues. In this line, manure waste management chain is maybe the most important issue to take into account, in order to minimise the huge amounts of livestock wastes generated on farms.

In the Mediterranean countries, the pig farms constitute a key area in the livestock production sector in terms of slurries production, due to the intensification of the production systems and the great number of animals. The nature of pig slurries, liquid and/or solid fraction, needs an accurate management due to nitrate leaching, gaseous emissions, odours, volume for storage and transportation and moisture content. Development of added value products derived from waste management of animal manures and especially recovery of nutrients and organic matter for soils through the preparation of biofertiliser products, and compost is a very promising line to produce win-win strategies by reduction of GHG emissions and synthetic fertiliser's inputs to the soil and increase the C sequestration in the amended soils and avoid other environmental problems.

The objectives of this thesis are the development of the most optimal methods to produce high quality biofertilisers by co-composting the pig slurry with plant residues, as bulking agents, optimising, in quality, the composting conditions and finally assess the biofertilising capacities in agronomic conditions. This objective is quite complex due to the multiple scenarios to be demonstrated or validated, and for this reason we stablish several specific objectives to contribute to a deeper acknowledge, listed below:

- Assess the biodegradability of the solid fraction of pig slurry for composting and the influence of the bulking agent on degradation and the CO_2 emissions.
- Assess the production of fertiliser products by composting of solid fraction of pig slurry in a real scale scenario and the CO_2, N_xO, CH_4 and NH_3 emissions during the process.
- Validate new instrumental technics (thermogravimetric analysis, FT-IR spectroscopy and CP-MAS 13C-NMR spectroscopy) as useful

tools in the structural knowledge of organic matter transformations during the composting process by comparing the efficiency front of the traditional analytic technics.

- Assess the nutrient values of the compost produced and define the adequate use of the compost. Identification of the C-conservation in the soil by the use of compost and the N-dynamics in agricultural soils.

In order to achieve the previous objectives, the research activities proposed were divided in four major tasks (Figure 19):

Prior the beginning of experiment 1, the input materials selected were fully characterised for chemical and physico-chemical properties.

Experiment 1 was sub-divided in 3 tasks including biodegradability and calibration tests, as well a small scale composting to understand the nature, composition and significant residual fluxes of the input materials to compost the solid fraction of pig slurry and assess the best materials for composting in experiment 2.

- Task 1.1 To assess the biodegradability of the solid fraction of pig slurry mixed with four different bulking agents (maize stalks, cotton gin waste, garden pruning and barley straw) in the laboratory by determining the CO_2 emission;
- Task 1.2 To identify the best combination solid fraction of pig slurry and bulking agent for composting using laboratory self-heating experiments in 5L reactors;

Experiment 2 consists on a pilot scale composting experiment upscaling experiment 1, where the best mixture of solid fraction of pig slurry and bulking agent were tested in a pilot scale composting using static pile system. The aim is to understand the dynamic, stability and degree of degradation of organic matter during the composting process, as well, compare the differences between the laboratory scale composting and the real scale composting.

- Task 2.1 The evolution of the temperature and chemical and physico-chemical properties of the piles were assessed during the composting process;
- Task 2.2 Assessment of the quality of the composts produced and environmental implications in terms of gaseous emissions during the thermophilic phase of the composting process.

Experiment 3 A transversal activity, where the advanced instrumental techniques, such as thermal analysis, CP-MAS and FT-IR spectroscopy were used to study the organic matter changes during several stages of the co-composting of the solid fraction of pig slurry with cotton gin waste in different scenarios, proportions of raw materials and composting systems applied.

Experiment 4 To assess the agronomic value of the composts and the nitrate leaching risk.

- Task 4.1 The nutrient availability of the compost produced in experiment 3 were tested in an agronomic pot experiment under glasshouse conditions. Nutrient efficiency of compost according to the bulking agent and application rate was evaluated, together with the potential risk of NO_3^--N leaching. This task was realised as a secondment in the University of Lisbon, Instituto Superior de Agronomía, in the Environmental Chemistry Research Unit.
- Task 4.2 The availability of N from compost and implication of compost application in the soil C was assessed by preforming two parallel incubations of soil amended with compost and the original waste materials (composts, cotton gin waste and SPS) using in one of them, ^{15}N to identify the amount of N in each pool. Evolution of inorganic N of the amended soils and C mineralisation by CO2 emissions were studied. This task was realised at the Faculty of Science at University of Copenhagen, as a secondment, in the Department of Plant and Environmental Sciences.

The results obtained in the experiments are reflected in the five publications mentioned below:

CARBON CONSERVATION STRATEGY FOR THE MANAGEMENT OF PIG SLURRY COMPOSTING: INITIAL STUDY OF THE BULKING AGENT INFLUENCE.

Estrategias de manejo para la conservación del carbono durante el compostaje del purín de cerdo: Estudio inicial de la influencia de los agentes estructurantes.

André Santos, Mª Ángeles Bustamante, Raul Moral, Mª Pilar Bernal.

***Mitigation and Adaptation Strategies for Global Change*, DOI 10.1007/s11027-014-9593-0**

GASEOUS EMISSIONS AND PROCESS DEVELOPMENT DURING COMPOSTING OF PIG SLURRY: INFLUENCE OF THE PROPORTION OF COTTON GIN WASTE.

Emisiones gaseosas y desarrollo del proceso durante el compostaje del purín de cerdo: Influencia de la proporción de desmotado de algodón.

André Santos, Mª Ángeles Bustamante, Germán Tortosa, Raul Moral, Mª Pilar Bernal.

Journal of Cleaner Production*,* DOI:10.1016/j.jclepro.2015.08.084

SUSTAINABLE MANAGEMENT OF PIG SLURRY USING DIFFERENT COMPOSTING SCENARIOS: ASSESSMENT OF THE ORGANIC MATTER CHANGES.

Manejo sostenible del purín de cerdo mediante diferentes escenarios de compostaje: Evaluación de los cambios en la materia orgánica.

Julio Martín-Mata, Carolina Lahoz-Ramos, Mª Ángeles Bustamante, Frutos Carlos Marhuenda-Egea, Raul Moral, André Santos, José António Sáez, Mª Pilar Bernal

Environmental Science and Pollution Research (*under review*)

AGRICULTURAL EFFICIENCY OF THE NUTRIENTS FROM PIG SLURRY COMPOST AND NITRATE LEACHING RISKS

Eficiencia agronómica de los nutrientes del compost de purín de cerdo y riesgos de lixiviación de nitratos.

André Santos, David Fangueiro, Raul Moral, Mª Pilar Bernal.

Biology and Fertility of Soils, 2016 (*under review*)

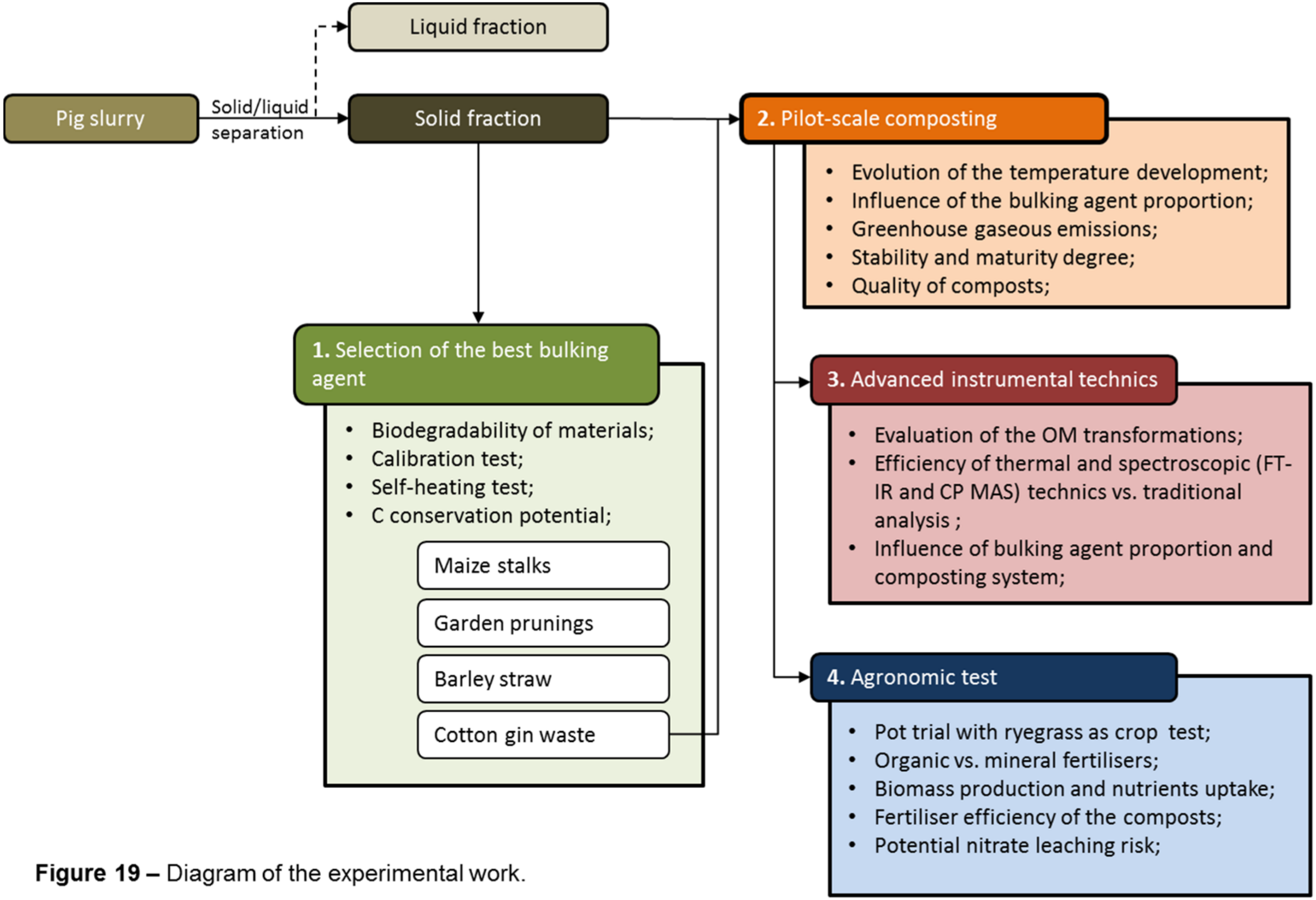

Figure 19 – Diagram of the experimental work.

3. Experimental part

3.1 Carbon conservation strategy for the management of pig slurry by composting: Initial study of the bulking agent influence.

Communication in Mitigation and Adaptation Strategies for Global Change.
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ORIGINAL ARTICLE

Carbon conservation strategy for the management of pig slurry by composting: Initial study of the bulking agent influence

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Abstract The intensification of the livestock production systems implies a potential environmental risk, associated with the great generation of animal wastes and slurries and their storage and management. Manure management is associated with considerable emissions of ammonia (NH_3) and greenhouse gases (GHG). However, the potential for GHG mitigation is highly dependent on the waste treatment strategy considered. This laboratory study aims to evaluate the influence of the type of bulking agent used on the potential reduction of the carbon dioxide (CO_2) emission, dealing with carbon (C) conservation when the solid fraction of pig (*Sus scrofa domesticus*) slurry is managed by composting. For this, a composting experiment in batch reactors was run with four mixtures elaborated using the solid fraction of pig slurry (SPS) and different materials (maize (*Zea mays*) stalks, barley (*Hordeum vulgare* L.) straw, cotton (*Gossypium hirsutum*) gin and garden prunings) as bulking agents. The potential C conservation in the mixtures was evaluated by determining the CO_2 emissions; the evolution of the mixtures, the thermal profile developed and the thermodynamics of the process were also studied. The mixtures elaborated with cotton gin and garden prunings showed the fastest temperature development, and also the highest CO_2 emissions. However, the use of maize stalks as bulking agent reduced CO_2 emissions due to its slow degradability: this could constitute a suitable strategy to promote C conservation during the management of pig slurry by composting.

Keywords C conservation · Cereal straw · Cotton gin · Degradability · Garden prunings · Maize stalks · Manure management

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1 Introduction

Agriculture constitutes one of the main sources of greenhouse gases (GHGs), representing about 13.5 % of worldwide (IPCC 2007) anthropogenic emissions; livestock production contributes 8 to 18 % (depending on the estimation method used) of global GHG emissions (O'Mara 2011). In this sense, the European Union of 27 Member States (EU-27), which maintains one of the greatest livestock densities in the world, has an impact on global warming with about 10 % of total GHG emissions (Lesschen et al. 2011). Pigs (*Sus scrofa domesticus*), together with cattle (*Bos primigenius taurus*) and poultry (*Gallus gallus domesticus*), constitute the dominant world livestock. The EU-27 produced 22 % of the world's pork in 2008 (FAO 2008). According to Lesschen et al. (2011), pigs had a contribution to GHG emission in the EU-27 during the period 2003–2005 of 3.5 kg of carbon dioxide (CO_2) equivalent (eq.) per kilogram of product, a value only exceeded by the GHG emission associated with beef production, and this represents 16 % of GHG emissions in the EU-27. In Spain, 51 % of the GHG emissions associated with animal manures came from pig rearing (FAO 2010).

There is a large potential for reducing the ammonia (NH_3) and GHG emissions from manure management, between 25 and 80 %, the mitigation strategies being mainly based on appropriate management and treatment (Cole et al. 1997; VanderZaag et al. 2013). Manure storage and/or land application constitute one of the most usual practices to manage animal wastes; however, these practices also imply an important contribution to global GHG emission. Manure emits methane (CH_4) and CO_2 during storage, depending on the aeration conditions, and contributes to nitrous oxide (N_2O) and CO_2 emissions after soil application (Bertora et al. 2008).

However, there are different slurry treatments that may improve the agricultural value and reduce the environmental impact of pig slurry, representing an opportunity for GHG mitigation and promotion of carbon (C) sequestration (Duchateau and Vidal 2003). Composting could be considered a feasible method to manage animal waste, such as pig slurry, and reduce GHG emissions, even considering the emissions associated due to the characteristics of the composting process, principally due to its potential for C sequestration. Brown et al. (2008) reported the impact of composting of animal manures (among a wide range of feedstocks) on GHG emissions, concluding that even in a worst-case scenario, the emissions during composting are minimal compared to the benefits associated with the reduction of CH_4 emissions when manure is stored under anaerobic conditions. Also, Vanotti et al. (2008) reported a reduction of 99 % of CH_4 emissions and of 75 % of N_2O emissions with the separation of swine slurry into solid and liquid portions and later treatment of the solids by aerated composting. The application of pig slurry to soil implies the incorporation of easily degradable organic C that can both sustain denitrification and induce anaerobic conditions by stimulating biological oxygen (O_2) demand, promoting increases in N_2O and nitric oxide (NO) emissions from soil following application (Vallejo et al. 2006). Kariyapperuma et al. (2012) observed a 57 % decrease in soil N_2O emissions with composted compared to liquid pig manure. However, the conclusions regarding the mitigation potential or impact of composting compared to other slurry treatment scenarios seem to be contradictory (Lopez-Ridaura et al. 2009; Macías and Camps 2010; Hoeve et al. 2014). This could be due to the lack of available data for the assessment of the CO_2 emission potential during composting and to the use of different strategies to promote C conservation within the composting process. Therefore, the aim of this laboratory study was to evaluate the influence of the type of bulking agent used on the reduction of the CO_2 emissions, and thus on the promotion of C conservation, during pig slurry management by composting.

2 Materials and methods

2.1 Experimental procedure

Four mixtures (M1, M2, M3 and M4) were prepared using the solid fraction of pig slurry (SPS) with different bulking agents: maize (*Zea mays*) stalks (MS), barley (*Hordeum vulgare* L.) straw (BS), cotton (*Gossypium hirsutum*) gin waste (CW), garden pruning wastes (mixture 1:1 of white mulberry (*Morus alba*) and jacaranda (*Jacaranda mimisifolia*)) (PW). The SPS was collected from a sows and piglets farm in Guazamara (Almería, Spain), after a solid–liquid separation using a screw-press. The MS and BS came from the same farm as the SPS, the CW was collected from the cotton industry in Seville (Spain) and the mixture of garden pruning wastes came from a company responsible for public gardens maintenance in Murcia (Spain).

Prior to its use in the mixtures, the SPS was homogenised. The bulking agents were also crushed to 5 cm particle size, except CW (that was only homogenised) and the garden pruning wastes, which were crushed by a mechanical mill to 5 mm particle size, and mixed in the proportion 1:1. The main physico-chemical and chemical characteristics of the raw materials used in the experiment are shown in Table 1. The proportions of the mixtures, on a fresh weight basis, were the following:

$$\begin{aligned} &M1 : 83\%SPS + 17\%CW \\ &M2 : 92\%SPS + 8\%MS \\ &M3 : 94\%SPS + 6\%BS \\ &M4 : 87\%SPS + 13\%PW \end{aligned}$$

The proportions of the mixtures were adjusted in order to use the maximum amount of SPS, but also considering an initial carbon to nitrogen (C/N) ratio of 20–25 and a moisture content of 55–80 %, adequate for composting (Bernal et al. 2009). Then, the SPS was thoroughly mixed with the corresponding bulking agent, using a mixer, and the mixtures obtained were placed in the respective batch reactors of 5 L (in duplicate for each mixture). The batch reactors consist of thermal insulated cylinders with 14 cm inner-diameter and 40 cm height. Laboratory temperature probes connected to a data logger were placed in the centre, inside the reactors,

Table 1 Physico-chemical and chemical characteristics of the raw materials used

–	SPS	CW	MS	BS	PW
Moisture (%)	76.5	13.9	8.83	9.52	53.8
DM (%)	23.5	86.1	85.8	92.1	46.2
pH	7.35	6.97	6.31	7.47	6.50
EC (dS m^{-1})	1.26	7.15	4.81	3.89	3.40
OM (%)	69.4	87.9	91.7	93.1	92.7
TOC (g kg^{-1})	335	411	462	471	462
C_w (g kg^{-1})	7.7	nd	nd	nd	nd
TN (g kg^{-1})	19.0	5.1	7.4	7.8	12.6
NH_4^+-N (mg kg^{-1})	11895	nd	nd	nd	nd
C/N	17.7	81.2	62.4	60.4	36.9

SPS, solid phase of pig slurry; *CW*, cotton gin waste; *MS*, maize stalk; *BS*, barley straw; *PW*, mixture of garden pruning waste (mixture 1:1 of mulberry and jacaranda)

DM, dry matter; *EC*, electrical conductivity; *OM*, organic matter; *TOC*, total organic carbon; C_w, water-soluble carbon; *TN*, total nitrogen; *nd*: not determined and temperature was registered automatically. The external temperature was also registered. The initial weight, height and density of the different mixtures inside the batch reactors are shown in Table 2. Only the mixtures elaborated with PW and MS were turned at day 7, when the temperature of these mixtures dropped to values close to ambient values, to improve the homogeneity and porosity of the mixtures. The turning was carried out by emptying completely the batch-reactor, thoroughly mixing the inner fraction of each mixture with the outer fractions and placing the new mixture inside the corresponding batch-reactor. The experiment was considered finished when the temperature of the mixtures was close to the ambient and re-heating did not occur, lasting approximately 15 days.

Composite representative samples were taken at the beginning and end of each batch experiment. Each representative sample was divided into three fractions in the laboratory: one of them was dried in a drying-oven at 105ºC for 24 h to determine the moisture content, the second was immediately frozen (−18ºC) and kept for the determination of ammonium nitrogen (NH_4^+-N) and the third was freeze-dried and ground to less than 0.5 mm for the rest of the analytical determinations.

The energy produced by microorganisms (q), responsible for the temperature heating in the reactors, was calculated considering the specific heat capacity of the samples (Cp_s) according to Sundberg (2005). For that, the increase in temperature of water after immersing a bag of sample was determined, considering that:

$$q_s = m_s.Cp_s.(100-T_f) \tag{1}$$

$$q_{water} = m_w.Cp_w.(T_i-T_f) \tag{2}$$

where $\mathbf{m_s}$ and $\mathbf{m_w}$, are the mass of sample and water in grammes (g), respectively, and $\mathbf{Cp_s}$ and $\mathbf{Cp_w}$ are the specific heat capacity of the sample and water (4.184 J g^{-1} ºC^{-1}), respectively; T_i is the temperature of water at room temperature and T_f the final temperature after immersing the heated bag of compost, being $T_f > T_i$. The energy gained from the water will be equal to the energy lost from the compost:

$$q_s = q_{water} \tag{3}$$

Then, the $\mathbf{Cp_s}$ of sample can be calculated. The energy produced by the microbial activity during the experiment was calculated as:

$$q(J) = m_c.Cp_s.\Sigma\Delta T \tag{4}$$

$\mathbf{m_c}$ being the mass (dry weight) of the mixture in the reactor and $\mathbf{\Sigma\Delta T}$ the accumulated increase of temperature, from the difference between the ambient temperature and the internal temperature of the mixture.

Table 2 Physical characteristics of the mixtures inside the batch reactors

–	M1	M2	M3	M4
Weight (kg f.w.)	2.3	3.0	2.3	3.0
Height (m)	0.31	0.30	0.31	0.31
Density (kg m^{-3})	479	652	479	625

M1: 83 % solid fraction of pig slurry+17 % cotton gin waste; M2: 92 % solid fraction of pig slurry+8 % maize stalk; M3: 94 % solid fraction of pig slurry+6 % barley straw; M4: 87 % solid fraction of pig slurry+13 % garden pruning waste (mixture 1:1 mulberry:jacaranda). *f.w.*, fresh weight

2.2 Analytical methods

The potential C conservation at the beginning and end of the experiment was evaluated by measuring the CO_2 emissions in the different mixtures at the beginning and end of the batch reactor experiment. Briefly, 5-g aliquots of the mixtures were incubated in the dark for 10 days at 26°C in hermetic 500-mL glass vessels, trapping the CO_2 evolved with 10 mL of 0.5 mol L^{-1} sodium hydroxide (NaOH) in small tubes placed inside the hermetic vessels. Empty vessels were used as blanks. The small tubes were changed every 2–3 days and the amount of CO_2 evolved was quantified by titrating the unreacted NaOH with 0.5 mol L^{-1} hydrochloric acid (HCl), after precipitation of the carbonates formed with an excess of barium chloride ($BaCl_2$). Each sample and blank was replicated three times.

In the freeze-dried samples, electrical conductivity and pH were determined in a water-soluble extract 1:10 (weight/volume (w/v)); organic matter (OM) was assessed by loss-on ignition at 550 °C for 24 h. Total organic carbon (TOC) and total nitrogen (TN) were determined by automatic microanalysis (EuroVector EuroEA 3000 elemental analyser), according to the method described by Navarro et al. (1991). Water-soluble organic carbon (C_w) was determined in a water extract of 1:10 (w/v), after filtration through a synthetic filter with a pore diameter of 0.45 μm, by using an automatic analyser for liquid samples (TOC-V CSN Analyser, Shimadzu). Ammonium-N was extracted from the frozen samples with 2 mol L^{-1} potassium chloride (KCl) (1:20, w/v) and determined by a colorimetric method based on Berthelot's reaction (Sommer et al. 1992).

2.3 Statistical analysis

The one-way analysis of variance (ANOVA) test was used to assess the significant differences among the values of each parameter studied during composting, while the Tukey test at significance $(P)<0.05$ was used to test the statistically significant differences in the parameters studied among the mixtures at the beginning and end of the experiment. Normality and homogeneity of the variances were checked using the Kolmogorov-Smirnov and Levene test, respectively, before ANOVA. The standard error of the mean values was also determined. Also, Pearson's correlation coefficient was obtained between the energy released, C_w concentration and carbon from carbon dioxide (CO_2-C) emissions for all the mixtures and both samplings (number of samples $(n)=8$). Data analysis was carried out using the SPSS v.19.0 statistical software package.

3 Results and discussion

3.1 Characteristics of the raw materials

The solid fraction of pig slurry was rich in OM and TOC, with 7.7 g kg^{-1} of water-soluble C (2.3 % of TOC), showing a low C/N ratio (Table 1) due to the high concentration of TN, mainly as NH_4^+-N (11.9 g kg^{-1}; 62.6 % of TN). Also, the SPS had a high moisture content (76.5 %), which, together with the high TN proportion as NH_4^+-N, could complicate its management by composting without a bulking agent.

All the bulking materials used were characterised by high organic matter concentrations (Table 1), with values ranging between 87.9 and 93.1 %, high concentrations of TOC and thus high C/N ratios (36.9 - 81.2). These values were similar to those found by other authors in similar bulking materials and agricultural wastes such as vine shoot prunings and cereal straw (Paredes et al. 1996; Bustamante et al. 2013). The PW showed the highest TN concentration, and therefore the lowest C/N ratio.

These materials showed suitable characteristics, especially the high C/N ratio, for the co-composting of nitrogen (N) rich wastes such as pig slurry, and improve the retention of the excess of moisture and provide structural support. Also, they are lignocellulosic materials; then, their C source will be slowly consumed by microorganisms, maintaining the C/N ratio and preventing N-losses (Doublet et al. 2012; Paredes et al. 1996). Other authors have reported the suitability of these materials as bulking agents for the co-composting of the solid fraction of pig slurry, such as cereal straw (Szanto et al. 2007; Mc Carthy et al. 2011), sawdust (Fukumoto and Inubushi 2009; Mc Carthy et al. 2011), cotton gin (Paredes et al. 1996; Vanotti et al. 2006) and garden prunings (Estevez-Schwarz et al. 2012).

3.2 Thermal profile of the mixtures

Analysing the thermal profile of the mixtures during the batch experiment (Fig. 1), it can be observed that the mixture elaborated with CW (M1) led to the highest temperatures and a quick temperature development in the first day, increasing 12 ºC with respect to the external values, in comparison with the 8, 7 and 3 ºC increases for the mixtures M4. M3 and M2, with pruning waste, barley and maize, respectively. This indicates higher microbial activity in the M1 mixture. All the mixtures were able to maintain the rise in temperature for at least 3–4 days, before it started to decrease. At day 7, only the mixtures M4 and M2, with garden pruning and maize stalks, were turned as the temperature dropped to values close to the external values, to improve the homogeneity and the aeration of the mixtures. After this, although re-heating occurred, the temperature increased very little in both mixtures, showing a small second peak of temperature, which indicated that the material was still biologically active. Georgacakis et al. (1996) also found that mixtures of the solid fraction of pig slurry with cotton gin reached higher temperatures during composting (45–55 ºC) than mixtures prepared with cereal straw (40–45 ºC) or with peat (30–35 ºC).

After the quick increase of temperature during the first 2 days, a constant temperature profile was observed in the mixture M3, maintaining≈4 ºC above the external values at the end of the experiment, while in the mixture M4, the temperature decreased quickly after 6 days. Such different behaviour of the mixtures does not seem to be related to the bulk density (Table 2), but it may be related to the degradability of the chemical compounds present in the bulking agents.

The energy produced by the microorganisms was calculated using the differences in temperature between the internal reactor and the external values (equation 4). The accumulative energy production showed a smooth initial curve for the mixture M2, with maize stalks (Fig. 2), indicating slower degradation of the material compared with the other materials studied. The mixture with cotton gin showed a quick energy production for the first day of experiment, indicating fast microbial activity. Also, the mixtures with cotton gin and garden prunings presented the highest energy production in the first 24 h of the experiment, reaching a production of 157 kJ and 111 kJ, while those with barley straw and maize stalks produced only 65 kJ and 36 kJ, respectively. A reduction in the size of the maize particles could increase the breakdown surface and, therefore, may speed-up the degradation. After 10 days, the energy produced by the mixtures increased in the order (kJ): M2 (96)<M4 (166)<M3 (296)<M1 (398).

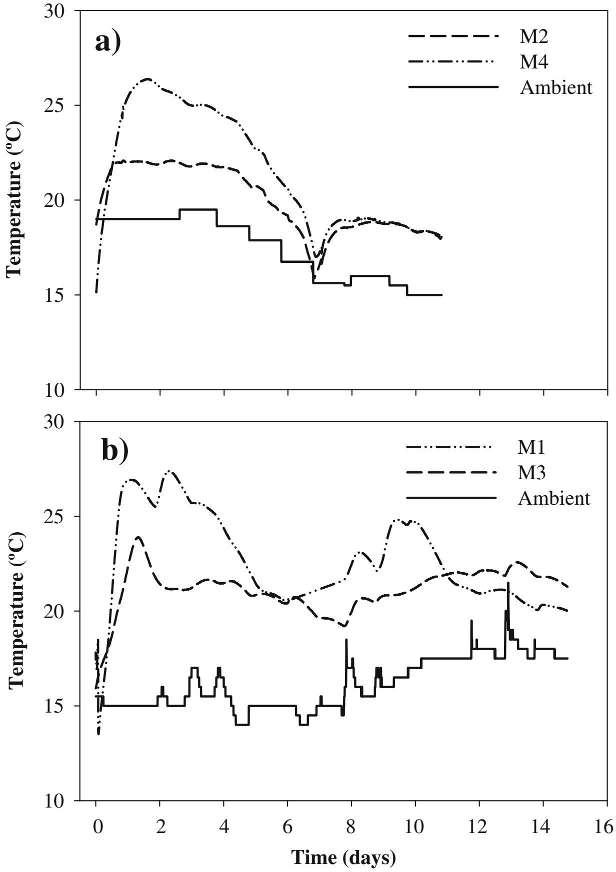

Fig. 1 Thermal profile of the mixtures during the experiment: **a** M2: solid fraction of pig slurry+maize stalk and M4: solid fraction of pig slurry+garden pruning waste (mixture 1:1 mulberry:jacaranda); **b** M1: solid fraction of pig slurry+cotton gin waste and M3: solid fraction of pig slurry+barley straw

3.3 Evolution of the mixtures

Regarding the initial characteristics of the mixtures, the moisture contents ranged between 65.1 and 69.8 % (Table 3), within an acceptable range for good development of the composting process (Bernal et al. 2009). Despite the high water content of SPS (76.5 %), the incorporation of the bulking agents adjusted the values of the mixtures to a range more suitable for composting, in order to avoid excess humidity and leaching during the process (Liao et al. 1993). Throughout the experiment, the moisture content of the mixtures did not change significantly in any of the samples (Table 3).

The initial pH values in the mixtures were within the range 6 – 8, suggested as suitable for composting (Bernal et al. 2009), and, in general, lower than 7.5, which reduces the potential emission of ammonia in conditions of high temperatures, therefore, favouring mitigation by composting. At the end of the process, all the mixtures also had final pH values within this range. The electrical conductivity values were higher than 4 dS m^{-1} in all the mixtures at the beginning of the experiment, showing an increase at the end of the process derived from OM degradation, due to the production of inorganic compounds (Bustamante et al. 2008).

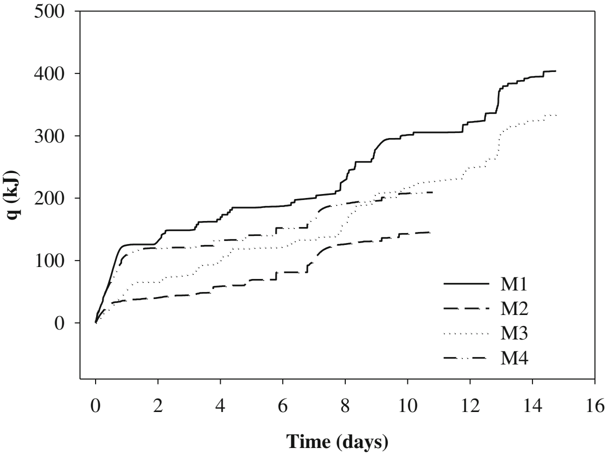

Fig. 2 Accumulated energy (q) produced by the microbial activity in the different mixtures throughout the experiment. M1: solid fraction of pig slurry+cotton gin waste; M2: solid fraction of pig slurry+maize stalk; M3: solid fraction of pig slurry+barley straw; M4: solid fraction of pig slurry+garden pruning waste (mixture 1:1 mulberry:jacaranda)

In relation to the OM concentrations, the initial values ranged between 72.5 %, for M2 (elaborated with MS) and 77.7 %, for M1 (prepared using CW). Also, M1 showed the highest decrease in the OM concentrations at the end of the experiment, and the same occurred for the concentrations of water-soluble C, coinciding with the fastest development and the highest values of the temperature observed in this mixture. Paredes et al. (1996) also found greater OM degradation during composting of olive-mill wastewater sludge when cotton gin was used as a bulking agent, compared to the use of maize straw.

The concentrations of C_w varied widely in the initial mixtures, from 22 g kg^{-1}, for M4 (with PW), to 8.6 g kg^{-1} in M3 (with BS). Throughout the experiment, the concentration of C_w decreased practically in all the mixtures, indicating the degradation of simple, water-soluble organic compounds, such as sugars, amino acids and peptides. This behaviour is usually found during composting (Bustamante et al. 2008) and this parameter has been established as a maturity index for composts (Bernal et al. 2009).

The initial concentrations of TN in the mixtures ranged between 14.5 g kg^{-1}, for M3 (with BS), and 20.1 g kg^{-1}, for M1 (with CW). The TN contents did not change statistically in the mixtures during the experiment, indicating low or no N-losses, which could be a consequence of the initial values of the C/N ratio, higher than 20, except for M1 (with CW). In a study of the effect of a low initial C/N ratio on aerobic composting of pig manure with rice straw, Zhu (2007) reported high N-losses when the C/N ratio was lower than 20. The NH_4^+-N concentrations decreased in all the mixtures during the experiment; however, this was not clearly reflected by a decrease in the TN values in all the mixtures. Thus, the N losses by NH_3-volatilization probably were relatively small, since the pH values of the piles were <7.5 during the process, and, at such pH, the ammonium form prevails over ammonia. Then, these decreases in ammonia content could be due to microbial immobilization. Initial NH_4^+-N immobilization by microorganisms during composting of NH_4^+-N rich wastes, such as animal manure and slurry, has been reported (Paillat et al. 2005; Liang et al. 2006; Bernal et al. 2009), being a key-factor for the control of NH_3 volatilization and thus the reduction of ammonia emission during composting.

Table 3 Physico-chemical and chemical characteristics of the mixtures at the beginning and end of the experiment (mean values±standard deviation (n=2))

Mixtures	Sampling time	Moisture	pH	EC	OM	TOC	C_w	TN	NH_4^+-N	C/N
		(%)		(dS m^{-1})	(%)	(g kg^{-1})	(g kg^{-1})	(g kg^{-1})	(mg kg^{-1})	
M1	Initial	65.1±0.3	7.7±0.0ab	4.9±0.1c	77.7±0.3a	324±4b	21.5±0.5a	20.1±1.2	271±22ab	16.1±0.7
	End	69.8±0.2	7.7±0.0a	6.2±0.2a	73.2±0.6bc	371±5a	11.9±1.1ab	20.1±6.1	73±12b	19.8±6.1
M2	Initial	69.4±0.2	7.2±0.0d	4.2±0.1d	72.5±0.4c	327±5b	8.8±0.4bc	15.3±0.6	353±63a	21.4±0.5
	End	60.0±4.1	7.4±0.0 cd	4.7±0.2c	72.8±1.0bc	331±20b	6.4±1.9c	17.8±9.1	144±99ab	23.6±13.1
M3	Initial	69.7±0.5	7.5±0.0bc	4.1±0.0d	73.7±0.1bc	350±2ab	8.6±1.8bc	14.5±2.5	368±17a	24.4±4.3
	End	74.2±0.4	7.3±0.2 cd	5.5±0.1b	71.7±1.9c	343±15ab	10.9±1.1bc	14.4±3.6	275±316ab	25.1±7.0
M4	Initial	68.7±0.4	7.2±0.0d	4.4±0.1 cd	76.2±0.3ab	370±9a	22.0±0.3a	16.8±0.7	334±85a	22.1±1.5
	End	57.9±4.4	7.7±0.0ab	4.5±0.1 cd	73.0±1.0bc	343±2ab	7.2±2.3bc	12.5±1.8	139±109ab	28.0±4.1
ANOVA		n.s.	***	***	***	**	***	n.s	*	n.s

M1: 83 % solid fraction of pig slurry+17 % cotton gin waste; M2: 92 % solid fraction of pig slurry+8 % maize stalk; M3: 94 % solid fraction of pig slurry+6 % barley straw; M4: 87 % solid fraction of pig slurry+13 % garden pruning waste (mixture 1:1 mulberry:jacaranda)

EC. electrical conductivity; *OM*. organic matter; *TOC*, total organic carbon; C_w, water-soluble carbon; *TN*, total nitrogen

n.s., not significant $P>0.05$; *, **, ***: significant at $P<0.05$, 0.01, 0.001 respectively

For each parameter, values followed by the same letter are not statistically significant according to the Tukey test

3.4 Assessment of the C conservation potential

The potential C conservation can be ascertained using respiration tests based on the CO_2-C production or O_2 consumption, procedures commonly used for determining compost stability and maturity (Hue and Liu 1995; Barrena-Gómez et al. 2006). Adani et al. (2006) correlated the dynamic respiration index with temperature and airflow rate, for determining the biological stability of compost. In this sense, these tests are also useful to determine the biodegradability of the material, since temperature and CO_2 concentrations are directly related to microbial activity (Qiu et al. 2005). Therefore, the potential C conservation in the mixtures before and after the experiment was assessed by measuring the CO_2 released from the samples during 10 days of aerobic incubation (Barrena-Gómez et al. 2006). The results indicate a clear reduction in the CO_2-C production in the mixtures M1 and M4 at the end of the experiment in comparison with the beginning (Table 4). The reduction of the CO_2-C emission was more significant in the mixture M4, elaborated with garden prunings, being 57 %, which indicates higher stabilisation of the mixture at the end of the process. Since CO_2-C emission is a sign of microbial activity and OM degradation, its slowdown indicates that easily accessible compounds were already degraded. However, it is important to remark that these mixtures (M1 and M4) also showed the highest CO_2-C emissions at the beginning of the experiment, compared with the mixtures elaborated with the other materials, the mixture with MS (M2) having the lowest value. These results are in agreement with those found by Paredes et al. (1996) in a study to assess the influence of the bulking agent on the degradation of olive-mill wastewater sludge during composting. These authors observed that the mixture with cotton gin consumed more O_2, producing more CO_2-C, than the mixture elaborated using maize stalks as bulking agent.

At the end of the experiment, the mixtures with cotton gin and barley straw (M1 and M3, respectively) had evolved similar CO_2-C values (Table 4), with no statistical difference in their C_w values (Table 3). However, in the mixture M2, with maize stalks, the CO_2 emission did not change statistically during the experiment, and this mixture reached low temperature values (the lowest energy produced after 1 and 10 days of the experiment; Fig. 2) and had a low C_w concentration in the initial mixture, indicating slow degradability. The C_w contains the simple, water-soluble organic compounds such as sugars, amino acids and peptides, which are easily metabolised by microorganisms during composting (Bernal et al. 1996). Several authors referred to the decrease in time of C_w, due to its high degradability (Bernal et al. 1996; Bustamante et al. 2008). In fact, C_w decreased for all the mixtures, except for the mixture with

Table 4 CO_2-C emission values of the mixtures at the beginning and end of the experiment (mg CO_2-C/g dry matter). Mean values±standard deviation (n=3)

Sampling time	M1	M2	M3	M4	ANOVA
Initial	26.7±7.0a	12.1±3.6b	17.8±1.3ab	24.2±2.2a	*
End	15.6±3.6b	12.6±1.4ab	15.6±3.8a	10.8±0.2b	*
ANOVA	*	n.s.	n.s.	**	–

M1: 83 % solid fraction of pig slurry+17 % cotton gin waste; M2: 92 % solid fraction of pig slurry+8 % maize stalk; M3: 94 % solid fraction of pig slurry+6 % barley straw; M4: 87 % solid fraction of pig slurry+13 % garden pruning waste (mixture 1:1 mulberry:jacaranda)

n.s., not significant $P>0.05$; *, **: significant at $P<0.05$ and 0.01, respectively

Values followed by the same letter for each sampling time and for each mixture are not statistically significant according to the Tukey test maize stalks (M2), which may be due to the liberation of simple, soluble organic compounds exceeding their degradation (Castaldi et al. 2005). A positive, highly significant correlation (standard error of the correlation coefficient (r)=0.935; $P<0.001$) between the CO_2-C released and the C_w concentration for all the mixtures at the beginning and end of the experiment was found, indicating that a decrease in C_w is associated with a decrease in CO_2-C production, reflecting degradability. Also, the energy produced by the microorganisms after 1 day of the experiment correlated with the CO_2-C release of the initial samples (r=0.966; $P<0.01$), while the energy produced after 10 days correlated to the CO_2-C released from the samples at the end of the experiment. Therefore, both parameters - the energy released as heat and the CO_2-C production - indicated the degradability of the material.

The absence of significant changes in the CO_2-C production for the mixtures with maize stalks and barley straw (M2 and M3) during the experiment indicates that these mixtures may have more recalcitrant compounds, more resistant to degradation. Both these bulking agents are lignocellulosic materials, and cellulose and hemicellulose are the main C sources for the microbial activity responsible for most of the CO_2 and heat produced. Lignin is an integral cell wall constituent which provides plant strength and resistance to microbial degradation (Argyropoulos and Menachem 1997), and is the most recalcitrant component of the plant cell wall, where the higher the proportion of lignin, the higher the resistance to chemical and enzymatic degradation (Taherzadeh and Karimi 2008). But, the larger particle size of both cereal straws, in comparison with cotton gin and garden prunings, may have rendered the internal part of the particles physically inaccessible for microbial attack. So, the 15–day duration of the experiment could have acted as a pre-treatment for breaking down the surface of the straw and stalk particles, making the internal part accessible to microbes and, thus, degradable. Similar results were reported by Paredes et al. (1996), who, in an experiment of co-composting of olive-mill wastewater sludge with different bulking agents, observed greater degradation in the mixture elaborated using cotton gin as bulking agent, due to its small particle size. Also, Nolan et al. (2011) concluded that woodchips, due to the presence of recalcitrant lignin and the large surface area, were not a suitable bulking agent, but - when mixed with sawdust - provided good quality compost.

The results indicate that cotton gin and garden prunings enhanced the composting of the solid fraction of pig slurry, speeding-up the process. However, this fast degradation of the organic matter may have a strong impact on the environment, due to a high CO_2 emission rate. Also, high CO_2 emission implies strong TOC degradation and mineralisation of the organic matter, which may produce compost with low OM and TOC. Then, from the point of view of GHG mitigation and C conservation, maize stalks and barley straw seem to be the best materials, although slow composting can be expected. These materials will guarantee C conservation when the derived compost is incorporated into soil, due not only to the C concentrations but also to the presence of stable organic C compounds produced through OM humification during the maturation phase of composting (Bernal et al. 2009). Bernal (2008) evaluated the balances of organic C during composting and after application to the soil, indicating that for C conservation in the soil system, compost incorporation into soils is preferable to the direct application of an untreated (fresh) manure, since fresh manures possess higher amounts of C_w (an easily degradable C source) than compost, hastening the depletion of available C.

4 Conclusions

The thermal profile of composting materials at the laboratory scale and the microbial degradation measured by CO_2-C emissions are adequate parameters to define the degradability of the material and, especially, to predict the potential C conservation during composting. Although the mixtures elaborated with the mixture of garden pruning waste and cotton gin waste showed a quick temperature development and high degradability, their fast organic matter degradation significantly increased the CO_2 release into the atmosphere, also producing composts with low concentrations of organic matter and total organic C. The use of maize stalks as bulking agent for the composting of the solid fraction of pig slurry produced a thermal profile with low temperature development, but also implied a low impact on the environment due to its slow degradation, helping to promote C conservation while significantly reducing CO_2 emissions and producing compost rich in organic matter. However, these findings should be corroborated at an industrial scale in order to confirm the efficiency of maize stalks regarding C conservation in the composting of the solid phase of pig slurry.

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References

Adani F, Ubbiali C, Generini P (2006) The determination of biological stability of composts using the dynamic respiration index: the results of experience. Waste Manag 26:41–48

Argyropoulos DS, Menachem SB (1997) Lignin. In: Eriksson, K-E.L. (Ed.), Adv Biochem Eng Biot 57: 127–158.

Barrena-Gómez R, Lima FV, Ferrer AS (2006) The use of respiration indices in the composting process: a review. Waste Manag Res 24:37–47

Bernal MP (2008) Compost: production, use and impact on carbon and nitrogen cycles. Monograph nº. 631, International Fertiliser Society, York. ISBN 987-0-85310-268-7

Bernal MP, Navarro AF, Roig A, Cegarra J, García D (1996) Carbon and nitrogen transformation during composting of sweet sorghum bagasse. Biol Fert Soil 22:141–148

Bernal MP, Alburquerque JA, Moral R (2009) Composting of animal manures and chemical criteria for compost maturity assessment. a review. Bioresour Technol 100:5444–5453

Bertora C, Alluvione F, Zavattaro L, van Groenigen JW, Velthof G, Grignani C (2008) Pig slurry treatment modifies slurry composition, N2O, and CO2 emissions after soil incorporation. Soil Biol Biochem 40:1999–2006

Brown S, Kruger C, Subler S (2008) Greenhouse gas balance for composting operations. J Environ Qual 37: 1396–1410

Bustamante MA, Paredes C, Marhuenda-Egea FC, Pérez-Espinosa A, Bernal MP, Moral R (2008) Co-composting distillery wastes with animal manure: carbon and nitrogen transformations and evaluation of compost stability. Chemosphere 72:551–557

Bustamante MA, Restrepo AP, Alburquerque A, Pérez-Murcia MD, Paredes C, Moral R, Bernal MP (2013) Recycling of anaerobic digestates by composting: effect of the bulking agent used. J Clean Prod 47:61–69

Castaldi P, Alberti G, Merella R, Mellis P (2005) Study of the organic matter evolution during municipal solid waste composting aimed at identifying suitable parameters for the evaluation of compost maturity. Waste Manag 25:209–213

Cole CV, Duxbury J, Freney J, Heinemeyer O, Minami K, Mosier A, Paustian K, Rosenberg N, Sampson N, Sauerbeck D, Zhao Q (1997) Global estimates of potential mitigation of greenhouse gas emissions by agriculture Nutr. Cycl Agroecosyst 49:221–228

Doublet J, Francou C, Poitrenaud M, Houot S (2012) Influence of bulking agents on organic matter evolution during sewage sludge composting; consequences on compost organic matter stability and N availability. Bioresour Technol 102:1298–1307

Duchateau K, Vidal C (2003) Between 1990 and 2000, European agriculture has reduced its greenhouse gas emissions by 6.4 %. Environment and Energy. Theme 8–1/2003.

Estevez-Schwarz I, Seoane S, Núñez A, López-Mosquera ME (2012) Production and characterization of a compost made from garden and other types of waste. Pol J Environ Stud 21(4):43–52

FAO (2008) FAOSTAT. Food and Agriculture Organization of the United Nations, Rome, Italy. www.faostat.fao.org/. Cited 16 May 2014.

FAO (2010). Greenhouse gas emissions from the dairy sector. A life cycle assessment. Food and Agriculture Organization of the United Nations, Rome, Italy.

Fukumoto Y, Inubushi K (2009) Effect of nitrite accumulation on nitrous oxide emission and total nitrogen loss during swine manure composting. Soil Sci Plant Nutr 55:428–434

Georgacakis D, Tsavdaris A, Bakouli J, Symeonidis S (1996) Composting solid swine manure and lignite mixtures with selected plant residues. Bioresour Technol 56:195–200

Hoeve M, Hutchings NJ, Peters GM, Svanström M, Jensen LS, Bruun S (2014) Life cycle assessment of pig slurry treatment technologies for nutrient redistribution in Denmark. J Environ Manag 132:60–70

Hue NV, Liu J (1995) Predicting compost stability. Compos Sci Util 3:8–15

IPCC (2007) Intergovernmental Panel on Climate Change. In: Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA (eds) Climate Change 2007: Working Group III: Mitigation of Climate Change. Cambridge University Press, Cambridge

Kariyapperuma KA, Furon A, Wagner-Riddle C (2012) Non-growing season nitrous oxide fluxes from an agricultural soil as affected by application of liquid and composted swine manure. Can J Soil Sci 92:315–327

Lesschen JP, van den Berg M, Westhoek HJ, Witzke HP, Oenema O (2011) Greenhouse gas emission profiles of European livestock sectors. Anim Feed Sci Technol 166–167:16–28

Liang Y, Leonard JJ, Feddes JJR, McGill WB (2006) Influence of carbon and buffer amendment on ammonia volatilization in composting. Bioresour Technol 97:748–761

Liao PH, Vizcarra AT, Chen A, Lo KV (1993) Composting separated solid swine manure. J Environ Sci Health A 28:1889–1901

Lopez-Ridaura S, van der Werf H, Paillat JM, Le Bris B (2009) Environmental evaluation of transfer and treatment of excess pig slurry by life cycle assessment. J Environ Manag 90:1296–1304

Macías F, Camps M (2010) Soil carbon sequestration in a changing global environment. Mitig Adapt Strateg Glob Chang 15:511–529

Mc Carthy G, Lawlor PG, Coffey L, Nolan T, Gutierrez M, Gardiner GE (2011) An assessment of pathogen removal during composting of the separated solid fraction of pig manure. Bioresour Technol 102:9059–9067

Navarro AF, Cegarra J, Roig A, Bernal MP (1991) An automatic microanalysis method for the determination of organic carbon in wastes. Commun Soil Sci Plant Anal 22:2137–2144

Nolan T, Troy SM, Healy MG, Kwapinski W, Leahy JJ, Lawlor PG (2011) Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. Bioresour Technol 102: 7131–7138

O'Mara FP (2011) The significance of livestock as a contributor to global greenhouse gas emissions today and in the near future. Anim Feed Sci Technol 166–167:7–15

Paillat JM, Robin P, Hassouna M, Leterme P (2005) Predicting ammonia and carbon dioxide emissions from carbon and nitrogen biodegradability during animal waste composting. Atmos Environ 39:6833–6842

Paredes C, Bernal MP, Roig A, Cegarra J, Sánchez-Monedero MA (1996) Influence of bulking agent on the degradation of olive-mill wastewater sludge during composting. Int. Biodeterior Biodegrad 38:205–210

Qiu S, McComb AJ, Bell RW, Davis JA (2005) Response of soil microbial activity to temperature, moisture, and litter leaching on a wetland transect during seasonal refilling. Wetl Ecol Manag 13:43–54

Sommer SG, Kjellerup V, Kristjansen O (1992) Determination of total ammonium nitrogen in pig and cattle slurry: sample preparation and analysis. Acta Agric Stand, Sect Bull, Soil Plant Sci 42:146–151

Sundberg C (2005) Improving Compost Process Efficiency by Controlling Aeration, Temperature and pH. Swedish University of Agricultural Sciences (http://pub.epsilon.slu.se/950/1/CeSu103fin0.pdf).

Szanto GL, Hamelers HVM, Rulkens WH, Veeken AHM (2007) NH_3, N_2O and CH_4 emissions during passively aerated composting of straw-rich pig manure. Bioresour Technol 98:2659–2670

Taherzadeh MJ, Karimi K (2008) Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. Int J Mol Sci 9:1621–1651

Vallejo A, Skiba UM, García-Torres L, Arce A, López-Fernández S, Sánchez-Martín L (2006) Nitrogen oxides emission from soils bearing a potato crop as influenced by fertilization with treated pig slurries and composts. Soil Biol Biochem 38:2782–2793

VanderZaag AC, MacDonald JD, Evans L, Vergé XPC, Desjardins RL (2013) Towards an inventory of methane emissions from manure management that is responsive to changes on Canadian farms. Environ Res Lett 8

Vanotti M, Millner P, Szogi A, Campbell C, Fetterman L (2006) Aerobic Composting of Swine Manure Solids Mixed with Cotton Gin Waste. ASABE, St. Joseph, Mich, ASABE Paper No. 064061

Vanotti MB, Szogi AA, Vives CA (2008) Greenhouse gas emission reduction and environmental quality improvement from implementation of aerobic waste treatment systems in swine farms. Waste Manag 28:759–766

Zhu N (2007) Effect of low initial C/N ratio on aerobic composting of swine manure with rice straw. Bioresour Technol 98:9–13

3.2 Gaseous emissions and process development during composting of pig slurry: the influence of the proportion of cotton gin waste.

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Gaseous emissions and process development during composting of pig slurry: the influence of the proportion of cotton gin waste

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ABSTRACT

Composting is a feasible, environmentally-friendly management tool for the treatment of animal manures based on nutrient recovery. However, the liquid character of the pig slurry, with low dry matter, requires previous solid–liquid separation and the mixture of the solid fraction with an adequate bulking agent in the correct ratio. This work studies the influence of the bulking agent proportion on the composting of the solid fraction of pig slurry, focussing on the development of the process and on the greenhouse gas emissions. For this, two mixtures of the solid fraction of pig slurry and cotton gin waste, in different proportions, were prepared (4:3 and 3:4 solid fraction of pig slurry:cotton gin waste, v:v) and composted by the Rutgers static pile system in a pilot plant (2000 kg each pile). The temperature profiles of the composting piles were similar, but the pile with the greater proportion of bulking agent showed higher temperatures and a longer thermophilic phase, with greater aeration demand. The specific heat capacity of cotton is lower than those of other bulking agents used frequently for animal manure composting, which means that this material requires less energy from microbial activity for its temperature to increase. However, the easily degradable organic matter present in the pig slurry explained the faster organic matter mineralisation occurred in the pile with the higher proportion of solid fraction of pig slurry; in pile with higher proportion of bulking agent, the mineralisation process was slower due to the lignocellulosic character of the cotton gin waste. The organic matter mineralisation was closely related to the gaseous emissions (mainly as carbon dioxide): significant methane emissions were detected when the highest organic matter degradation occurred in the pile with the greater proportion of solid fraction of pig slurry, together with the highest nitrogen oxide emissions – indicating the existence of anaerobic pockets within the composting mass. So, it can be concluded that the thermal properties of the bulking agent were responsible for the temperature development and aeration demand, while the gaseous emissions were related to the organic matter degradation process. The composts produced were stable, with a good degree of maturation; the compost with the higher proportion of solid fraction of pig slurry had greater organic matter humification and higher nutrient concentrations.

1. Introduction

The management of animal manures is one of the main problems that the current intensive farm production systems have to deal with in developed countries. According to Eurostat (2015), Spain is the country with the second-greatest pig production in Europe (after Germany). Within Spain, Murcia is the region with the fourth-greatest pig production (INE, 2015), with about 1.8 × 10^6 pigs (CARM, 2015). The annual pig slurry production in Murcia exceeds 6.5 million m^3, concentrated mainly in two areas: Guadalentin Valley and Fuente Álamo (CARM, 2015), both with declared nitrate-vulnerable zones. This situation – the high concentration of pig farms within nitrate vulnerable areas – has led to the production of pig slurry in excess of the amount which can be applied directly to agricultural soil. Then, in order to avoid possible negative impacts on the environment and to comply with the national legislation, treatment technologies for the management of the pig slurry need to be established (Burton and Turner, 2003). There are different technologies for pig slurry treatment, based either on the

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recovery of plant nutrients or on their elimination (Sommer et al., 2014; Flotats et al., 2009).

Composting is a feasible, environmentally-friendly management tool for the treatment of these residues based on nutrient recovery (Huang et al., 2001), where organic matter (OM) is degraded into a stable and humified final product, free of pathogens and malodours, rich in nutrients, beneficial for plant growth and with agricultural value as a fertiliser (Bernal et al., 2009). Composting can minimise the potential environmental problems that can occur during storage of animal manures and after their direct soil application, such as greenhouse gas (GHG) emissions, the spread of pathogens and nutrient leaching into superficial and ground waters (Brown et al., 2008; Moral et al., 2005; Vinnerås, 2013).

However, pig slurry is a liquid material with low dry matter (<5%) and is rich in N (Moral et al., 2005). Thus, prior to composting, the physical and chemical properties should be improved by solid–liquid separation and the addition of a bulking agent (Nolan et al., 2011); for example, by adjusting the air space of the matrix, reducing the excessive moisture of the solid fraction of pig slurry (SFP) and adjusting the carbon to nitrogen (C/N) ratio, as high values lead to high N losses during composting (Bernal et al., 2009; Georgacakis et al., 1996; Nolan et al., 2011). Due to their availability on farms and ability to provide the optimal conditions for the development of the process, lignocellulosic materials such as barley and rice straws (Qian et al., 2014), maize stalks and other woody materials – sawdust and wood shavings (Huang et al., 2001; Ros et al., 2006) – have been used as bulking agents for pig slurry composting (Bernal et al., 1993; Hang et al., 2004; Nolan et al., 2011). According to Vanotti et al. (2006), the use of wood chips and cotton gin waste helped to reduce the bulk density of the pile and the moisture content, increasing the porosity and C/N ratio. Nolan et al. (2011) found that the addition of a bulking agent (sawdust, green waste or barley straw) to maintain the initial water content below 60% was necessary for composting of SFP at a low C/N ratio; they concluded that wood chips were not a suitable bulking agent due to the presence of recalcitrant lignin and its large surface area. The proportion of bulking agent appropriate for pig slurry composting depends on the initial characteristics of the separated solids, which are determined by the efficiency of the solid–liquid separator. Huang et al. (2004) concluded that increasing the proportion of sawdust in a mixture with pig manure increased the C/N ratio of the mixture, reducing the composting time and the salinity of the compost produced – the latter is mainly responsible for the phytotoxic effects in compost with a low proportion of bulking.

Also, the incorporation of a bulking agent has been reported as one of the most-effective measures to reduce GHG emissions during composting – since it improves the structure of the pile (waste or manure heap) while simultaneously reducing methane (CH_4) and nitrous oxide (N_2O) emissions (53% and 71%, respectively), without increasing substantially the N losses through ammonia (NH_3) volatilisation (Pardo et al., 2015). For reducing ammonia losses, Bernal et al. (1993) highlighted the relevance of the C supplied by the bulking agent and its particle size in the composting of pig manure.

A preliminary laboratory study for bulking agent selection for SFP composting, based on thermal evaluation in a self-heating test, revealed that cotton gin waste was a better bulking agent than cereal straw, maize stalks or pruning wastes, to control the excessive moisture content of the SFP and temperature development (Santos et al., 2014). Also, cotton gin waste has proved to be an adequate material to control the excessive moisture content of certain liquid wastes (Paredes et al., 1996), promoting the development of thermophilic temperatures during the composting process and hence ensuring the sanitation of the final product.

Therefore, the aim of this study was to assess the influence of the proportion of cotton gin waste on the thermal profile, chemical evolution of the solid fraction of pig slurry during composting and the environmental implications regarding GHG emissions.

2. Material and methods

The solid fraction of pig slurry (SFP) was obtained from a fattening pig farm after a solid–liquid separation with a screw press. Cotton gin waste was used as a bulking material. The main characteristics of both initial materials are shown in Table 1.

2.1. Experimental design and conditions

Two composting mixtures (M1 and M2) were prepared by mixing SFP with cotton gin waste, considering the moisture content and C/N ratio of both materials: M1, with a ratio of 4:3 (SFP:cotton gin; v/v); and M2, with a ratio of 3:4 (SFP:cotton gin). The experiment was run in a pilot-scale composting plant. The mixtures were set up in trapezoidal piles of 2000 kg each, with a base of 2.7 × 3.7 m and a height of 1 and 1.2 m, for M1 and M2, respectively, and composted using the Rutgers static pile composting system with forced aeration at temperature demand, set to 65 °C. Aeration was programmed, occurring every 120 min for: 1 min if $T < 55$ °C; 2 min if 55 °C $< T < 60$ °C; 3 min if 60 °C $< T < 65$ °C; and continuously if $T \geq 65$ °C, until $T \leq 60$ °C. The ventilation demand was calculated as the time (hours per day) that the pump was blowing continuously ($T > 65$ °C). The piles were turned twice throughout the process, when the temperature started to decrease, in order to improve both the homogeneity of the materials and the composting process. The moisture of the piles was controlled weekly by adding the amount of water necessary to keep the moisture content above 40%. The evolution of the temperature was monitored using two temperature probes for each pile, at different places in the pile. The bio-oxidative phase of composting was considered finished when the temperature inside the pile was close to the external temperature and re-heating did not occur after turning. Then, the ventilation was turned off and the composts were left to mature over a period of two months.

During the 167 days that the composting process lasted, ten samples were taken to assess the evolution of the mixtures. The samples were taken by mixing seven sub-samples from seven representative sites of the pile, from the whole profile (from the top to the bottom of the pile). Each representative sample was divided into three fractions in the laboratory: one was dried in a drying-oven at 105 °C for 24 h to determine the moisture content, the second was immediately frozen (−18 °C) and kept for the

Table 1
Characteristics of the initial materials (dry weight basis).

	Cotton gin waste	Solid fraction of pig slurry
pH	6.97	7.31
EC (dS m^{-1})	7.15	6.85
Moisture (%)[a]	14	75
OM (%)	87.9	68.6
TOC (g kg^{-1})	534	356
C_w (g kg^{-1})	n.d.	5.41
TN (g kg^{-1})	10.4	32.8
NH_4^+-N (g kg^{-1})	0.33	10
C/N ratio	51.3	10.9
Lignin (%)	49.9	n.d

EC: electrical conductivity; OM: organic matter; TOC: total organic carbon; C_w: water-soluble carbon; TN: total nitrogen.
n.d.: not determined.
[a] Calculated based on fresh weight.

determination of ammonium nitrogen (NH_4^+-N) and the third was freeze-dried and ground to less than 0.5 mm for the rest of the analytical determinations.

2.2. Physico-chemical and chemical analysis

The raw materials and the composting samples were analysed according to standard procedures: electrical conductivity (EC) and pH in a water-soluble extract 1:10 (w/v); OM by loss-on ignition at 550 °C for 24 h; total organic carbon (TOC) and total nitrogen (TN) by automatic microanalysis (EuroVector EuroEA 3000 elemental analyser) (Navarro et al., 1991); water-soluble organic carbon (C_w) in a 1:10 (w/v) water extract, extractable carbon (C_{ext}) in a 1:20 (w/v) sodium hydroxide (NaOH) extract and fulvic acid-C (C_{FA}) after precipitation of the humic acid-C (C_{HA}) at pH < 2 using sulphuric acid (H_2SO_4), all analysed by an automatic analyser for liquid samples (TOC-V CSN Analyser, Shimadzu); ammonium nitrogen (NH_4^+-N) by a colorimetric method based on Berthelot's reaction (Sommer et al., 1992), after potassium chloride (2 M KCl) 1:20 (w/v) extraction; nitrate with a selective electrode in a 1:20 water extract; cation exchange capacity (CEC) with barium chloride ($BaCl_2$)-triethanolamine (Lax et al., 1986); and macro and micronutrients by inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Elemental Co. Iris Intrepid II XDL) after nitric acid and hydrogen peroxide (HNO_3—H_2O_2) digestion in a microwave oven. The germination index (GI) was determined using seeds of *Lepidium sativum* L., according to Zucconi et al. (1981).

The emission flow of the GHGs (carbon dioxide — CO_2, methane — CH_4 and nitrous oxide — N_2O) was measured at the surface of the pile using the closed static chamber system (Sommer et al., 2004; Sánchez-Monedero et al., 2010). For this, two chambers (both 0.055 m^2 and 0.01 m^3) were placed at two different points of the pile. The gas samples were taken every 5 min for 30 min with a syringe and the gas sampled was injected into two different containers: 30 ml into a 0.1 M NaOH trap, for CO_2 determination by HCl titration, and 10 ml into a vacuum tube (Vacutainer) for CH_4 and N_2O determination by gas chromatography (HP5890, column HP Innovax with Flame Ionization Detector for CH_4, and HP 4890D equipped with an electron capture detector — ECD for N_2O). The flow rate emissions ($g\ m^{-2}\ day^{-1}$) were calculated according to Hao et al. (2001). All the samples were taken after turning off the ventilation system. All the analytical determinations were performed at least in duplicate.

The energy produced by microbial activity during the composting process was calculated according to the Eq. (1) (Santos et al., 2014):

$$q = m \times c \times \Delta T \quad (1)$$

where q is the energy produced (kJ), m is the mass of compost (kg), c is the heat capacity of the compost ($kJ\ kg^{-1}\ K^{-1}$) and ΔT is the increase in temperature from the room to the internal values of the composting mass.

The OM-loss by mineralisation was calculated, using the initial (X_1) and final (X_2) ash concentrations, with the following the Eq. (2) (Bernal et al., 1996):

$$OM\ loss\ (\%) = 100 - \frac{100[X_1(100 - X_2)]}{[X_2(100 - X_1)]} \quad (2)$$

2.3. Statistical analysis

The standard error of the means was calculated for the chemical and physico-chemical characteristics of the composting samples; one-way analysis of variance (ANOVA) and least significant difference (LSD) were used for determining changes of the parameters during composting. The normality and homogeneity of the variances were checked using the Shapiro—Wilk and Levene test, respectively, before ANOVA. The IBM SPSS Statistics v.19 software package was used for the statistical analyses. The OM mineralisation (OM-loss) data were fitted to a first-order kinetic model (Eq. (3)) by a non-linear least-square technique (Marquardt—Levenberg algorithm), using the SigmaPlot v. 12.0 Systat Software Inc.:

$$OM_{min} = A \times \left(1 - e^{-kt}\right) \quad (3)$$

where OM_{min} is the mineralised OM (%) at the composting time t (day), A is the potentially mineralisable OM (%) and k is the rate constant (day^{-1}). The goodness of curve fitting was estimated according to the residual mean square (RMS) and the significance of the F-value of the ANOVA.

3. Results and discussion

The solid fraction of pig slurry had a slightly alkaline character (Table 1) with an excessive moisture content (75%) for composting without a bulking agent (Bernal et al., 2009), which could cause leaching and anaerobic conditions within the composting mass. The low moisture content of the cotton gin waste (Table 1) can compensate the excess moisture of the SFP. Both materials were rich in OM, but SFP was richer in Cw (easily degradable by microorganisms) and TN (30.5% as NH_4^+-N) with a low C/N ratio for composting; all these factors could lead to high ammonia losses by volatilisation if not equilibrated by the bulking agent (Bernal et al., 2009).

3.1. Evaluation of the thermal profiles of the composting piles

The thermal profiles of both composting piles showed a fast increase in temperature during the first week of experiment, when both piles achieved values close to 65 °C (Fig. 1a). Such quick increases indicate fast biodegradation of the materials due to the presence of easily-degradable forms of TOC in the mixtures (Bernal et al., 2009). During the thermophilic phase, both piles showed a similar trend (Fig. 1a), reaching temperatures above 55 °C for more than 35 days, longer than the time required to ensure hygienic conditions in the compost (European Commission, 2001; JRC and IPTS, 2012). However, the thermophilic phase was shorter in M1 than in M2 (50 and 80 days, respectively). The increment of temperature with respect to the external values indicates that the exothermic process was stronger in M2 (1640 °C Mg^{-1}DM) than in M1 (1190 °C Mg^{-1}DM), which may be due to the thermal properties of the cotton gin waste — present in a greater proportion in M2. Similar results were found by Yañes et al. (2009) during composting of sewage sludge with garden prunings; mixtures with a greater proportion of bulking agent showed a longer thermophilic phase. Also, Huang et al. (2001) found that partial substitution of sawdust by garden waste (leaves), in the composting of pig manure, improved composting efficiency by shortening the time required for maturation. However, Ros et al. (2006) found a two-week delay in the temperature development during composting of SFP, with or without wood shavings as a bulking agent. All these findings indicate that the proportion and characteristics of the bulking agent affect the temperature development during composting.

Temperature variations during composting are the result of the thermal balance between the heat generated by the microorganisms and the heat loss through convection, conduction, evaporation and radiation (Haug et al., 1993). Thus, the energy generated by

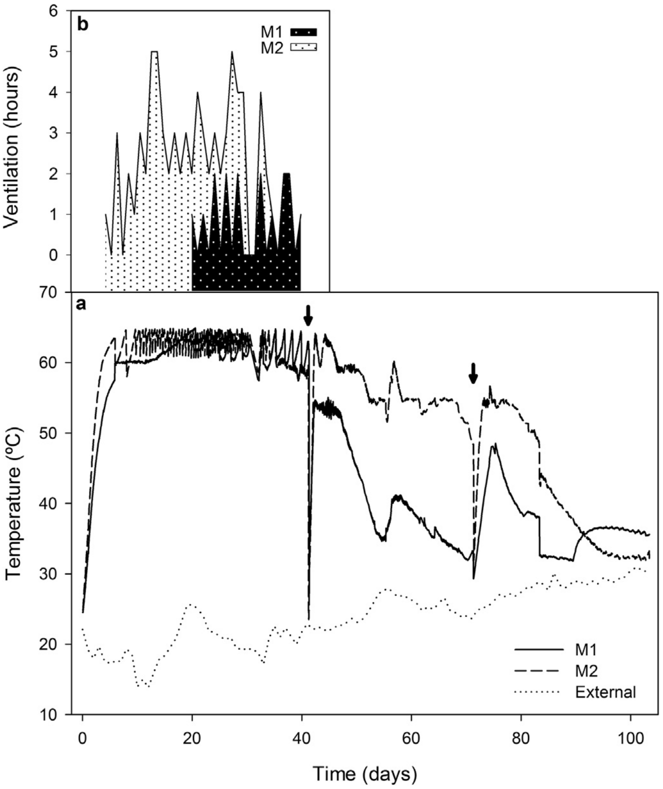

Fig. 1. Thermal profile of the composting piles (a); and ventilation demand to maintain the temperature of the piles below 65 °C during the bio-oxidative phase of the composting process (b). M1: solid fraction of pig slurry + cotton gin waste (4:3, v:v); M2: solid fraction of pig slurry + cotton gin waste (3:4, v:v). Arrows indicate the turnings.

microorganisms and its effect on the temperature of the composting mass depend on the thermal properties of the bulking agent and its proportion. Cotton gin waste is a material with good thermal properties, with a calorific value of 14.7 MJ kg^{-1} (Zabaniotou et al., 2007), higher than wood chips (12.2 MJ kg^{-1}) (Francescato et al., 2008). Also, the specific heat capacity of cotton (1.34 kJ kg^{-1} K^{-1}) is comparable to those of several kinds of wood and other biomasses (soybean straw or corn stalks), but is lower than those of wheat straw, silage, oat straw, alfalfa hay and leaves and wood shavings, which are frequently used as bulking agents for animal manure composting (Bernal et al., 2009; Ros et al., 2006), and beef manure or turkey litter (Ahn et al., 2009) – which means that this material requires less energy for its temperature to increase. This property is directly related to the moisture content (Ahn et al., 2009); thus, SFP would have a higher specific heat capacity than cotton gin waste, and the higher the proportion of SFP in the mixture the greater the energy necessary to increase its temperature. The specific heat capacity may also explain the delay in reaching thermophilic temperatures when composting SFP with wood shavings (Ros et al., 2006), showing cotton gin waste to be a more-adequate bulking agent.

The energy produced in the composting mass was higher in M2 than in M1 (8556 and 7837 MJ, respectively; calculated according to Eq. (1)); this is related to the greater length of the thermophilic phase in M2, due to the high microbial activity and the thermal properties of the cotton gin waste. Ventilation demand is a good indicator of microbial activity during the composting process (Haug, 1993). In the present experiment, the high amount of energy produced by the microbial activity and converted into heat meant that the ventilation demand was higher in M2 than in M1 (74 and 16 h of continuous air-blowing, respectively, during the thermophilic phase; Fig. 1b). This was associated with the higher proportion of bulking agent in M2 and the thermal properties of the cotton waste. Then, in M2, the energy generated by microbial activity was efficiently converted into heat within the composting mass, requiring greater ventilation for temperature control. During the extra-ventilation period in M2 a great amount of heat was lost and the oxygen concentration within the mass was enhanced.

The temperature increased after each turning in both piles, especially for the second turning at day 71, indicating that the piles were still microbiologically active. The reactivation of the composting process by the turnings was also observed during composting of the solid fraction of anaerobically-digested pig slurry or animal manure with different bulking agents (Bustamante et al., 2013; Tortosa et al., 2012). This is due to the incorporation of poorly-degraded material from the external part of the pile into the internal part, where biological activity is greatest. During composting, as the OM becomes more stabilised, the microbial activity and the OM decomposition rate decrease and the temperature gradually decreases to the ambient level (Haug, 1993; Ros et al., 2006; Paredes et al., 2001), indicating the end of the bio-oxidative phase, which in the present experiment occurred at 103 days.

3.2. *Evolution of the physico-chemical and chemical parameters and GHG emissions during the composting process*

In both piles, most of the physico-chemical and chemical parameters showed a similar pattern along the process (Table 2). The pH slowly decreased during the first 56 days, probably due to the degradation of the OM and NH_3-volatilisation, with a quick decrease after this day until the end of the composting process due to nitrification, an acidification process (Tarre and Green, 2004). Similar results were found when sawdust was composted with raw and digested pig manure (Troy et al., 2012), and are frequently found during composting (Bernal et al., 2009).

The EC values increased during the process (Table 2), as OM mineralisation leads to an increase in inorganic compounds in the compost matrix (Moreno and Moral, 2008). According to Eq. (2), such OM mineralisation gave a reduction in the OM concentration of 64.4 and 50.5% (M1 and M2, respectively) during the process. As a microbial-mediated process, the OM mineralisation can be described by a first-order kinetic model (Paredes et al., 2001; Bernal et al., 1996; Haug, 1993), in which the rate of decomposition depends on the concentration of potentially degradable substrate (OM): $d\mathrm{OM}/dt = -\mathrm{K} \times \mathrm{OM}$.

The integration of the expression from time 0 to "t" gives the usual form of the equation shown in Eq. (3). The use of such a model allows us to discuss the degradation process in kinetic terms. The experimental data of OM degradation in both piles fitted the first-order kinetic model (Eq. (3)) with a high probability level ($p < 0.0001$) (Fig. 2), and the following parameters were obtained:

M1: $A = 56.4 \pm 2.5$; $k = 0.0803 \pm 0.0183$; RMS = 33.186, F = 91.03, $p < 0.0001$, $R^2_{adj} = 0.909$;
M2: $A = 57.4 \pm 8.0$; $k = 0.0235 \pm 0.0084$; RMS = 71.208, F = 56.76, $p < 0.0001$, $R^2_{adj} = 0.861$.

Therefore, an increase in the proportion of bulking agent did not statistically change the concentration of degradable OM (parameter *A* did not differ statistically between the piles), but led to a significant decrease in the degradation rate (the rate constant, *k*, decreased from M1 to M2). The product of $A \times k$ indicates that the initial OM mineralisation rate was faster for M1 (4.53% OM d^{-1}), elaborated with a higher proportion of SFP, than for M2 (1.35% OM d^{-1}),

Table 2

Evolution of the physico-chemical and chemical parameters of the two piles (M1 and M2) during the composting process (mean ± standard deviation).

Composting time (days)	pH	EC (dS m^{-1})	OM (%)	TOC (g kg^{-1})	C_w (g kg^{-1})	TOC/TN
M1: SFP + cotton gin waste (4:3, v:v)						
0	7.43 ± 0.03	5.73 ± 0.10	79.1 ± 0.8	363 ± 3	27.5 ± 0.7	18.6 ± 0.6
6	7.32 ± 0.02	5.64 ± 0.14	72.3 ± 1.1	359 ± 8	14.9 ± 1.0	15.8 ± 1.7
15	7.35 ± 0.03	6.65 ± 0.05	69.1 ± 1.0	355 ± 13	21.3 ± 1.3	13.8 ± 1.2
32	7.27 ± 0.02	7.19 ± 0.16	68.4 ± 1.2	355 ± 5	21.4 ± 1.2	11.4 ± 0.6
41	7.28 ± 0.03	6.80 ± 0.20	65.5 ± 0.8	347 ± 12	20.1 ± 1.1	11.0 ± 0.4
56	7.28 ± 0.03	6.44 ± 0.15	62.1 ± 0.8	336 ± 13	14.9 ± 0.1	10.9 ± 1.3
70	7.12 ± 0.02	6.67 ± 0.06	61.1 ± 1.1	335 ± 7	12.1 ± 0.8	10.1 ± 0.2
83	6.92 ± 0.02	5.80 ± 0.10	58.3 ± 1.1	316 ± 7	9.2 ± 0.15	10.3 ± 0.3
103	6.78 ± 0.02	9.43 ± 0.14	56.7 ± 0.6	311 ± 14	7.8 ± 0.20	9.3 ± 0.3
167	6.77 ± 0.02	10.70 ± 0.17	57.3 ± 0.6	303 ± 10	7.0 ± 0.10	8.6 ± 0.3
ANOVA	***	***	***	***	***	***
LSD	0.04	0.23	1.6	17	1.35	1.5
M2: SFP + cotton gin waste (3:4, v:v)						
0	7.81 ± 0.02	6.23 ± 0.19	73.3 ± 0.9	357 ± 6	24.7 ± 0.3	16.3 ± 0.4
6	7.52 ± 0.02	5.70 ± 0.19	71.9 ± 0.3	339 ± 8	19.3 ± 1.0	15.6 ± 0.4
15	7.57 ± 0.03	6.55 ± 0.06	70.9 ± 0.8	333 ± 5	21.1 ± 2.0	14.7 ± 1.2
32	7.57 ± 0.03	6.64 ± 0.06	63.9 ± 1.0	327 ± 8	19.3 ± 1.2	11.1 ± 0.2
41	7.55 ± 0.04	6.19 ± 0.09	62.2 ± 0.8	336 ± 11	18.9 ± 1.5	12.2 ± 0.5
56	7.43 ± 0.02	5.13 ± 0.07	56.2 ± 1.7	308 ± 7	18.0 ± 2.0	11.1 ± 0.5
70	7.36 ± 0.04	5.76 ± 0.05	55.2 ± 1.1	307 ± 9	12.5 ± 1.9	10.6 ± 1.2
83	7.18 ± 0.03	6.86 ± 0.17	56.0 ± 1.7	305 ± 10	10.3 ± 0.7	9.7 ± 0.7
103	6.92 ± 0.02	7.80 ± 0.13	57.3 ± 1.2	298 ± 11	8.1 ± 1.0	9.1 ± 0.4
167	6.85 ± 0.03	10.06 ± 0.25	57.2 ± 1.4	292 ± 8	7.3 ± 0.8	9.4 ± 0.3
ANOVA	***	***	***	***	***	***
LSD	0.05	0.24	2.0	15	2.30	1.1

EC: electrical conductivity; OM: organic matter; TOC: total organic carbon; C_w: water-soluble carbon; TN: total nitrogen. SFP: solid fraction of pig slurry.
***: significant at $p < 0.001$. LSD: least significant difference at $p < 0.05$.

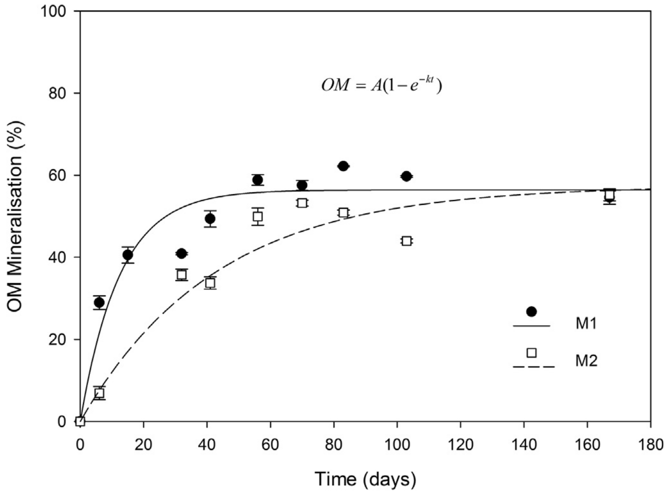

Fig. 2. Organic matter mineralisation during composting of the two piles, M1: solid fraction of pig slurry + cotton gin waste (4:3, v:v); M2: solid fraction of pig slurry + cotton gin waste (3:4, v:v). The dots are the experimental data and the lines are the curve fittings.

showing quick mineralisation in the first 20 days and reaching its maximum after 40 days of composting. However, M2 showed a slower OM mineralisation rate, stabilising after 60 days. The quicker OM mineralisation in M1 was associated with high microbial activity at the beginning of the process, as observed in the temperature profile (Fig. 1a), a consequence of the high amount of easily-degradable material from the SFP. In M2, the higher amount of recalcitrant compounds, such as lignin, provided by the cotton gin waste can explain the slower OM mineralisation. However, the temperature remained at thermophilic values for a long time, which may be due to the thermal characteristics of cotton gin waste and also the degradation of polymers (cellulose) from cotton. Similar results were found by Nolan et al. (2011), when composting the solid fraction of pig slurry with several different bulking agents at a low C/N ratio; they observed lower OM mineralisation for the mixtures made with materials rich in lignin, such as sawdust, shredded green waste, chopped straw and wood chips. Also, Doublet et al. (2010) found that increasing the proportion of bulking agent slowed down the OM mineralisation rate. The degradation rates found in M1 were similar to those found by Paredes et al. (2001) and Bernal et al. (1996) (4.48 and 4.00% OM d^{-1}) when co-composting sewage sludge with cotton gin waste and animal manure with sorghum bagasse, respectively.

The OM mineralisation was also manifested in the TOC concentration (Table 2), which was reduced by 16.5 and 18.2% in M1 and M2, respectively. A lesser reduction in the TOC concentration occurred when wood shavings were used as a bulking agent (12%; Ros et al., 2006), reflecting their more-lignified and degradation-resistant character. Taken into account the mass-loss of the piles, the TOC losses by mineralisation at the end of the process averaged 50% (52 and 47% for M1 and M2, respectively), indicating the consumption of the easily-degradable forms of C, due to the high microbial activity during the thermophilic phase. The water-soluble organic compounds (C_w) are the readily-available C source for microorganisms, as their metabolism occurs in the liquid phase. At the beginning of the composting process, the C_w concentration decreased in both piles (Table 2), but formation of soluble organic compounds was detected after 15 days, mainly in M1, indicating the hydrolysis of complex, insoluble organic compounds, such as hemicellulose or cellulose (Charest et al., 2004; Ros et al., 2006). According to Ros et al. (2006), the microorganisms responsible for the composting process use water-soluble compounds as energy sources for their growth and multiplication. This suggests that newly-formed glucose or other forms of C_w may have originated from microorganisms during this process – giving an alternate decrease and increase in the C_W concentration during the degradation process, as found in M1 and M2 at 15d, related to the synthesis of new carbohydrates of microbial origin. The C_W concentrations were lower in M2 than in M1 during the thermophilic phase, due to the lower proportion of SFP and higher proportion of lignocellulosic cotton gin waste in M2. Tortosa et al. (2012) also found a lower C_W concentration when a higher proportion of bulking agent was used in the composting of two-phase olive mill waste with two different types of animal manure. At the end of the process, the C_W concentration had decreased by 84% (86 and 82% for M1 and M2, respectively), indicating the consumption of readily-degradable OM; this parameter is considered a compost maturity index (Bernal et al., 1998).

The TN concentration increased in both piles during the process (Fig. 3), mainly due to a concentration effect as a result of the weight reduction of the mass, caused by the OM degradation. Huang et al. (2001) and Zhu et al. (2004) also found an increase in the TN concentration along the process, when composting SFP with leaves and rice straw, respectively. The evolution of TOC and TN decreased the TOC/TN ratio during the composting process (Table 2). Fels et al. (2014) explained that the C/N decrease can be attenuated if high losses of N as ammonia occur during the thermophilic phase. However, at the end of the process, the TN losses were around 20%, lower in M1 (17%) than in M2 (22%). Such values are in the low part of the range reported for the composting of pig slurry or pig manure, as reviewed by Bernal et al. (2009). Similar losses were found by Paredes et al. (1996), when composting poultry manure with cotton gin waste, and by Bustamante et al. (2008), when composting cattle manure with distillery wastes. At the beginning of the process (15 days) the TN loss was lower in M1 (5%) than in M2 (10%), which can be due to the higher ventilation demand in M2, promoting water evaporation and NH_3-volatilisation. It is well known that high temperatures and aeration, together with alkaline pH and a high NH_4^+-N concentration in the material during the thermophilic phase, favour NH_3-volatilisation (Bernal et al., 2009; Tiquia et al., 2002). In fact, the NH_4^+-N concentration decreased along the composting process in both mixtures (M1 and M2), but the decrease was faster in M2 (Fig. 3).

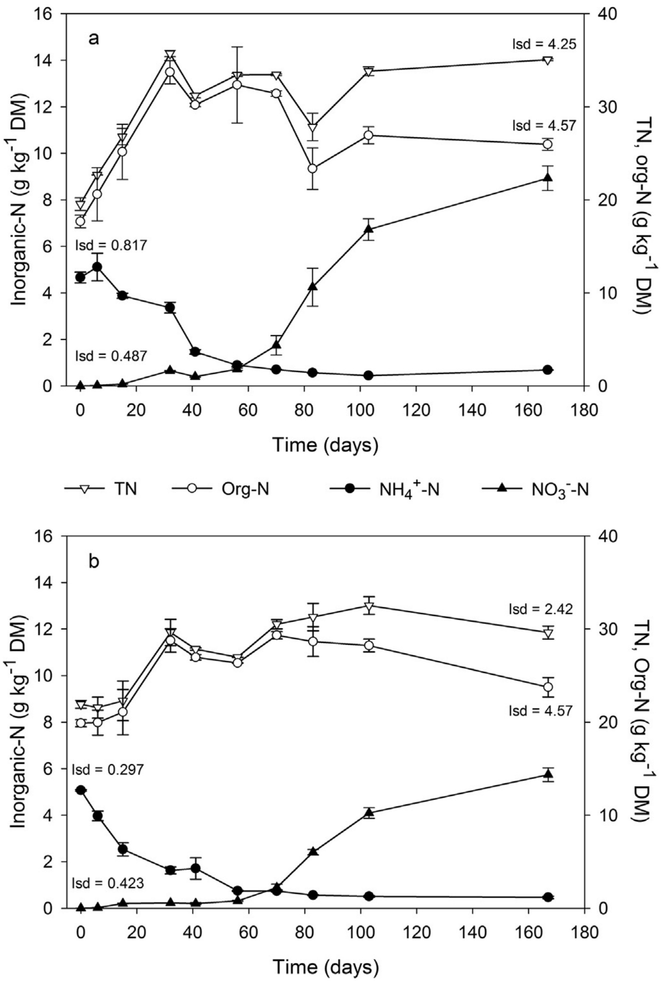

Fig. 3. Evolution of the N-forms during the composting process in M1 [solid fraction of pig slurry + cotton gin waste (4:3, v:v)] (a) and M2 [solid fraction of pig slurry + cotton gin waste (3:4, v:v)] (b). Right-hand axes for TN and organic-N, left-hand axes for inorganic-N (NH_4^+-N, NO_3^--N).

Losses of N can be due to NH_3-volatilisation, denitrification, nitrification and NO_3^- leaching; microbial N-immobilisation could also occur, mainly at the beginning of the composting process, when NH_4^+-N-rich materials are co-composted with a C-rich material (Bernal et al., 1996; Ros et al., 2006). The composting conditions – the number of turnings, aeration of the piles, temperatures obtained during the thermophilic phase, initial NH_4^+-N concentration and bacterial nitrification activity – affect N-losses (Bernal et al., 2009). According to Sánchez-Monedero et al. (1996), the Rutgers static system can reduce N-losses by NH_3-volatilisation, with respect to the turning systems, due to the direct contact of the internal gaseous phase with the atmosphere during turning. However, recent meta-analysis studies revealed the existence of high NH_3 losses during static pile composting (Pardo et al., 2015). Also, no or little NO_3^--N leaching could have occurred in the present experiment, and at the beginning of the process the NO_3^--N concentration remained very low, because high temperatures inhibit the activity of nitrifiers (Tiquia et al., 2002). Hence, NH_3-volatilisation should be the main factor responsible for N-losses at the beginning of the process. Further losses can be due to denitrification, which can occur in anaerobic microsites within the material, although the aeration programme applied, dependent on the temperatures, should have ensured adequate aerobic conditions.

The NO_3^--N concentration increased during the composting process for both mixtures (Fig. 3), when the internal temperature of the piles started to decrease from thermophilic values (Tiquia et al., 2002; Ros et al., 2006; Bernal et al., 2009). Nitrification occurs when temperatures are <40 °C and the aeration is favourable (Sánchez-Monedero et al., 2001), consistent with the static composting system and the observed formation of nitrate after the drop in temperature. Similar results were found by other authors when co-composting SFP (Zhu et al., 2004; Ros et al., 2006; Bernal et al., 2009) or sewage sludge (Fels et al., 2014) with several bulking agents.

The mass balances in both piles indicate that a high proportion of the initial inorganic N (up to 80%) was lost during the thermophilic phase, but formation of inorganic-N (as nitrate) was detected as the temperature went down, especially in M1 during the maturation phase, giving net organic-N mineralisation. As for TN, there was a balanced result for the inorganic-N during the process in M1: although, initially, a high proportion of inorganic-N (pre-existing and formed by mineralisation) was lost, the later formation gave a similar proportion of TN as of inorganic-N in the mature compost, with respect to the initial mixture. However, the mass balance for M2 indicates an overall loss of inorganic-N in the mature compost, equivalent to 27% of that initially present, with scarce organic-N mineralisation during maturation. So, the proportion of TN present as inorganic-N was reduced from 18.8% in the initial mixture to 14% in the mature compost (Table 2). These results

Table 3
Flow rates of the gaseous emissions from piles M1 and M2 during the thermophilic phase of composting.

Composting time (days)	CO_2-C ($g\ m^{-2}\ d^{-1}$)	CH_4-C ($g\ m^{-2}\ d^{-1}$)	N_2O-N ($g\ m^{-2}\ d^{-1}$)
M1: SFP + cotton gin waste (4:3, v:v)			
0	104	–	–
6	131	<0.01	–
15	253	0.46	5.99
32	459	11.6	11.3
41	245	0.67	4.69
56	22	<0.01	0.08
M2: SFP + cotton gin waste (3:4, v:v)			
0	–	–	–
6	88	0.30	1.6
15	167	–	0.97
32	141	2.44	4.02
41	147	4.20	6.04
56	27	<0.01	0.05

can be very relevant for the agronomic value of the composts as fertilisers.

Gaseous emissions of anthropogenic CO_2 and GHGs (N_2O and CH_4) were measured during the thermophilic phase (Table 3), before the second turning (active phase). The main gases generated by the microbial degradation of OM during composting are CO_2 and CH_4, and N_2O is formed through both nitrification and denitrification of the NH_4^+-N and NO_3^--N contained in the composting mixtures, when oxygen is limited (Sánchez-Monedero et al., 2010; Szanto et al., 2007; Kampschreur et al., 2009). Carbon dioxide emissions increased during the first 32 days in M1, which showed higher emissions than M2-associated with the already-discussed intense OM mineralisation caused by the high amount of SFP in M1 (Table 3). The values decreased after 56 days, in both piles. The results are well related to the OM mineralisation (losses of TOC and C_w) and the kinetic parameters of the process (Fig. 2), which indicate maximum OM mineralisation in M1 after 40 days (with the maximum CO_2 emission) and slower OM mineralisation in M2. Similar results were reported by Hao et al. (2004) when composting cattle manure, but higher values were found during sheep manure composting (Sánchez-Monedero et al., 2010) and when SFP was composted without any bulking agent (Pampuro et al., 2014), using the turning system.

Methane is formed in anaerobic microsites that occur inside the piles due to insufficient aeration associated with intense microbial activity and O_2 consumption and/or the compaction of the pile due to its excessive height (Fukumoto et al., 2003; Beck-Friis et al., 2000; Sommer and Moller, 2000). The CH_4 emissions were greatest at 32 days in M1 (Table 3), when microbial activity was intense and the ventilation demand was also high in this pile, indicating high oxygen demand for microbial degradation of the OM. However, the values of CH_4-C were very low in comparison with CO_2-C, indicating that the degradation of the OM occurred in a mainly aerobic environment. The CH_4-C emission values were lower than those found by Hao et al. (2004) and Sánchez-Monedero et al. (2010), during composting of animal manures, and by Pampuro et al. (2014) when SFP was composted without bulking agent using the turning pile system. Only the result on day 32 in M1 was close to the results found by Pampuro et al. (2014). It has been proved that CH_4 is oxidised to CO_2 when air passes through the pile, especially in the Rutgers static composting system – where air is blown from the bottom of the pile (Hao et al., 2001). In the turning system, the CH_4 emission rate decreases immediately after each turning operation (Pampuro et al., 2014), as most of the emissions occur during the turnings. Brown et al. (2008) suggested that the gases present in the interior of the piles were released as the material from the interior was brought to the surface during turning; but, in static systems, diffusion of these gases to the atmosphere through the pile was limited by decomposition of the compounds in the aerated surface section of the pile. In M2, the CO_2-C and CH_4-C values followed a similar pattern but were lower than in M1, although M2 required longer extra ventilation periods than M1. As previously discussed, OM mineralisation was slower in M2 (with a higher proportion of bulking agent) than in M1, indicating that the thermal characteristics of the cotton gin waste conditioned the temperature reached during the process and the heat diffusion by air ventilation (Keener et al., 1993).

The highest CH_4 and N_2O emission rates were found before the first turning in M1 (Table 3), indicating the presence of anaerobic microsites – probably due to pile settlement (in M1, with less bulking agent) that reduced the pore spaces and consequent O_2 availability, although the extra ventilation by temperature demand should have provided an O_2 concentration sufficient to guarantee aerobic conditions. During the composting of the solid fraction of pig slurry with wood chips, Vázquez et al. (2015) found that a low proportion of bulking agent reduced the O_2 concentration in the pile, which could have created anaerobic conditions. The proportion of bulking agent in the mixture and the turning frequency of the pile in a turned windrow system were key factors determining the O_2 concentration inside the composting pile (Vázquez et al., 2015). Substantial CH_4 emissions after the first turning event, during composting of dairy manure, were also reported by Ahn et al. (2011).

Also, as mentioned before, N_2O can be formed through both nitrification and denitrification of NH_4^+-N and NO_3^--N in the material, when the O_2 concentration is limited. The N_2O emissions found before the first turning were much higher than those found by other authors (Hao et al., 2004; Sánchez-Monedero et al., 2010), perhaps due to the high NH_4^+-N concentration provided by the SFP. The most-probable mechanism of N_2O formation was through nitrification, since the nitrate concentration during the bioactive phase was low and NH_4^+-N was the predominant form of inorganic-N. It seems that N_2O emissions were responsible for a relevant fraction of the TN losses. After 41 days, the emissions were reduced drastically, indicating that the turning event supplied the O_2 needed to eliminate anaerobic microsites (emissions of CH_4 and N_2O were not detectable).

3.3. *Compost maturity and quality*

Compost maturity is considered a compost quality indicator (Bernal et al., 1998). In this sense, several parameters have been established to define compost maturity (Bernal et al., 1998, 2009; Itavaara et al., 2002; Benito et al., 2003; Chang and Chen, 2010). Both composts reached adequate values for the maturity indices (Table 4): NH_4^+-N/NO_3^--N ratio < 0.16, C_w concentration $< 10\ g\ kg^{-1}$, C_w/TN ratio < 0.7, water-soluble C/N < 16, CEC > 67 meq 100 g^{-1} OM, CEC/TOC ratio > 1.7 and GI $> 50\%$, all indicative of a good degree of maturation. The only exception was the NH_4^+-N concentration (higher in M1 than in M2), which was slightly higher than the limit value ($<0.4\ g\ kg^{-1}$) established (Zucconi and de Bertoldi, 1987; Bernal et al., 1998). Hence, M1 seems to have required a maturation period longer than two months, due to the high concentration of inorganic-N of the SFP.

Maturation implies the formation of humic-like substances, and the degree of OM humification (HR, HI, PHA and PI) is commonly used as a criterion for compost maturity (Bernal et al., 2009). However, most of the limits established for these parameters were not applicable for all materials, as some authors found that such limits can be reached in early stages of animal manure composting

Table 4
Characterisation of the mature composts obtained from piles M1 and M2 (dry weight basis).

Maturity indices	M1	M2	Agronomic criteria	M1	M2
GI (%)	81.5 ± 4.7	85.0 ± 9.7	pH	6.77 ± 0.02	6.85 ± 0.03
NH_4^+-N (mg kg^{-1})	679 ± 8	466 ± 6	EC (dS m^{-1})	10.70 ± 0.17	10.06 ± 0.25
NH_4^+-N/NO_3^--N	0.08 ± 0.01	0.08 ± 0.01	OM (%)	57.3 ± 0.6	57.2 ± 1.4
C_w (g kg^{-1})	7.0 ± 0.1	7.3 ± 0.8	TOC (g kg^{-1})	303 ± 10	292 ± 8
C_w/TN	0.19 ± 0.01	0.22 ± 0.03	TN (g kg^{-1})	35.4 ± 0.5	31.1 ± 1.1
C_w/N_w	1.05 ± 0.03	1.28 ± 0.13	NH_4^+-N (mg kg^{-1})	679 ± 8.1	466 ± 6.2
C_{ex}	33.8 ± 5.1	24.8 ± 0.8	NO_3^--N (mg kg^{-1})	8932 ± 528	5740 ± 294
C_{ex}/C_w	4.90 ± 0.24	3.20 ± 0.25	C/N ratio	8.56 ± 0.63	9.40 ± 0.14
C_{FA} (g kg^{-1})	16.3 ± 0.4	15.1 ± 0.3	Ca (g kg^{-1})	51 ± 1.0	46 ± 5.3
C_{HA} (g kg^{-1})	17.5 ± 2.5	9.7 ± 1.2	K (g kg^{-1})	22 ± 0.2	22 ± 2.3
CEC (meq 100 g^{-1} OM)	90 ± 1	100 ± 5	Mg (g kg^{-1})	9.32 ± 0.72	7.47 ± 0.99
CEC/TOC ratio	1.89 ± 0.04	1.95 ± 0.02	Na (g kg^{-1})	2.19 ± 0.02	1.88 ± 0.24
HI (%)	5.77 ± 0.38	3.32 ± 0.36	P (g kg^{-1})	15 ± 0.1	11 ± 0.4
HR (%)	11.1 ± 0.1	8.49 ± 0.42	Cd (mg kg^{-1})	0.35 ± 0.01	0.18 ± 0.01
PHA (%)	51.8 ± 2.9	39.0 ± 2.3	Cr (mg kg^{-1})	14 ± 0.1	35 ± 1.8
PI	1.08 ± 0.13	0.64 ± 0.06	Cu (mg kg^{-1})	326 ± 1	262 ± 28
			Fe (mg kg^{-1})	2304 ± 10	2506 ± 466
			Mn (mg kg^{-1})	358 ± 1	292 ± 35
			Pb (mg kg^{-1})	10 ± 1.0	8.5 ± 0.01
			Zn (mg kg^{-1})	947 ± 5	720 ± 67

M1: Solid fraction of pig slurry + cotton gin waste (4:3, v:v); M2: Solid fraction of pig slurry + cotton gin waste (3:4, v:v).
GI: germination index; N_w: water-soluble N; C_{ex}: extractable organic C; C_{HA}: humic acid-like C; C_{FA}: fulvic acid-like C; CEC: cation exchange capacity; HI: humification index; HR: humification ratio; PHA: percentage of humic acids; PI: polymerisation index.

(Bernal et al., 1996, 1998; Paredes et al., 2001). For instance, the C_{HA}:C_{FA} ratio or polymerisation index (PI > 1) was established for city refuse and sewage sludge composting, while the humification index (HI > 30) was established for agro-industrial and farm wastes. The values obtained in M1 were similar to those found by Bustamante et al. (2008) when composting distillery wastes with animal manures, except for the higher HR in M1. In general, the results indicate a good degree of humification of the OM in both composts.

The agronomic quality of the composts was evaluated using the values of chemical parameters relevant to agricultural use. The composts obtained presented pH values close to neutrality, relatively-high concentrations of TOC and TN and high concentrations of macro and micronutrients, providing the essential elements for plant nutrition. Similar results were found for other composts produced from manures (Zhu et al., 2004; Huang et al., 2004) and sewage sludge (Paredes et al., 2001; Fels et al., 2014). The C/N ratio values met the requirements established by the Spanish legislation for composts (<20) (BOE, 2013) and the value considered as a limit for mature composts by several authors (<12: Bernal et al., 2009). However, slightly-high values of moisture content were found, which can be easily reduced during maturation and storage. High values were found for the EC and Cu and Zn concentrations (higher in M1 than in M2 due to the greater proportion of SFP in the former), limiting the quality of the compost (Table 4). The concentrations of Zn and Cu found in mature compost produced from the solid phase of anaerobically-digested pig slurry by Bustamante et al. (2013) were higher than in the present experiment, due to the occurrence of these elements in the pig slurry. No limit has been established for the EC (soluble salts) in compost to be used as fertiliser, because salts can be easily washed away by rainfall after compost application to soil. The Cu and Zn concentrations were above the values suggested for the End-of-waste criteria in Europe (100 and 400 mg kg^{-1}, respectively; JRC and IPTS, 2012), and both composts can be classified as class C (Cu and Zn < 400 and 1000 mg kg^{-1}, respectively) according to the Spanish legislation for fertiliser products (BOE, 2013), which limits their agricultural use to 5 Mg ha^{-1} per year. However, the germination index (GI) was high > 80% – indicating the absence of phytotoxicity. Considering an application limited to 5 t/ha, the annual input of Cu and Zn to the soil would be, respectively, 1.63 and 4.75 kg ha^{-1} with compost M1 and 1.31 and 3.6 kg ha^{-1} with M2. These amounts are well below the limit values for the quantities of metals introduced annually into the soil (12 and 30 kg ha^{-1} of Cu and Zn, respectively) established by the European Union for the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (Directive 86/278/CEE; CEE, 1986). These elements are supplied to pigs to prevent several diseases and to improve growth (Zhang et al., 2012), and are later recovered in the pig slurry and concentrated in the solid phase after solid–liquid separation. Therefore, to ensure a compost of acceptable agricultural quality derived from pig slurry, the first action required is to reduce the amount of Cu and Zn at the origin – the amount supplied to the animals. Then, a management strategy at the farm/production system level – based on selection of the SFP with low metal contents for composting – should be implemented, using other recycling treatments for the metal-rich pig slurry.

4. Conclusions

The temperature evolution during the SFP composting process has been shown to rely on the thermal properties of the bulking agent, while the gaseous emissions were very well related to the OM degradation process. The use of cotton gin waste as bulking agent balanced the excessive moisture of the SFP, favouring good development of the composting process, as shown by the thermal profiles. An increase in the proportion of cotton gin waste led to higher temperatures and ventilation demand, prolonging the thermophilic phase, due to the thermal properties of the cotton gin waste. With the higher proportion of bulking agent, the energy generated by the microbial activity was quickly and efficiently converted into heat in the composting mass, requiring high aeration for thermal diffusion and therefore a high energy cost for management. The higher proportion of bulking agent reduced gaseous emissions during composting, especially of CO_2, CH_4 and N_2O. However, total-N losses were greater in the pile with the higher proportion of bulking agent, since the intense aeration required to maintain the ceiling temperature favoured ammonia emissions. Based on the process performance, the 4:3 proportion of SFP:bulking agent (v/v) was the most adequate for composting the

SFP, giving a compost with high OM humification and nutrient concentrations. However, the production of quality compost at the industrial or farm level will be conditioned by the concentration of Cu and Zn in the pig slurry. Increasing the proportion of bulking agent has a dilution effect on such elements in the compost, but the process will have a greater energy cost for aeration of the composting mass. The use of SFP with low Cu and Zn concentrations will be the best way to ensure the production of high-quality compost appropriate for commercial use.

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References

Ahn, H.K., Mulbry, W., White, J.W., Kondrad, S.L., 2011. Pile mixing increases greenhouse gas emissions during composting of dairy manure. Bioresour. Technol. 102, 2904–2909.

Ahn, H.K., Sauer, T.J., Richard, T.L., Glanville, T.D., 2009. Determination of thermal properties of composting bulking materials. Bioresour. Technol. 100, 3974–3981.

Beck-Friis, B., Pell, M., Sonesson, U., Jönsson, H., Kirchmann, H., 2000. Formation and emission of N_2O and CH_4 from compost heaps of organic household waste. Environ. Monit. Assess. 62, 317–331.

Benito, M., Masaguer, A., Moliner, A., Arrigo, N., Palma, R.M., 2003. Chemical and microbiological parameters for the characterisation of the stability and maturity of pruning waste compost. Biol. Fert. Soils 37, 184–189.

Bernal, M.P., Alburquerque, J.A., Moral, R., 2009. Composting of animal manures and chemical criteria for compost maturity assessment. A review. Bioresour. Technol. 100, 5444–5453.

Bernal, M.P., Lopez-Real, J.M., Scott, K.M., 1993. Application of natural zeolites for the reduction of ammonia emissions during the composting of organic wastes in a composting simulator. Bioresour. Technol. 43, 35–39.

Bernal, M.P., Navarro, A.F., Roig, A., Cegarra, J., García, D., 1996. Carbon and nitrogen transformation during composting of sweet sorghum bagasse. Biol. Fert. Soils 22, 141–148.

Bernal, M.P., Paredes, C., Sánchez-Monedero, M.A., Cegarra, J., 1998. Maturity and stability parameters of compost prepared with a wide range of organic wastes. Bioresour. Technol. 63, 91–99.

BOE, 2013. Real Decreto 506/2013, de 28 de junio, sobre productos fertilizantes. Boletín Oficial del Estado 164, 51119–51207.

Brown, S., Kruger, C., Subler, S., 2008. Greenhouse gas balance for composting operations. J. Environ. Qual. 37, 1396–1410.

Burton, H., Turner, C., 2003. Treatment strategies for sustainable agriculture. Manure Management, second ed. Silsoe Research Institute, Lister and Durling Printers, Flitwick, Bedford, UK.

Bustamante, M.A., Paredes, C., Marhuenda-Egea, F.C., Pérez-Espinosa, A., Bernal, M.P., Moral, R., 2008. Co-composting distillery wastes with animal manure: carbon and nitrogen transformations and evaluation of compost stability. Chemosphere 72, 551–557.

Bustamante, M.A., Restrepo, A.P., Albuquerque, J.A., Pérez-Murcia, M.D., Paredes, C., Moral, R., Bernal, M.P., 2013. Recycling of anaerobic digestates by composting: effect of the bulking agent used. J. Clean. Prod. 47, 61–69.

CARM, 2015. Estadística Agraria de Murcia: Producciones ganaderas – serie histórica. Available at: http://www.carm.es/web/pagina?IDCONTENIDO=1377&IDTIPO=100&RASTRO=c1355$m1174 (June, 2015).

CEE, 1986. Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). Off. J. Eur. Commun L 181, 6–12.

Chang, J.I., Chen, Y.J., 2010. Effects of bulking agents on food waste composting. Bioresour. Technol. 101, 5917–5924.

Charest, M.H., Antoum, H., Beauchamp, C.J., 2004. Dynamics of water-soluble carbon substances and microbial populations during the composting of de-inking paper sludge. Bioresour. Technol. 91, 53–67.

Doublet, J., Francou, C., Poitrenaud, M., Houot, S., 2010. Sewage sludge composting: influence of initial mixtures on organic matter evolution and N availability in the final composts. Waste Manage. 30, 1922–1930.

European Commission, 2001. Working Document. Biological Treatment of Biowaste, 2nd Draft. Available at: http://europa.eu.int/comm/environment/waste/facts_en.htm.

Eurostat, 2015. Available at: http://ec.europa.eu/eurostat (June 2015).

Fels, L., Zamama, M., Asli, A., Hafidi, M., 2014. Assessment of biotransformation of organic matter during co-composting of sewage sludge-lignocellulosic waste by chemical, FTIR analyses, and phytotoxicity tests. Int. Biodeter. Biodeg. 87, 128–137.

Flotats, X., Bonmatí, A., Fernández, B., Magrí, A., 2009. Manure treatment technologies: on farm versus centralized strategies. NE Spain as case study. Bioresour. Technol. 100, 5519–5526.

Francescato, V., Antonini, E., Ziccoli, L., 2008. Wood Fuel Handbook. In: Production, Quality Requirements, Trading. AIEL- Italian Agroforestry Energy Association, Legnano, Italy.

Fukumoto, Y., Osada, T., Hanajima, D., Haga, K., 2003. Patterns and quantities of NH_3, N_2O and CH_4 emissions during swine manure composting without forced aeration—effect of compost pile scale. Bioresour. Technol. 89, 109–114.

Georgacakis, D., Tsavdaris, A., Bakouli, J., Symeonidis, S., 1996. Composting solid swine manure and lignite mixtures with selected plant residues. Bioresour. Technol. 56, 195–200.

Hao, X., Chang, C., Larney, F.J., 2004. Carbon, nitrogen balances and greenhouse gas emission during cattle feedlot manure composting. J. Environ. Qual. 33, 37–44.

Hao, X., Chang, C., Larney, F.J., Travis, G.R., 2001. Greenhouse gas emissions during cattle feedlot manure composting. J. Environ. Qual. 30, 376–386.

Haug, R.T., 1993. The Practical Handbook of Compost Engineering. Lewis Publishers, Boca Raton, FL.

Huang, G.F., Fang, M., Wu, Q.T., Zhou, L.X., Liao, X.D., Wong, J.W.C., 2001. Co-composting of pig manure with leaves. Environ. Technol. 22, 1203–1212.

Huang, G.F., Wong, J.W.C., Wu, Q.T., Nagar, B.B., 2004. Effect of C/N on composting of pig manure with sawdust. Waste Manag. 24, 805–813.

INE, 2015. Instituto Nacional de Estadística. Available at: http://ine.es (June 2015).

Itavaara, M., Venelampi, O., Vikman, M., Kapanen, A., 2002. Compost maturity – problems associated with testing. In: Insam, H., Riddech, N., Klammer, S. (Eds.), Microbiology of Composting. Springer, Heidelberg, pp. 373–382.

JRC, IPTS, 2012. Technical Report for End-of-waste Criteria on Biodegradable Waste Subject to Biological Treatment, 3rd Working Document. Available at: http://susproc.jrc.ec.europa.eu/activities/waste/documents/IPTS_EoW_Biodegradable_waste_3rd_working_document_wo_line_nr.pdf.

Kampschreur, M.J., Poldermans, R., Kleerebezem, R., van der Star, W.R.L., Haarhuis, R., Abma, W.R., Jetten, M.S.M., van Loosdrecht, M.C.M., 2009. Emission of nitrous oxide and nitric oxide from a full-scale single-stage nitritation-anammox reactor. Water Sci. Technol. 60, 3211–3217.

Keener, H.M., Marugg, C., Hansen, R.C., Hoitink, H.A.J., 1993. Optimizing the efficiency of the composting process. In: Hoitink, H.A.J., Keener, H.M. (Eds.), Science and Engineering of Composting. Renaissance Publications, Worthington, Ohio, pp. 59–94.

Lax, A., Roig, A., Costa, F., 1986. A method for determining the cation-exchange capacity of organic materials. Plant Soil 94, 349–355.

Moral, R., Perez-Murcia, M.D., Perez-Espinosa, A., Moreno-Caselles, J., Paredes, C., 2005. Estimation of nutrient values of pig slurries in Southeast Spain using easily determined properties. Waste Manag. 25, 719–725.

Moreno, J., Moral, R., 2008. Compostaje. Ediciones Mundi-Prensa, Madrid. Madrid.

Navarro, A.F., Cegarra, J., Roig, A., Bernal, M.P., 1991. An automatic microanalysis method for the determination of organic carbon in wastes. Commun. Soil Sci. Plant Anal. 22, 2137–2144.

Nolan, T., Troy, S.M., Healy, M.G., Kwapinski, W., Leahy, J.J., Lawlor, P.G., 2011. Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. Bioresour. Technol. 102, 7131–7138.

Pampuro, N., Dinuccio, E., Balsari, P., Cavallo, E., 2014. Gaseous emissions and nutrient dynamics during composting of swine solid fraction for pellet production. Appl. Math. Sci. 129, 6459–6468.

Pardo, G., Moral, R., Aguilera, E., del Prado, A., 2015. Gaseous emissions from management of solid waste: a systematic review. Glob. Change Biol. 21, 1313–1327.

Paredes, C., Bernal, M.P., Roig, A., Cegarra, J., Sánchez-Monedero, M.A., 1996. Influence of bulking agent on the degradation of olive-mill wastewater sludge during composting. Int. Biodeter. Biodegr. 38, 205–210.

Paredes, C., Bernal, M.P., Roig, A., Cegarra, J., 2001. Effects of olive mill wastewater addition in composting of agroindustrial and urban wastes. Biodegradation 12, 225–234.

Qian, X., Shen, G., Wang, Z., Guo, C., Liu, Y., Lei, Z., Zhang, Z., 2014. Co-composting of livestock manure with rice straw: characterization and establishment of maturity evaluation system. Waste Manage. 34, 530–535.

Ros, M., Garcia, C., Hernández, T., 2006. A full-scale study of treatment of pig slurry by composting: kinetic changes in chemical and microbial properties. Waste Manage. 26, 1108–1118.

Sánchez-Monedero, M.A., Bernal, M.P., Roig, A., Cegarra, J., García, D., 1996. The effectiveness of the Rutgers system and the addiction of bulking agent in reducing N-losses during composting. In: Van Cleemput, O., Hofman, G., Vermoesen, A. (Eds.), Progress in Nitrogen Cycling Studies. Kluwer, Netherlands, pp. 133–139.

Sánchez-Monedero, M.A., Roig, A., Paredes, C., Bernal, M.P., 2001. Nitrogen transformation during organic waste composting by the Rutgers system and its effects on pH, EC and maturity of the composting mixtures. Bioresour. Technol. 78, 301–308.

Sánchez-Monedero, M.A., Serramiá, N., Civantos, C.G., Fernández-Hernández, A., Roig, A., 2010. Greenhouse gas emissions during composting of two-phase olive mill wastes with different agroindustrial by-products. Chemosphere 81, 18–25.

Santos, A., Bustamante, M.A., Moral, R., Bernal, M.P., 2014. Carbon conservation strategy for the management of pig slurry by composting: initial study of the bulking agent influence. Mitig. Adapt. Strateg. Glob. Chang. http://dx.doi.org/10.1007/s11027-014-9593-0 (in press).

Sommer, S.G., Christensen, M.L., Schmidt, T., Jensen, L.S., 2014. Animal Manure Recycling: Treatment and Management. Wiley, Chichester, UK.

Sommer, S.G., Kjellerup, V., Kristjansen, O., 1992. Determination of total ammonium nitrogen in pig and cattle slurry: sample preparation and analysis. Acta Agric. Scand. Sect. B, Soil Plant Sci. 42, 146–151.

Sommer, S.G., McGinn, S.M., Hao, X., Larney, F.J., 2004. Techniques for measuring gas emissions from a composting stockpile of cattle manure. Atmos. Environ. 38, 4643–4652.

Sommer, S.G., Møller, H.B., 2000. Emission of greenhouse gases during composting of deep litter from pig production effect of straw content. J. Agric. Sci. 134, 327–335.

Szanto, G.L., Hamelers, H.V.M., Rulkens, W.H., Veeken, A.H.M., 2007. NH_3, N_2O and CH_4 emissions during passively aerated composting of straw-rich pig manure. Bioresour. Technol. 98, 2659–2670.

Tarre, S., Green, M., 2004. High-rate nitrification at low pH in suspended- and attached-biomass reactors. Appl. Environ. Microbiol. 70, 6481–6487.

Tiquia, S.M., Richard, T.L., Honeyman, M.S., 2002. Carbon, nutrient, and mass loss during composting. Nutr. Cycl. Agroecosys 62, 15–24.

Tortosa, G., Albuquerque, J.A., Ait-Baddi, G., Cegarra, J., 2012. The production of commercial organic amendments and fertilisers by composting of two-phase olive mill waste ("alperujo"). J. Clean. Prod. 26, 48–55.

Troy, S.M., Nolan, T., Kwapinski, W., Leahy, J.J., Healy, M.G., 2012. Effect of sawdust addition on composting of separated raw and anaerobically digested pig manure. J. Environ. Manage. 111, 70–77.

Vanotti, M., Millner, P., Szogi, A., Campbell, C., Fetterman, L., 2006. Aerobic composting of swine manure solids mixed with cotton gin waste. In: ASAE Annual Meeting. Paper number 064061 2006.

Vázquez, M.A., de la Varga, D., Plana, R., Soto, M., 2015. Integrating liquid fraction of pig manure in the composting process for nutrient recovery and water re-use. J. Clean. Prod. 104, 80–89.

Vinneras, B., 2013. Sanitation and hygiene in manure management. In: Sommer, S.G., Christensen, M.L., Schmidt, T., Jensen, L.S. (Eds.), Animal Manure Recycling: Treatment and Management. Wiley Publishing, West Sussex, pp. 91–104.

Yañes, R., Alonso, J.L., Díaz, M.J., 2009. Influence of bulking agent on sewage sludge composting process. Bioresour. Technol. 100, 5827–5833.

Zabaniotou, A.A., Skoulou, V.K., Koufodimos, G.S., Samaras, Z.C., 2007. Investigation study for technological application of alternative methods for the energy exploitation of biomass/agricultural residues in Northern Greece. Therm. Sci. 11, 125–134.

Zhang, F.S., Li, Y.X., Yang, M., Li, W., 2012. Content of heavy metals in animal feeds and manures from farms of different scales in northeast China. Int. J. Environ. Res. Pub. Health 9, 2658–2668.

Zhu, N., Deng, C., Xiong, Y., Qian, H., 2004. Performance characteristics of three aeration systems in the swine manure composting. Bioresour. Technol. 95, 319–326.

Zucconi, F., de Bertoldi, M., 1987. Compost specifications for the production and characterization of compost from municipal solid waste. In: de Bertoldi, M., Ferranti, M.P., L'Hermite, P., Zucconi, F. (Eds.), Compost: Production, Quality and Use. Elsevier, Barking, pp. 30–50.

Zucconi, F., Pera, A., Forte, M., de Bertoldi, M., 1981. Evaluating toxicity of immature compost. Biocycle 22, 54–57.

3.3 Sustainable management of pig slurry using different composting scenarios: assessment of the organic matter changes.

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Sustainable management of pig slurry using different composting scenarios: assessment of the organic matter changes

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Highlights

Thermal analysis, IR-TF and NMR can be used to assess OM changes during composting.

FT-IR, useful technique to follow OM biotransformations by ‘signaling’ compounds.

NMR and FT-IR showed powerful capacities to understand the evolution of C pools.

Composting system effect on OM changes was only detected by these techniques.

Abstract

In this work, the association of different analytical techniques (thermal analysis, ^{13}C cross polarization magic angle spinning (CPMAS) NMR and Fourier transform infrared (FT-IR) spectroscopy) has been used to study the organic matter changes during the co-composting of pig slurry with cotton gin waste, developed in several scenarios, with different proportions of the raw materials and different type of composting system used. Also, the thermal stability index (R1) has been determined before and after a water-extraction method to eliminate water-soluble inorganic salts, to evaluate the effect of this procedure in the samples prior to thermal analysis. The results of the thermal methods showed the degradation of the most labile organic matter during composting; R1 increased in all cases, without showing any influence on the presence of water-soluble inorganic ions in the sample. NMR showed during composting a decrease of the carbohydrate molecules and an increase of the aliphatic materials due to a concentration effect. Also, FT-IR spectroscopy was a useful technique to study the trend of polysaccharides and nitrates as compounds indicative of organic matter transformations during composting.

Keywords: pig slurry, organic matter, compost, ^{13}C-NMR, FT-IR, thermal analysis.

1. Introduction

In Europe, during the last 20 years, pig farms have been increasing in size, concentrating the activity in certain areas (Burton et al., 2003), which frequently leads to an accumulation of manure in areas without enough agricultural land for its recycling in the soil-plant system. Pig slurry is rich in organic matter (OM) and beneficial plant nutrients, mainly nitrogen and phosphorous (Moral et al., 2005), but also it presents several characteristics, such as pathogens and unpleasant odours, among others, which limit its direct agricultural use, and safe transport to land.

Composting is a friendly environmental and economical alternative and a value enhancement strategy for treating organic wastes, also obtaining a stabilised, mature, deodorised, hygienic product, free of pathogens and plant seeds, and rich in humic substances that is easy to store and marketable as organic amendment or fertiliser (Bernal et al., 2009). However, compost quality and stability strongly depend on the properties of the raw materials, the time of composting and the oxidative conditions of treatment, which influence microbial activities, resulting in different degrees of degradation and transformation of the initial organic mixtures (Fuentes et al., 2007). Therefore, the understanding of organic matter transformations throughout the composting process is an essential aspect for successful utilisation of composts.

During composting, labile organic compounds, such as simple carbohydrates, fats and aminoacids, are degraded quickly in the first stage of composting; other, more resistant organic substrates, such as cellulose, hemicellulose and lignin are partially degraded and transformed at a lower rate. Therefore, composting involves a partial mineralisation of the organic substrate, leading to carbon losses throughout the process; this is compensated by the high stabilisation degree of the remaining organic compounds (Bernal et al., 2009). Also, during the humification process, singular structural changes and features occur, these changes being classically attributed to increases in aromatic content in humic substances, although other studies have shown that the accumulation of recalcitrant aliphatic structures also takes place during composting (Almendros et al., 2000). This shows that the evaluation of the real degree of the organic matter evolution during composting is complicate and requires a wide and complete knowledge of the processes and of the factors that condition the transformation of the organic matter. Therefore, the association of thermal and spectral techniques can be an accurate way to complement the chemical methods and to provide a precise knowledge of the processes involved during the changes that organic matter undergo throughout the composting process.

Thermal analysis (TA) has been proposed as a method to characterise the organic matter of composted materials and of humic and fulvic acids of different origin and nature (Drussi et al., 2009; De Oliveira et al., 2002), as well as of biomass (Mothè et al., 2009; Dos Reis Orsini et al. 2011) and soil organic matter (Barros et al., 2011; Fernández et al., 2011). Thermal techniques, such as thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA), have been applied as a reproducible, informative and rapid, low-cost and small-sample consuming method to elucidate structural features of heterogeneous organic matter (Smidt and Lechner, 2005), providing important information about the chemical characteristics of the sample and about the progressive biodegradation of biopolymers during the compost process (Provenzano et al., 2000; Otero et al., 2002). However, several interferences related to the catalytic role of ammonia salts should be taking in to account. In this sense, Blanco and Almendros (1994) suggested comparative studies with bulk and washed samples.

Solid-state ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic angle spinning (CPMAS NMR) has a great strength to provide information about the carbon molecules in a complex sample without any chemical or physical fractionation (Preston, 1996; Preston et al., 1998). This technique can be used to detect C types, such as carbohydrates and alkyl, aromatic, or carboxyl carbons for complex samples (Almendros et al., 2000; Pichler et al., 2000; Chen, 2003; Castaldi et al., 2005; Tang et al., 2006; Gómez et al., 2007). The integration of the CP-MAS spectra of the compost samples showed that the modification of the carbon distributions is related to the transformation of the organic matter during the composting process. The fundament of FT-IR is the interaction of infrared light with matter, and it is sensitive to the chemical functional groups present in the sample (Smith, 1999).

FT-IR has similar advantages respect the sample preparation and relatively lower cost than thermal analysis.

Therefore, this study aimed to evaluate the efficiency of the association of thermal analysis and spectral techniques to identify organic matter changes throughout the management of pig slurry by co-composting with cotton gin waste in different conditions, according to the proportion of the raw materials and to the type of composting system used.

2. Materials and methods

2.1. Experimental procedure

Three piles (P1, P2 and P3) were prepared using the solid fraction of pig slurry (SFP) coming from two different pig farms, and cotton gin waste (CW) as bulking agent, using different composting systems (static pile with forced aeration and turning composting system). The SFP of P1 and P2 was collected from a fattening farm located in Orihuela (Alicante, Spain) (SFP1) and that of P3 (SFP2), from a sows and piglets farm in Guazamara (Almería, Spain), after a solid-liquid separation using a screw-press (without flocculants) in both cases, and CW was collected from a cotton industry in Seville (Spain). The main characteristics of the starting materials were: moisture 76.5%, pH 7.4, 1.26 dS m^{-1} for EC, 69.4% OM, 33.5% total organic carbon (TOC) and 1.90% total nitrogen (TN), for SFP1; moisture 85.8%, pH 6.8, 3.00 dS m^{-1} for EC, 80.5% OM, 39.0% TOC and 2.84 % TN, for SFP2; and moisture 8.2%, pH 7.6, 3.80 dS m^{-1} for EC, 81.0% OM, 40.7% TOC and 2.18% TN, for CW.

The piles P1, P2 and P3 were elaborated in the proportions of SFP:CW (v:v, fresh mass basis): 4:3, 3:4 and 3:1, respectively, in order to compost the maximum weight of SFP with a sufficient amount of CW, as bulking agent. Piles P1 and P2 (2000 kg fresh weight) were composted by the Rutgers static pile composting system, with forced aeration on temperature demand, which maintains a temperature ceiling (65 ºC) in the pile, involving on-demand ventilation through temperature feedback control. In P1 and P2, the bio-oxidative phase lasted for 103 days and during this period, both piles were turned twice, when the temperature inside the piles started to decrease, in order to homogenize the mixture and improve the composting process (Figure 1).

The mixture P3 was elaborated using the turning system in a trapezoidal pile (19.2 m^3) in the pig farm. Thermophilic temperatures occurred during 70 days, reaching values higher than 60ºC (Figure 1). The bio-oxidative phase lasted for 146 days, during which the pile was turned five times.

In all piles, the bio-oxidative phase of composting was considered finished when the temperature of the piles was stable and near to that of the atmosphere. Then, all the piles were allowed to mature for 2 months. The moisture of the piles was controlled weekly by adding the necessary amount of water to keep the moisture at a value > 40 %. The samples were taken by mixing seven sub-samples from seven sites of the pile, from the whole profile (from the top to the bottom of the pile). The sampling was made at the beginning of the process at day 0 (initial sample – I), two times at the thermophilic phase (beginning – BT and advanced thermophilic – T), at the end of the bio-oxidative phase (EB) and after the maturation period (M).

2.2. Chemical analysis

Total organic carbon (TOC) and total-N (TN) were determined by automatic microanalysis. Organic matter (OM) was calculated by loss-on ignition at 550 ºC for 24 h. Water-soluble organic carbon (C_w) was determined in a water extract of 1:10 (w/v), after filtration through a synthetic filter with a pore diameter of 0.45 µm, by using an automatic analyzer for liquid samples (TOC-V CSN Analyzer, Shimadzu). Humic-like fractions (0.1 mol L^{-1} NaOH-extractable organic carbon (C_{EX}), fulvic acid-like carbon (C_{FA}), and humic acid-like carbon (C_{HA}) were also determined, using an automatic carbon analyzer for liquid samples (TOC-V CSN Analyzer, Shimadzu). The humification ratio (HR), the humification index (HI), the percentage of humic acid-like carbon (P_{HA}) and the polymerization index (P_I) were calculated as (C_{EX}/Corg) × 100; (C_{HA}/Corg) × 100 and (C_{HA}/C_{EX}) × 100 and C_{HA}/C_{FA}, respectively. All parameters were determined in triplicate and according to the methods described in Bustamante et al. (2012).

2.3. Thermal and spectral analysis

Samples were air-dried, ground in an agate mill, then sieved through a 0.125 mm mesh, and milled again with a mortar with liquid N_2. Thermal analyses were performed with a Mettler Toledo (TGA/SDTA851e/LF/1600) and Pfeiffer Vacuum (Thermostar GSD301T) mass spectrometer that enables the recording of thermograms and mass spectra of combustion gases simultaneously. All samples were combusted with a mixing stream of oxygen/He (20/80%), a gas flow 100 ml min^{-1} within a temperature range from 25 to 650 °C, a heating rate 10 °C min^{-1}, a sample weight about 6-7 mg, Al_2O_3 pan, and self-controlled calibration.

In order to evaluate the effect of removing the compost water-soluble fraction in thermal analysis (Blanco and Almendros, 1994), 1 g of compost was suspended in 20 ml of water overnight with shaking. After centrifugation, the compost insoluble fraction was dried and ground in an agate mortar. Thermal analyses were carried out with the original compost samples and with the compost samples after the water-extraction process of the soluble fraction.

CPMAS ^{13}C NMR experiments were performed on a Bruker Advance DRX500 operating at 125.75 MHz for ^{13}C. Samples were packed into a 4 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 10000 ± 100 Hz. A conventional CPMAS pulse sequence (Wilson, 1987) was used with a 1.0 ms contact time. Between 2000 and 5000 scans were accumulated with a pulse delay of 1.5 s. Line broadening was adjusted to 50 Hz. Spectral distributions (the distribution of total signal intensity among various chemical shift ranges) were calculated by integrating the signal intensity in seven chemical shift regions: carbonyl (210−165 ppm), O-aromatic (165−145 ppm), aromatic (145−110 ppm), O_2-alkyl (110−95 ppm), O-alkyl (95−60 ppm), N-alkyl/methoxy (60−45 ppm), and alkyl (45 to −10 ppm) (Nelson and Baldock, 2005). The labels indicate only major types of C found in each region.

The FT-IR spectra were collected on a Bruker IFS 66 spectrometer. The resolution was set to 4 $cm^{-1,}$ and the operating range was 400−4000 cm^{-1}. Samples (7−10 mg) were mixed with 100 mg of dried KBr, and then the mixture was pressed into pellets. In all cases, 20 scans per sample were recorded, averaged for each spectrum, and corrected against the spectrum with ambient air as background.

2.4. Statistical analysis

The one-way analysis of variance (ANOVA) and least significant difference (LSD) test at $P < 0.05$ were used to assess the significant differences among the values of each parameter studied during composting. The two-way analysis of variance (two-way ANOVA) and Tukey HSD test ($p<0.05$) were used to assess the significant differences among the results of thermal analysis (T50 and R1) throughout the process. Normality and homogeneity of the variances were checked using the Shapiro-Wilk and Levene test, respectively, before ANOVA. The standard error of the mean values of each parameter was also determined. Also, the Pearson regression analysis was carried out between the thermostability index (R1) and classical parameters (OM, TOC, Cw, TN and TOC/TN ratio) usually used to study organic matter changes during composting. Data analysis was carried out using the SPSS v. 19.0 statistical software package.

3. Results and discussion

3.1 Development of the composting process

All the piles showed a typical composting temperature profile, reaching thermophilic temperatures (> 40ºC) during the first two weeks of composting, due to the microbial proliferation, and maintaining the thermophilic phase during more than two months (Fig. 1). For P1 and P2, the thermophilic phase was longer and the temperature values > 40 ºC were reached faster than in P3. Several studies of composting of manures have reported the lack of differences in the temperature profile due to the type of composting system used (Solano et al., 2001). Then, the differences observed could be due to the different characteristics of the solid fraction of pig slurry used, such as the initial highest moisture concentration of P3 (72.5 %), with respect to P1 (46.7 %) and P2 (63.7 %), which could have influenced the porosity and aeration of the mixture.

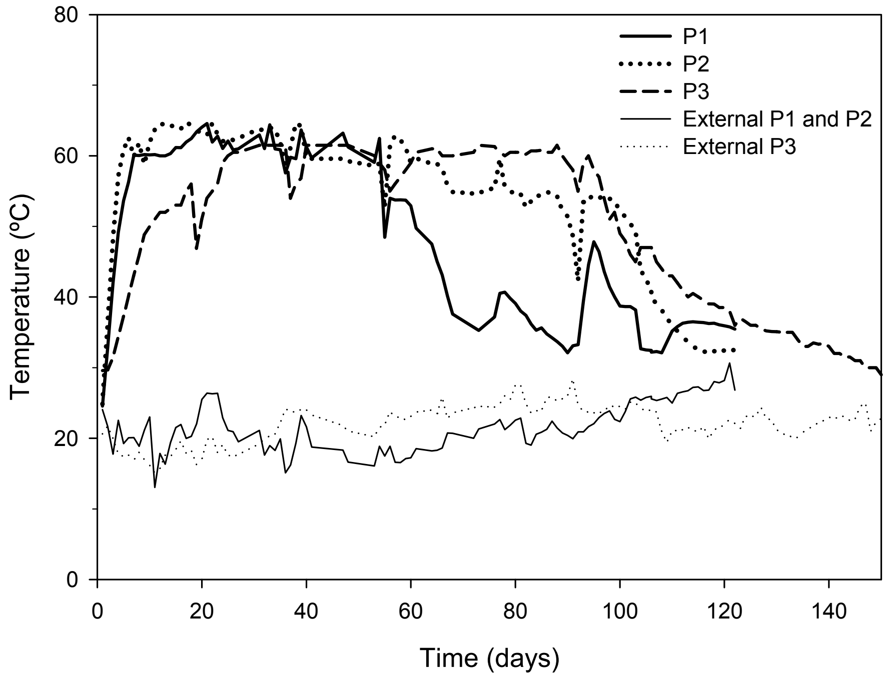

Figure 1 – Temperature profiles during composting of P1 [solid fraction of pig slurry + cotton gin waste (4:3, v:v)]; P2 [solid fraction of pig slurry + cotton gin waste (3:4, v:v)] and P3 [solid fraction of pig slurry + cotton gin waste (3:1, v:v)].

During composting, the OM concentration decreased 28%, 22% and 17 % in P1, P2 and P3, respectively, due to the microbial degradation of the labile organic compounds (Table 1). These led to OM losses (calculated by mass balance, taking into account the weight loss of the pile) that reached 64.4%, 50.5% and 54.7 % of OM in P1, P2 and P3, respectively. Most of the OM losses occurred at the beginning of the process, with the highest temperature values, which is indicative of the rapid decomposition of the readily biodegradable substrates and a high rate of microbial activity (Bustamante et al., 2012). Afterwards, a second stage was observed with low rate of OM loss, indicating the most resistant compounds to microbial activity degradation, such as polymers like lignin, remained in the mixture, which suggests that the OM content in the product became highly stabilised. This behaviour in OM degradation during composting of animal manure has been frequently observed in other studies (Paredes et al., 2000; Bustamante et al., 2012; Brito et al., 2012).

The concentrations of TOC and C_w decreased as the composting process progressed (Table 1). According to Bernal et al. (2009), TOC tends to decrease during composting due to the mineralisation of the OM caused by microbial degradation of the most labile forms of TOC, such as C_w. Similar results were reported by Nolan et al. (2011) and Szanto et al. (2007) when composting the solid fraction of pig slurry with several bulking agents. Furthermore, an increase of 49, 16 and 33 % in the TN concentration was found for P1, P2 and P3, respectively, during the composting period. This increase can be due to a concentration effect caused by the reduction of the compost mass and/or N-immobilisation processes (Bustamante et al., 2012). Similar results were found by Huang et al. (2001) when composting the pig slurry with leaves, where an increase in TN concentration was observed throughout the composting process. Then, the TOC/TN ratio decreased during the composting process, with the values reaching the limit value < 12, indicative of an acceptable degree of maturity (Bernal et al., 2009).

Several parameters, such as the concentrations of the different C fractions (C_{EXT}, C_{HA} and C_{FA}) and the humification indices (HI, HR, P_{HA}, P_I) have been used in different studies to evaluate organic matter humification and compost maturity (Bernal et al., 2009). The composts obtained from P1 and P3 showed higher concentrations of C_{HA} than the compost from P2 (P1= 17.5 g kg^{-1}, P2 = 9.7 g kg^{-1} and P3 = 18.1 g kg^{-1}), while the lowest concentration of C_{FA} occurred in P3 (P1= 16.3 g kg^{-1}, P2 = 15.1 g kg^{-1} and P3 = 11.3 g kg^{-1}).

Regarding the humification indices, the highest values of these parameters were also observed in the composts with the highest proportion of SFP, P1 and P3 (HR: 10.7%, 9.27%, 10.2% for P1, P2 and P3, respectively; HI: 5.78%, 3.61% and 6.27% for P1, P2 and P3, respectively; P_{HA}: 54.2%, 39.0% and 61.3%, for P1, P2 and P3; P_I: 1.08, 0.64 and 1.60 for P1, P2 and P3, respectively). However, all the composts showed values of these parameters higher than those established by different authors as indicative of compost maturity (Bernal et al., 2009).

Table 1 – Evolution of organic matter (OM), total organic carbon (TOC), water-soluble carbon (C_w), total nitrogen (TN) and total organic carbon to total nitrogen ratio (TOC/TN) of the piles during composting.

Composting phase	**Days**	**OM (%)**	**TOC ($g\ kg^{-1}$)**	**C_w ($g\ kg^{-1}$)**	**TN ($g\ kg^{-1}$)**	**TOC/TN**
Pile 1: solid fraction of pig slurry + cotton gin waste (4:3, v:v)						
I	0	79.1 ± 0.8	363 ± 3	27.5 ± 0.7	24.2 ± 0.6	18.6 ± 0.6
BT	15	69.1 ± 1.0	355 ± 13	21.3 ± 1.3	29.7 ± 2.6	13.8 ± 1.2
T	56	62.1 ± 0.8	336 ± 13	14.9 ± 0.1	32.1 ± 4.1	10.9 ± 1.3
EB	103	56.7 ± 0.6	311 ± 14	7.8 ± 0.2	34.0 ± 0.6	9.3 ± 0.3
M	167	57.3 ± 0.6	303 ± 10	7.0 ± 0.1	36.1 ± 0.5	8.6 ± 0.3
LSD		*2.46*	*36.7*	*1.18*	*4.42*	*1.83*
Pile 2: solid fraction of pig slurry + cotton gin waste (3:4, v:v)						
I	0	73.3 ± 0.9	357 ± 6	24.7 ± 0.3	27.0 ± 0.3	16.2 ± 0.4
BT	15	70.9 ± 0.8	333 ± 5	21.1 ± 2.0	25.3 ± 1.5	14.6 ± 1.2
T	56	56.2 ± 1.7	308 ± 7	18.0 ± 2.0	28.4 ± 0.6	11.1 ± 0.5
EB	103	57.3 ± 1.2	298 ± 11	8.1 ± 1.0	33.2 ± 0.7	9.1 ± 0.4
M	167	57.2 ± 1.4	292 ± 8	7.3 ± 0.8	31.5 ± 1.1	9.4 ± 0.3
LSD		*4.86*	*44.4*	*1.82*	*5.23*	*2.77*
Pile 3: solid fraction of pig slurry + cotton gin waste (3:1, v:v)						
I	0	76.6 ± 0.3	383 ± 1	30.9 ± 0.5	21.1 ± 2.8	18.2 ± 0.4
BT	41	69.2 ± 0.6	367 ± 14	21.7 ± 0.4	24.0 ± 0.2	15.3 ± 0.3
T	76	65.4 ± 0.4	348 ± 10	16.8 ± 0.8	29.8 ± 1.0	11.7 ± 1.4
EB	146	60.5 ± 0.2	293 ± 7	9.3 ±0.7	30.5 ± 0.9	9.7 ± 0.7
M	187	59.7 ± 0.7	288 ± 3	7.5 ± 0.6	28.1 ± 0.7	10.3 ± 0.8
LSD		*1.69*	*11.1*	*1.01*	*3.60*	*2.82*

I: initial phase of composting; BT: beginning of the thermophilic phase; T: advanced thermophilic phase; EB: end of the bio-oxidative phase; M: maturity phase.
Values reported as mean ± standard error. LSD: Least significant difference at P<0.05.

3.2 Thermal analysis

The TG curves (Figure 2) showed the typical combustion process of organic matter in a compost sample (Blanco and Almendros, 1994; Smidt and Lechner, 2005; Marhuenda-Egea et al., 2007). All the piles had a similar behaviour in the combustion process between 25 ºC and 600 ºC, showing an increase in the percentage of the inorganic residual fraction after the combustion process, related to the time of composting, also coinciding with the OM decrease (Table 1). The increase of the remaining inorganic fraction associated to the composting process (mature vs. initial samples) was lower for

P1 compared to P2 and P3, in the unwashed (8.9, 23.0 and 21.4 %, respectively) and washed samples (15.7, 22.6 and 16.9 %, respectively).

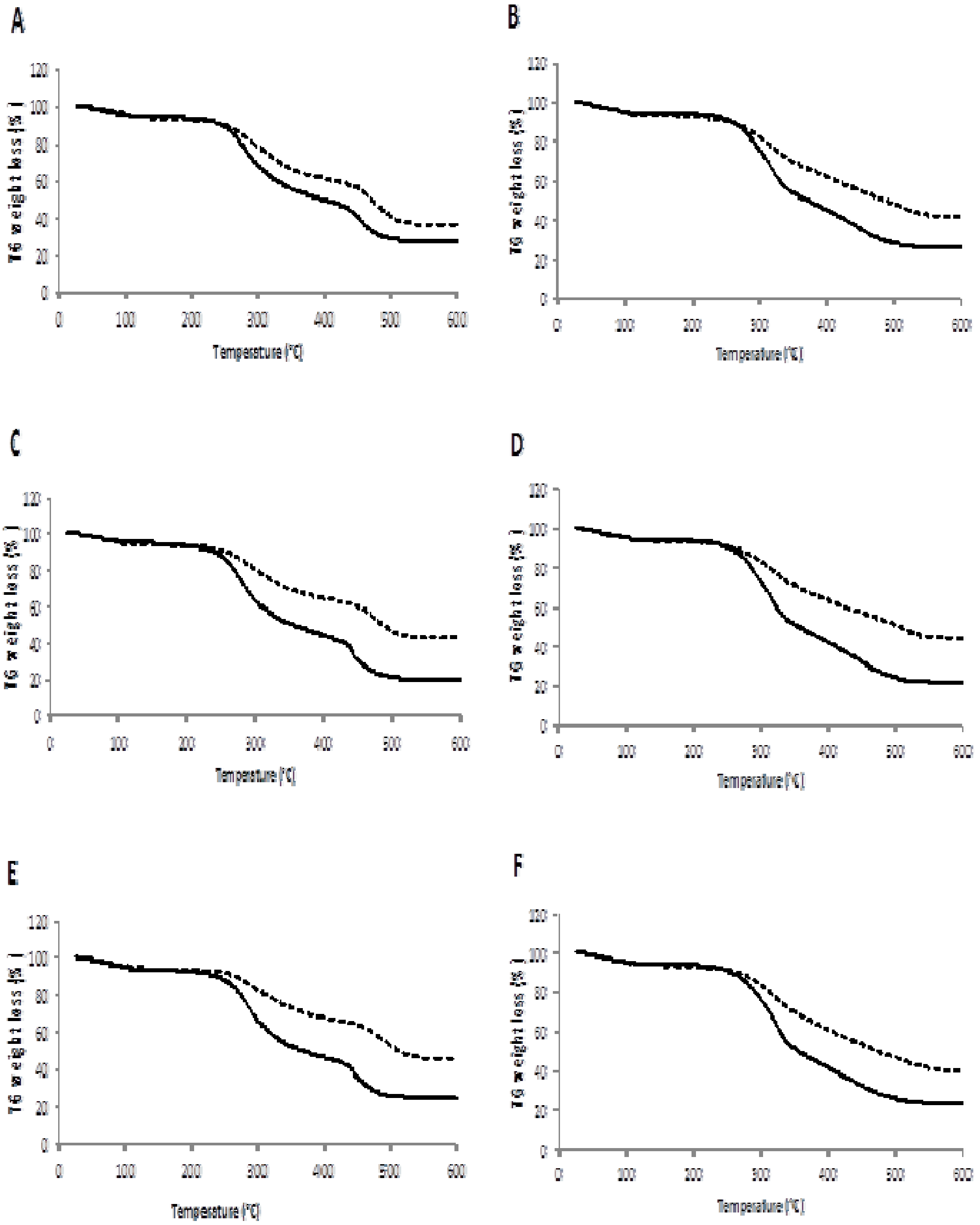

Figure 2 – Thermogravimetry (TG) curves of the compost samples after the water-extraction (AWE) and before the water-extraction (BWE) process, collected at the beginning (solid line) and end (dotted line) of the composting process. A) Pile 1, samples AWE process; B) Pile 1, samples BWE process; C) Pile 2, samples AWE

process; D) Pile 2, samples BWE process; E) Pile 3, samples AWE process; and F) Pile 3, samples BWE process.

The DTG curve shape was determined by the combustion of different organic compounds when the temperature increased (Figure 3). The weight loss in the temperature range between 25 and 105 ºC can be attributed to the loss of water. Dehydration within this range of temperature was also reported in other studies (Smidt and Lechner, 1994; Melis and Castaldi, 2004; Marhuenda-Egea et al., 2007). This dehydration is an endothermic process. Therefore, in order to minimise the effect of the endothermic process with the combustion of the organic matter at higher temperatures (exothermic process), a time of 10 min at 105 ºC was included in the thermogravimetry. After this region of the DTG curve, two different regions can be distinguished: a first region, between 200 ºC and 430 ºC, and a second region, between 430 ºC and 580 ºC. The first region can be attributed to the combustion of the more labile organic matter (probably carbohydrates, simple lipids and amino acids) (Rovira et al., 2008; Ali et al., 2012). The combustion of the more stable organic matter (such as aromatic compounds and polyphenols) was the cause of the weight loss in the second region (Blanco and Almendros, 1994, Rovira et al., 2008).

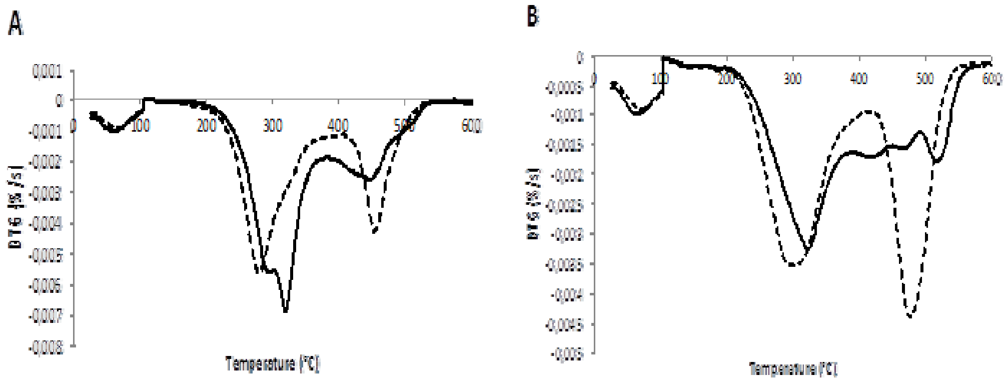

Figure 3. Derivative thermogravimetry (DTG) curves of the compost samples after the water-extraction (solid line) and before the water-extraction (dotted line) process: A) collected at the beginning and B) at the end of the composting process from Pile 1. See Supplementary Material for the other samples.

The range between 350-500 ºC has been also attributed by different authors (Smidt et al., 2005; Ali et al., 2012) to the degradation of complex aromatic structures, such as the humified organic matter. Thus, the samples with a higher degree of stabilisation use more energy for decomposition, e.g. to achieve the same mass losses, these samples require higher temperatures, as a consequence of the higher content in highly complex aromatic compounds compared to the initial ones, indicating OM stabilisation throughout the composting process.

The shape of the DTG curves showed differences between the samples before and after the water-extraction process (Figure 3). Similar DTG curves were obtained for the other piles (see Supplementary Material). The presence of water-soluble inorganic salts in the compost samples can modify the curve shape, by the catalytic effect of these inorganic salts in the combustion process (Blanco and Almendros, 1994). The probable catalytic effect of these inorganic salts also shifted the peaks in the DTG curves toward higher temperatures, i.e., for the pile P1 the maximum temperature peak in the first region shifted from 276 ºC to 292 ºC, comparing the sample before and after the water extraction. Other temperatures are shown in the Supplementary Material. The sharpening of the peaks was more evident in the region at the highest temperatures (between 430 and 580 ºC). This sharpening covered up the combustion of a molecular diversity in the compost samples before the water extraction process, since the peaks in the DTG curves of the water-extracted samples suggested the presence of this molecular diversity (Figure 3) (Blanco and Almendros, 1994). So, in the DTG curve of the sample after water-extraction at the end of the composting process three wide peaks can be distinguished (Figure 3).

The transformation of the organic matter during the composting process can be assessed by thermogravimetry, independently of the shape of the curves. If the area below the DTG curve in the different regions is determined, it is possible to obtain similar values in the original samples and in the water-extracted samples (Table 2). Therefore, it seems that the amount of the organic matter burned in the two regions of the temperatures was not conditioned by the catalytic effects of the water soluble salts. With these areas, the thermostability index (R1) can be calculated, which is the ratio between the mass losses associated with the two main exothermic peaks (Table 2). The thermostability index (R1) can be used to evaluate the transformation of the organic matter during the composting process (Rovira et al., 2008). This relation between the mass losses in the two exothermic peaks increased in the three piles (Table 2).

The increase of R1 in the composting process showed the high sensitivity of this parameter to the chemical changes induced by the bio-transformation of the organic materials in the composting piles, indicating the relative amount of the most thermally-stable fraction of the organic matter with respect to the less stable one. In the same way, the values of the R1 in the maturation stages of the composting process reached stable values, suggesting a good stability of the organic compounds in the composting pile. Statistically, the ANOVA analysis showed significant differences ($P<0.001$) between the initial samples and the rest of the samples (Table 2), decreasing those differences in the thermophilic samples and at the end of the bio-oxidative and after maturation phases (the two last ones without statistical differences).

The ANOVA analysis did not find any significant difference between R1 of the samples before and after water extraction ($P>0.05$; Table 2). As the water-extraction process did not have any effect on the R1 values, then, R1can be used to evaluate the composting process without eliminating the catalytic effect of the water-soluble ions (Table 2). In this sense, if the T50 (temperature at which 50% organic matter was burning) is considered (Rovira et al., 2008), the differences between the samples after and before the water-extraction process were scarce. The T50 increased for all piles during the composting process (Table 2). Statistically, only the initial samples had a lower T50 value than the rest of the samples; while in the samples after water-extraction the increase with composting was statistically significant. However, the water-extraction was not a statistically significant factor for the T50 results at the different composting times. Also, a Pearson regression analysis was carried out between R1 and the classical parameters usually used to estimate OM changes (OM, TOC, Cw, TN and TOC/TN ratio). Strong inverse correlations between R1 and such parameters were observed, indicating that recalcitrant organic matter was related to higher R1 values (Pearson correlation coefficient values = -0.88, -0.88, -0.94 and -0.90 vs. OM, TOC, C_w and TOC/TN, respectively in the unwashed samples; and -0.94, -0.97, -0.96 and -0.94 vs. OM, TOC, C_w and TOC/TN, respectively in the washed samples).

Table 2 - Temperature at which half of the exothermic mass was lost (T50) and the thermostability index (R1) values calculated for the composting samples.

Composting phase	Days	T50 (ºC) BWE	T50 (ºC) AWE	R1 BWE	R1 AWE
Pile 1: solid fraction of pig slurry + cotton gin waste (4:3, v:v)					
I	0	395	370	0.47	0.46
BT	15	450	376	0.61	0.55
T	56	479	462	0.61	0.59
EB	103	458	427	0.79	0.75
M	154	471	485	0.85	0.78
P2: solid fraction of pig slurry + cotton gin waste (3:4, v:v)					
I	0	353	354	0.47	0.47
BT	15	399	423	0.56	0.59
T	56	497	521	0.67	0.71
EB	103	469	476	0.69	0.74
M	167	486	506	0.72	0.76
P3: solid fraction of pig slurry + cotton gin waste (3:1, v:v)					
I	0	366	354	0.45	0.42
BT	41	460	394	0.58	0.54
T	76	456	462	0.59	0.59
EB	146	474	496	0.76	0.75
M	187	511	471	0.82	0.77
ANOVA analysis according to the composting stage					
I	0	371a	359a	0.46a	0.45a
BT	15	436b	397ab	0.58ab	0.56b
T	56	477b	481c	0.62ab	0.63b
EB	103	467b	466bc	0.75c	0.75c
M	167	489b	487c	0.80c	0.77c
F-ANOVA		*13.7****	*14.5****	*27****	*41****

BWE: before water-extraction; AWE: after water-extraction.
I: initial phase of composting; BT: beginning of the thermophilic phase; T: advanced thermophilic phase; EB: end of the bio-oxidative phase; M: maturity phase.

The DTA profiles showed different endothermic and exothermic peaks (Figure 4). These peaks were associated with the peaks in the DTG curves. The endothermic peak around 98 ºC corresponded to the dehydration process. The other two exothermic peaks in the region between 200 ºC to 430 ºC and in the region between 430 ºC to 580 ºC were associated to the combustion process of the organic matter (Rovira et al., 2008; Martínez-Sabater et al., 2009). The thermal degradation of carbohydrates and other labile molecules, related to the first exothermic peak in DTA curves, was higher in the initial samples and decreased throughout the composting process. This feature coincided with the decrease of O-alkyl C percentage (see NMR spectroscopy section). In this experiment, the second exothermic peak was associated to the combustion of more recalcitrant compounds, confirmed by the significant increase of alkyl C percentage during composting. The shape of the DTA curves was different for samples before and after the water -extraction process, such as the shape of the DTG curves showed (Figure 4). Also, the possible catalytic effect of the water-soluble ions in the exothermic reactions can be observed in the sharpening of the peaks.

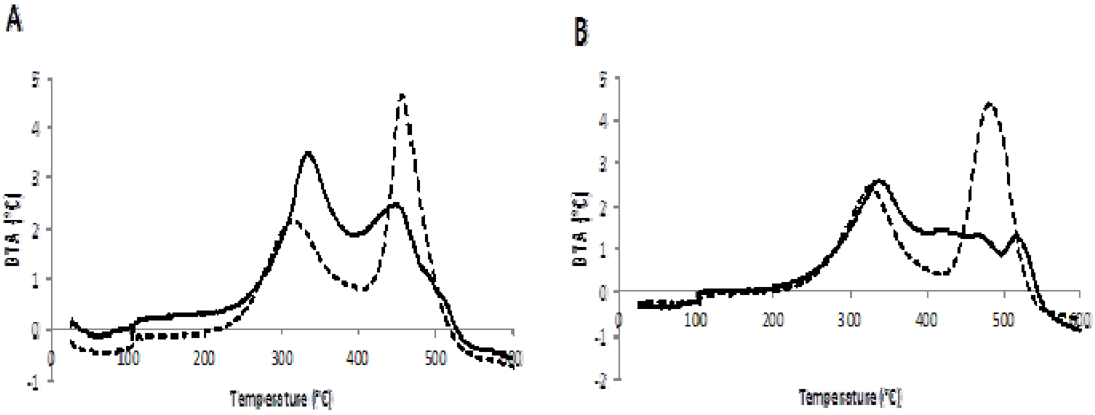

Figure 4 – Differential thermal analysis (DTA) curves of the compost samples after the water-extraction (solid line) and before the water-extraction (dotted line) process: A) collected at the beginning and B) at the end of the composting process from Pile 1. See Supplementary Material for the other samples.

3.3 NMR spectroscopy

The solid-state CPMAS ^{13}C NMR spectra of the compost samples at the different composting stages are displayed in Figure 5. The presence of materials from vegetal origin in the compost piles was clear by the visual inspection of the spectra. The spectra were dominated by the peaks around to 73 ppm, this peak being attributed to carbohydrates (cellulose and hemicellulose) (Nelson and Baldock, 2005). The ^{13}C NMR spectra were divided in different chemical shift regions, such as it was reported by Nelson and Baldock (2005): carbonyl (210-165 ppm), O-aromatic (165-145 ppm), aromatic (145-110 ppm), O_2-alkyl (110-95 ppm), O-alkyl (95-60 ppm), N-alkyl/methoxy (60-45 ppm), and alkyl (45 to -10 ppm). These divisions were dominated by types of C present in the different regions, although there were overlapping between the C types (Nelson and Baldock, 2005). The integration of the different chemical shift regions was obtained in order to follow the biotransformation of the organic matter in the composting piles (Table 3). The O-alkyl (D) region decreased, suggesting carbohydrate degradation during the composting process. For pile P3, a decrease was also observed in all the chemical shift regions (Fig. 5). The C types in other regions increased in the contribution to the spectra by a concentration effect throughout the composting process. Moreover, especial attention must be paid to the alkyl region (column A, Table 3), which mainly includes the most recalcitrant carbon pools. In this experiment, the relative intensity of alkyl C increased significantly during the composting process (e.g. 13 to 35 % in P1, 19 to 34 % in P2), coinciding this fact with the enrichment in recalcitrant compounds detected with the thermal analysis. Martínez-Sabater et al. (2009) also found an increase between initial and matured samples from 10 to 15 % in related experiments using winery and distillery wastes.

The evolution of the relative intensity between the most stable C fractions associated to alkyl region, and the labile C fractions, associated to O-alkyl region (carbohydrate and related molecules) is shown in Table 3. This ratio decreased for the piles P1 and P2, but it showed an erratic behaviour for the pile P3, indicating different patterns of biotransformation, which could be caused by the different SFP used and the different management during the composting process, since P1 and P2 were prepared using the static pile system with forced aeration and P3 was elaborated by the turning composting system, thus, carrying out periodical whirls (see Material and Methods section). This can be also observed only with a visual inspection of the ^{13}C NMR spectra of each composting pile, P3 showing lower intensity of the signals in the carbonyl (210-165 ppm), O-aromatic (165-145 ppm), and aromatic (145-110 ppm) regions.

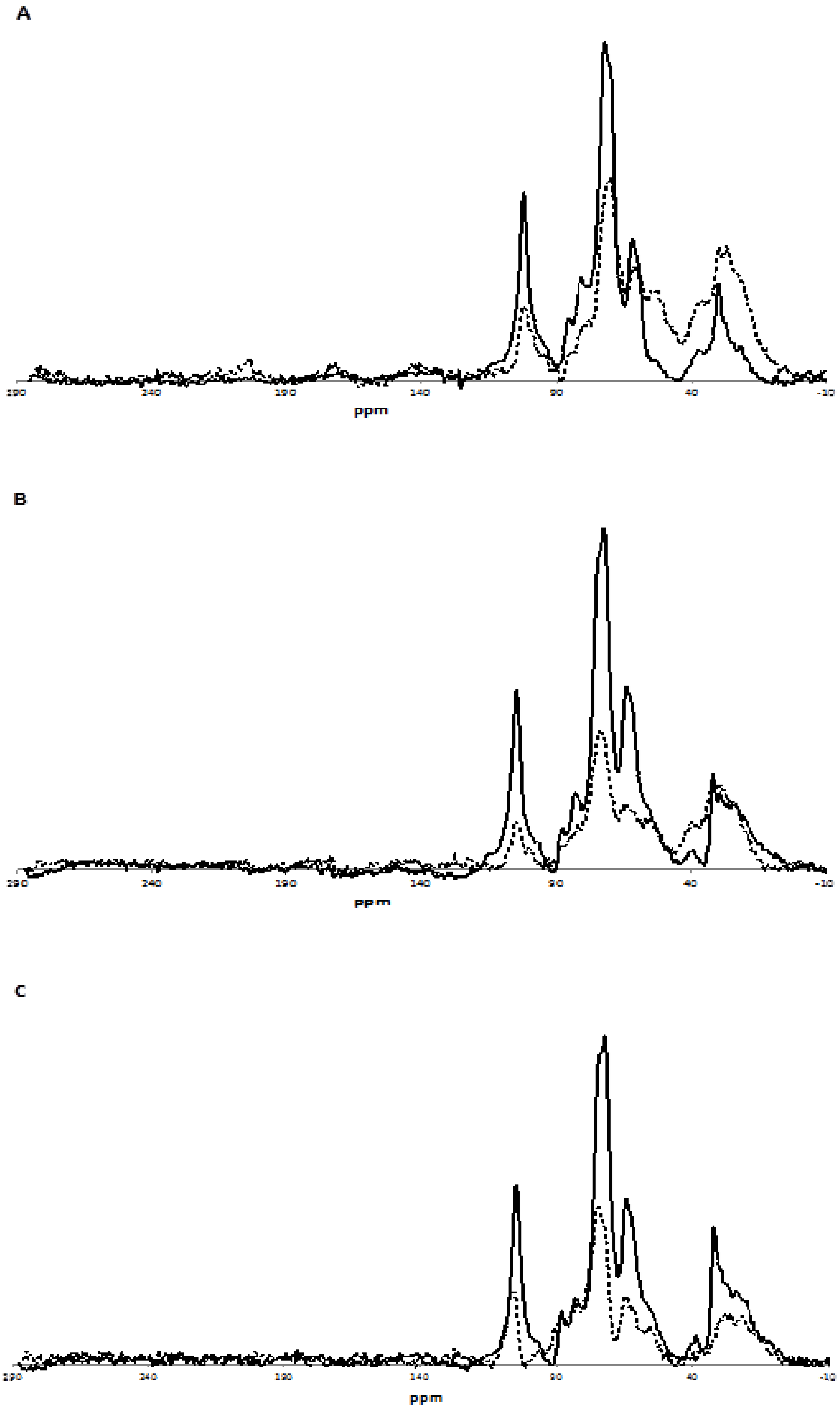

Figure 5 – Solid-state CPMAS 13C NMR spectra of compost samples collected at the beginning (solid line) and at the end (dotted line) of the composting process. A) Pile 1; B) Pile 2; C) Pile 3.

Table 3 – Relative intensity (%) of each C types by integration of solid-state ^{13}C NMR spectra of composting samples. The chemical shift regions were: A) alkyl (45 to -10 ppm); B) N-alkyl/methoxy (60-45 ppm); C) O-alkyl (95-60 ppm); D) O_2-alkyl (110-95 ppm); E) aromatic (145-110 ppm); F) O-aromatic (165-145 ppm); G) carbonyl (210-165 ppm).

Composting phase	**Days**	**Chemical shift regions**							**Alkyl /O-Alkyl ratio**
		A	B	C	D	E	F	G	
Pile 1: solid fraction of pig slurry + cotton gin waste (4:3, v:v)									
I	0	13.5	5.9	58.5	16.4	3.7	0.9	1.1	4.3
BT	15	17.5	8.2	49.3	13.4	5.3	1.8	4.5	2.8
T	56	26.0	12.3	43.0	8.2	4.2	2.5	3.9	1.7
EB	103	30.1	10.5	41.5	6.6	4.4	1.9	5.0	1.4
M	154	35.5	13.1	36.7	7.1	3.6	0.7	3.4	1.0
Pile 2: solid fraction of pig slurry + cotton gin waste (3:4, v:v)									
I	0	19.4	9.3	57.1	14.5	0.3	0.0	0.0	2.9
BT	15	13.6	7.1	56.3	15.3	5.5	1.0	1.2	4.1
T	56	18.7	4.7	49.1	12.8	7.4	3.2	4.1	2.6
EB	103	26.4	11.4	38.4	6.8	5.7	4.5	6.8	1.5
M	167	34.1	12.5	37.8	6.5	3.8	1.3	4.1	1.1
Pile 3: solid fraction of pig slurry + cotton gin waste (3:1, v:v)									
I	0	22.9	7.4	50.8	12.8	2.3	1.1	2.7	2.2
BT	41	24.9	9.3	48.8	10.3	0.9	2.0	3.9	2.0
T	76	21.0	9.3	55.4	10.1	1.1	0.9	2.2	2.6
EB	146	18.4	8.1	58.3	11.4	2.1	1.4	0.3	3.2
M	187	21.8	9.0	50.0	8.8	2.6	2.6	5.2	2.3

I: initial phase of composting; BT: beginning of the thermophilic phase; T: advanced thermophilic phase; EB: end of the bio-oxidative phase; M: maturity phase.

3.4 FT-IR spectroscopy

FT-IR spectra were used in order to evaluate the transformation of the organic and inorganic materials throughout the composting process. Only carrying out a visual inspection of the FT-IR spectra, similar profiles were observed for all samples, which shows that the variations of FT-IR spectra depending of the composting mixture were minor (Fig. 6). The changes in the functional chemical groups were followed in the FT-IR spectra measuring the relative intensity of the absorbance bands (Martínez-Sabater et al., 2009). The relative intensity of the select absorbance bands is shown in Table 4.

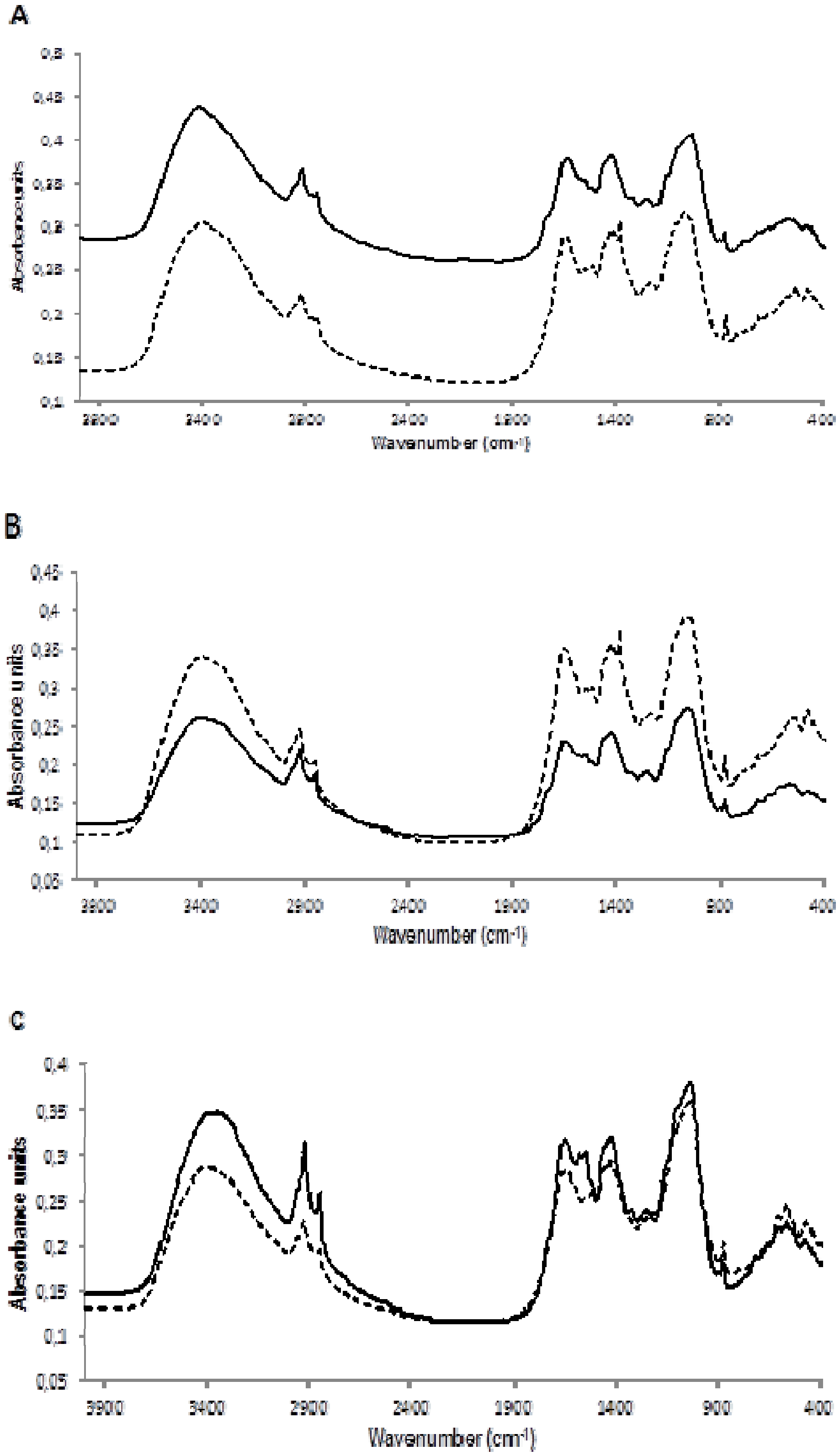

Figure 6 – FT-IR spectra of the compost samples collected at the beginning (solid line) and at the end (dotted line) of the composting process. A) Pile 1; B) Pile 2; C) Pile 3.

Table 4 – Relative absorbance in % of the sum of all peak heights of the FT-IR spectra of the composting samples.

Composting phase	**Days**	**Relative absorbance (%)** 2920 cm^{-1}	1730 cm^{-1}	1630 cm^{-1}	1510 cm^{-1}	1450 cm^{-1}	1384 cm^{-1}	1050 cm^{-1}	**1050/1384 ratio**
Pile 1: solid fraction of pig slurry + cotton gin waste (4:3, v:v)									
I	0	19.2	4.2	25.6	0.0	8.4	2.6	40.0	15.4
BT	15	16.2	1.7	28.3	2.5	8.3	2.8	41.3	14.6
T	56	12.0	2.0	25.4	2.7	8.3	5.3	38.6	7.3
EB	103	14.0	2.7	28.8	3.3	5.2	11.2	36.1	3.2
M	154	16.7	2.5	27.9	2.9	5.3	12.7	35.2	2.8
Pile 2: solid fraction of pig slurry + cotton gin waste (3:4, v:v)									
I	0	21.3	4.7	22.6	0.0	7.5	3.2	40.8	12.7
BT	15	18.4	2.3	26.3	2.2	8.2	3.4	39.4	11.7
T	56	16.4	1.7	25.4	3.2	8.6	4.2	40.5	9.7
EB	103	15.9	2.2	26.4	2.6	5.9	13.4	33.6	2.5
M	167	14.0	2.2	27.2	2.7	4.8	12.9	36.2	2.8
Pile 3: solid fraction of pig slurry + cotton gin waste (3:1, v:v)									
I	0	25.7	3.8	20.3	0.0	8.1	2.1	40.1	19.0
BT	41	18.4	2.9	23.0	1.8	7.4	3.2	43.4	13.6
T	76	15.5	1.4	23.4	3.1	7.3	3.5	46.0	13.3
EB	146	15.3	1.8	23.5	3.1	6.3	3.8	46.1	12.2
M	187	14.6	2.4	24.6	3.1	6.2	5.5	43.7	8.0

I: initial phase of composting; BT: beginning of the thermophilic phase; T: advanced thermophilic phase; EB: end of the bio-oxidative phase; M: maturity phase.

In accordance to the biodegradation of organic matter, significant increases in the band at 1384 cm^{-1} (band assigned to nitrates), and decreases in the bands at 2920 cm^{-1} and at 1050 cm^{-1} (assigned to the aliphatic C-H vibrations and to polysaccharides, respectively) were observed. Grube et al. (2006) also referenced the changes in the band at 2920 cm^{-1} as an effective way to assess the biotransformation of organic matter during composting. The region between 2930-2880 cm^{-1} could be attributed to aliphatic groups in fatty acids (Fialho et al., 2010) and its stationary behaviour during the composting indicated the presence of vegetable material highly resistant to microbiological degradation, probably associated to molecules of vegetable origin like cutines, suberines or lignins (Marhuenda-Egea et al., 2007). The ratio between the intensity of the bands of polysaccharides (1050 cm^{-1}) and nitrates (1384 cm^{-1}) decreased for all the piles with the time of composting and additionally was directly correlated with the C:N ratio (Table 4). However, the decrease for the pile P3 was different from those shown in piles P1 and P2, due to a different trend of organic matter transformation, this fact being also confirmed in the results obtained with the ^{13}C NMR spectra.

4. Conclusions

Thermogravimetric methods and classical analytical approaches seemed to be very synergic obtaining good correlations between thermostability index (R1) and C related parameters. NMR and FT-IR showed more powerful capacities to understand the evolution of C pools especially when recalcitrant C vs labile C pools are compared, e.g. Alkyl /O-Alkyl ratio. FT-IR spectroscopy was also more useful to follow the evolution of polysaccharides and nitrates as ‘signaling’ compounds of the organic matter biotransformation than classical techniques. The composting system seemed to produce differences in OM changes only detected by instrumental analysis, which can be also used to discriminate quality aspects in mature composts.

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6. References

Ali, M., Bhatia, A., Kazmi, A.A., Ahmed, N., 2012. Characterization of high rate composting of vegetable market waste using Fourier transform-infrared (FT-IR) and thermal studies in three different seasons. Biodegradation 23, 231–242.

Almendros, G., Dorado, J., Gonzáles-Vila, F. J., Blanco, M. J., Lankes, U., 2000. ^{13}C NMR assessment of decomposition patterns during composting of forest and shrub biomass. Soil Biol. Biochem. 32, 793-804.

Barros, N., Salgado, J., Villanueva, M., Rodriquez-Añón, J., Proupin, J., Feijoó, S., Martín-Pastor, M., 2011. Application of DSC–TG and NMR to study the soil organic matter. J. Therm. Anal. Calorim. 104(1), 53–60.

Bernal, M.P., Alburquerque, J.A., Moral, R., 2009. Composting of animal manures and chemical criteria for compost maturity assessment. A review. Bioresour. Technol. 100, 5444–5453.

Blanco, M.J., Almendros, G. J., 1994. Maturity assessment of wheat straw composts by thermogravimetric analysis. Agric. Food Chem. 42, 2454-2459.

Brito, L.M., Mourão, I., Coutinho, J., Smith, S.R. (2012). Simple technologies for on-farm composting of cattle slurry solid fraction. Waste Manage. 32(7):1332-1340.

Burton, H., Turner, C., 2003. Manure management, Treatment Strategies for Sustainable Agriculture (second ed.) Silsoe Research Institute, Lister and Durling Printers, Flitwick, Bedford, UK.

Bustamante, M.A., Alburquerque, J.A. Restrepo, A.P., de la Fuente, C., Paredes, C., Moral, R., Bernal, M.P. 2012. Co-composting of the solid fraction of anaerobic digestates, to obtain added-value materials in agriculture. Biomass Bioenerg. 43, 26-35.

Castaldi, P., Alberti, G., Merella, R., Melis, P., 2005. Study of the organic matter evolution during municipal solid waste composting aimed at identifying suitable parameters for the evaluation of compost maturity. Waste Manage. 25, 209-213.

Chen, Y. N., 2003. Nuclear magnetic resonance, infra-red and pyrolysis: application of spectroscopic methodologies to maturity determination of composts. Compost Sci. Util. 11, 152-168.

De Oliveira, S.C., Provenzano, M., Santiago-Silva, M.R., Senesi, N., 2002. Maturity degree of composts from domestic solid wastes evaluated by differential scanning calorimetry. Environ. Technol. 23, 1099-1105.

dos Reis Orsini, R., Moscardini Filho, E., Pita Mercuri, L., do Rosario Matos, J., de Carvalho, F.M.S., 2011. Thermoanalytical study of inner and outer residue of coffee harvest. Applications on biomass. J. Therm. Anal. Calorim. 106, 741–745.

Droussi, Z., Dorazio, V., Provenzano, M., Hafidi, M., Outmane, A., 2009. Study of the biodegradation and transformation of olive-mill residues during composting using FTIR spectroscopy and differential scanning calorimetry. J. Hazard. Mat. 164, 1281-1285.

Fernández, J.M., Plante, A.F., Leifeld, J., Rasmussen, C., 2011. Methodological considerations for using thermal analysis in the characterization of soil organic matter. J. Therm. Anal. Calorim. 104(1), 389–398.

Fialho, L.L., da Silva, W.T.L., Milori, D.M.B.P., Simões, M.L., Martin-Neto, L., 2010. Characterization of organic matter from composting of different residues by physicochemical and spectroscopic methods. Biores Technol. 101, 1927–1934.

Fuentes, M., Baigorri, R., González-Gaitano, G., García-Mina, J.M., 2007. The complementary use of 1H NMR, 13C NMR, FTIR and size exclusion chromatography to investigate the principal structural changes associated with composting of organic materials with diverse origin. Organic Geochem. 38, 2012–2023.

Gómez, X., Diaz, M. C., Cooper, M., Blanco, D., Morán, A., Snape, C.E., 2007. Study of biological stabilization processes of cattle and poultry manure by thermogravimetric analysis and C-13 NMR. Chemosphere 68, 1889-1897.

Grube, M., Lin, J.G., Lee, P.H., Kokorevicha, S., 2006. Evaluation of sewage sludge-based compost by FT-IR spectroscopy. Geoderma 130, 324-333.

Huang, G.F., Fang, M., Wu, Q.T., Zhou, L.X., Liao, X.D., Wong, J.W.C, 2001. Co-composting of pig manure with leaves. Environ. Technol. 22:10 1203-1212.

Marhuenda-Egea, F.C., Martínez-Sabater, E., Jordá, J., Sánchez-Sánchez, A., Moral, R., Bustamante, M.A., Paredes, C., Pérez-Murcia, M.D., 2007. Evaluation of the aerobic composting process of winery and distillery residues by thermal methods. Thermochim. Acta 454, 135-143.

Martínez-Sabater, E., Bustamante, M.A., Marhuenda-Egea, F.C., El-Khattabi, M., Moral, R., Lorenzo, E., Paredes, C., Gálvez, L. and Jordá, J., 2009. Study of the evolution of organic matter during composting of winery and distillery residues by classical and chemometric analysis. J. Agri. Food Chem. 57, 9613-9623.

Melis, P., Castaldi, P., 2004. Thermal analysis for the evaluation of the organic matter evolution during municipal solid waste aerobic composting process. Thermochim. Acta 413 (1-2), 209-214.

Moral, R., Perez-Murcia, M.D., Perez-Espinosa, A., Moreno-Caselles, J., Paredes, C., 2005. Estimation of nutrient values of pig slurries in Southeast Spain using easily determined properties. Waste Manage. 25, 719–725.

Mothè, C., Miranda, I., 2009. Characterization of sugarcane and coconut fibers by thermal analysis and FTIR. J Therm Anal Calorim. 97(2), 661–665.

Nelson, P. N., Baldock, J. A., 2005. Estimating the molecular composition of a diverse range of natural organic materials from solid-state 13C NMR and elemental analyses. Biogeochemistry. 72, 1-34.

Nolan, T, Troy, S.M., Healy, M.G., Kwapinski, W., Leahy, J.J., Lawlor, P.G., 2011. Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. Biores. Technol. 102: 7131-7138.

Otero, M., Calvo, L.F., Estrada, B., García, A.I., Morán, A., 2002. Thermogravimetry as a technique for establishing the stabilization progress of sludge from wastewater treatments plants. Thermochim. Acta 389, 121-132.

Paredes, C., Roig, A., Bernal, M.P., Sánchez-Monedero, M.A., Cegarra, J. 2000. Evolution of organic matter and nitrogen during co-composting of olive mil wastewater with solid organic wastes. Biol. Fert. Soils 32, 222-227.

Pichler, M., Knicker, H., Kogel-Knabner, I., 2000. Changes in the chemical structure of municipal solid waste during composting as studied by solid-state dipolar dephasing and PSRE 13C NMR and solid-state 15N NMR spectroscopy. Environ. Sci. Technol. 34, 4034-4038.

Preston, C. M., Trofymow, J. A., Niu, J., Fyfe, C. A., 1998. 13CPMAS-NMR spectroscopy and chemical analysis of coarse woody debris in coastal forests of Vancouver Island. For. Ecol. Manag. 111, 51-68.

Preston, C., 1996. Applications of NMR to soil organic matter analysis: history and prospects Soil Sci. 161, 144-166.

Provenzano, M., Outmane, A., Hafidi, M., Senesi, N., 2000. Differential scanning calorimetric analysis of composted materials from different sources. J. Therm. Anal. Calorim. 61, 607-614.

Rovira, P., Kurz-Besson, C., Coûteaux, M., Vallejo, V.R., 2008. Changes in litter properties during decomposition: a study by differential thermogravimetry and scanning calorimetry. Soil Biol. Biochem. 40,172-185.

Smidt, E., Eckhardt, K., Lechner, P., Schulten, H., Leinweber, P., 2005. Characterization of different decomposition stages of biowaste using FT-IR spectroscopy and pyrolysis-field ionization mass spectrometry. Biodegradation 16, 67–79.

Smidt, E., Lechner, P., 2005. Study on the degradation and stabilization of organic matter in waste by means of thermal analyses. Thermochim. Acta 438/1- 2, 22-28.

Smith, B., 1999. Infrared Spectral Interpretation, CRC Press: Boca Raton, Florida.

Solano, M.L., Iriarte, F., Ciria, P., Negro, M.J., 2001. Performance characteristics of three aeration systems in the composting of sheep manure and straw. J. Agric. Engin Res. Vol. 79, nº 3, July 1, 2001. pp. 317-329.

Szanto, G.L., Hamalers, H.V.M, Rulkens, W.H., Veeken, A.H.M., 2007. NH_3, N_2O and CH_4 emissions during passively aerated composting of straw-rich pig manure. Biores. Technol. 98. 2659-2670.

Tang, J.C., Maie, N., Tada, Y., Katayama, A., 2006. Characterization of the maturing process of cattle manure compost. Process Biochem. 41, 380-389.

Wilson, M. A., 1987. NMR Techniques and Applications in Geochemistry and Soil Chemistry, Pergamon Press: Oxford, U.K.

Supplementary Materials

Figure captions

Figure 1 – Derivative thermogravimetry (DTG) curves of the compost samples after the water-extraction (solid line) and before the water-extraction (dotted line) process: A) collected at the beginning and B) at the end of the composting process from Pile 2. C) collected at the beginning and B) at the end of the composting process from Pile 3.

Figure 2 – Differential thermal analysis (DTA) curves of the compost samples after the water-extraction (solid line) and before the water-extraction (dotted line) process: A) collected at the beginning and B) at the end of the composting process from Pile 2. C) collected at the beginning and B) at the end of the composting process from Pile 3.

3.4 Agricultural efficiency of the nutrients of pig slurry compost and nitrate leaching potential.

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Fertilizer value and potential nitrate leaching risks of pig slurry composts

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Fertilizer value and potential nitrate leaching risks of pig slurry composts

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Keywords: Nitrate; Organic fertilizer; Plant nutrient uptake; Relative agronomic efficiency; Ryegrass.

Abstract

The agronomic value of compost made from the solid fraction of pig slurry mixed with cotton gin waste was assessed in a pot trial using Italian ryegrass (*Lolium multiflorum* Lam.) as a plant test. The two composts differed in the proportions of pig slurry solid fraction and cotton gin waste used for their preparation. They were applied to a sandy loam soil at two different rates, based on the N supplied, and compared with a mineral fertilizer; unamended control soil was also tested. The potential risk of nitrate-N leaching in the soil after intense rainfall events was also evaluated. The experiment was carried out in double-layer pots, which allowed the collection of leachates from the pots. The results show that both composts were able to increase biomass production and soil fertility with respect to the control. The high Cu and Zn concentrations found in the composts did not affect negatively the development of the plants, as they acted as essential microelements for plant growth, without showing great accumulation in soil. Losses of N by leaching were very low in all treatments; the results suggest that the compost water holding capacity may affect the leaching risk. In comparison with the mineral fertilizer, the relative agronomic efficiency (RAE) of compost N reached 47.6 %, indicative of a partial N-mineralization of the compost organic-N; for compost-P the RAE reached 56 and 75 % for composts A and B, respectively. The high solubility of the K in the compost also gave high RAE values, demonstrating the nutrient fertilizer value of compost prepared from pig slurry. Therefore, both composts can be used as organic fertilizers in partial substitution of mineral fertilizers without a nitrate leaching risk.

1. Introduction

Macronutrients, such as nitrogen (N), phosphorus (P) and potassium (K), are required by plants for their correct growth, and are provided through mineral or organic fertilizers. Mineral fertilizers are the main source of macronutrients used in agriculture. The EU-27 consumption was estimated at 10.4, 1.0 and 2.2 million tons of N, P and K, respectively, in 2012 (*Fertilizers Europe*, 2014; *FAO*, 2015). The use of mineral fertilizers implies some economic and environmental costs. The economic costs are associated with the high fossil fuel and energy consumption (9 billion m^3 of natural gas were consumed in the USA in 2004; 23.45 MJ are required to produce one kilogram of urea) (*Abram and Forster*, 2005; *Fertilizers Europe*, 2008). The environmental costs associated with mineral fertilizers are derived from their production from non-renewable resources and the use of excessive amounts of water, energy and chemicals.

In order to reduce the use of mineral fertilizers, materials derived from organic residues, such as compost, constitute adequate alternatives as sources of plant nutrients. They can also improve soil physico-chemical and biological properties, increasing the available nutrients in the soil (*Bernal* et al., 2009a; *Biau* et al., 2012; *Egodowatta* et al., 2012; *Tejada and Gonzalez*, 2006), while simultaneously providing an efficient and cost-effective way of recycling these products (*Burgos* et al., 2006).

Traditionally, animal manures have been applied directly to soil as organic fertilizers in areas close to sites of livestock production. But, with the intensification of pig-production systems, solid-liquid separation of pig slurry has been adopted in many farms in order to obtain a liquid fraction, used directly on the farm, and a solid fraction that can be treated and exported to other farms. Composting has proved to be a feasible technology to treat the solid fraction of pig slurry (SFP), producing a stable final product, free of pathogens and rich in organic matter (OM), humic substances and nutrients (*Santos* et al., 2016). Compost application to soil enhances the recycling of nutrients in the soil-plant system (*Bernal* et al., 2009a; *Tiquia* et al., 2002), increasing biomass production and soil fertility by improving the physico-chemical and biological properties of the soils (*Bedada* et al., 2014; *Cordovil* et al., 2007; *Keener* et al., 2000; *Loecke* et al., 2004). Compared with other organic wastes (e.g. animal slurry, digestates or untreated plant residues), qualitatively high-class composts show clear benefits as soil amendments/fertilizers: reliable sanitization, a high proportion of stable humus and high concentrations of nutrients (*Bernal* et al., 2009a; *Moral* et al., 2009), the latter allowing a reduction in mineral fertilization.

One of the main limitations to compost utilization as organic fertilizer is the fact that the exact amount of N available to plants is not clearly known, which can induce an under- or over-application of N if the compost application rate is based on the total or mineral N content, respectively Indeed, total-N comprises both inorganic forms (mainly nitrate in mature compost; *Bernal* et al., 2009a), readily available to plants, and organic forms, which need to be mineralized in order to be available to plants. Then, when compost is applied on a total-N basis, the fertilizer efficiency may be lower than that of mineral fertilizers. Furthermore, the rate of organic-N mineralization should be such that available-N is produced when required by the crop, otherwise it will be lost to the environment, through nitrate leaching (*He* et al., 2000). The over-application of mineral and organic fertilizers to crops can lead to an excess of nutrients and consequent leaching into the surrounding environment (*Cavanagh* et al., 2011).

Even if the annual rainfall in Mediterranean climates is low, heavy storms in short time periods do occur, which can constitute a risk regarding nitrate pollution. Frequently, the amount of rainfall is not sufficient to wash the nitrate down into aquifers, and it accumulates in the vadose zone (*Jorge-Mardomingo* et al., 2015). The use of fertilizers in nitrate-vulnerable zones is regulated by EU legislation (Directive 91/676/EEC) limiting the application to 170 kg N ha^{-1} yr^{-1}; the good agricultural practices guidelines specify safety measures and practices to minimize the impacts of nitrate pollution, thereby increasing the effectiveness of organic fertilizers. These will contribute to decreased use of mineral fertilizers and to lower losses of nitrogen (*FAO*, 2015).

Jorge-Mardomingo et al. (2015) recently indicated that the potential contamination of groundwater by nitrate from N-fertilization is determined mainly by the stability of the amendment used, due to the mineralization rate of the organic-N, and the water input into the soil system, upon which the transport of nitrate to aquifers depends. Less-stable organic amendments have quicker mineralization rates, providing a higher concentration of inorganic-N to the soil in the short-term. Also, some physical properties of the composts, such as water holding capacity, can affect the water fluxes in the soil and thus the N-losses (*Corrêa* et al., 2005). In this sense, the use of stabilized composts could reduce the potential nitrate leaching, especially at high application rates.

Another limitation associated with the use of composted manures, and in particular, the solid fraction of pig slurry, is the high concentration of Cu and Zn. Both elements are supplied to piglets in great quantities to promote growth (Cu) and prevent diseases (Zn). However, almost 90 % is excreted in the feces (*Legros* et al., 2010). In this sense, the systematic application of composted pig manure as organic fertilizer could promote the accumulation of these elements in the soil (*Gräber* et al., 2005).

The main objective of this study was to assess the fertilizer value of two composts produced from the solid fraction of pig slurry and cotton gin waste, and the potential nitrate leaching following their soil application.

2. Materials and methods

2.1 Experimental design

A four-month pot trial with Italian ryegrass (*Lolium multiflorum* Lam.) was carried out in a greenhouse using a sandy loam soil collected from the 0-15 cm soil layer of an agricultural field at UTAD (Universidade de Trás-os-Montes e Alto Douro), Vila Real, Portugal. The soil was air-dried and sieved to 4 mm for the pot experiment and to 2 mm for analysis. Two composts (A and B) were produced using the solid fraction of pig slurry and cotton gin residues, at proportions of 4:3 and 3:4 (by volume), respectively. More details about the composts can be obtained in Santos et al. (2016). The composts were applied at two doses and compared with a standard NPK (10:10:10) commercial fertilizer. The main characteristics of the soil and composts are shown in Table 1.

Table 1 – Characteristics of the soil and composts (dry weight basis).

	Soil	**Compost A**	**Compost B**
pH	7.4	6.8	6.9
EC (dS m^{-1})	0.1	10.8	10.1
OM (%)	0.69	63	57
TOC (g kg^{-1})	5.0	303	288
TN (g kg^{-1})	0.4	35.1	34.8
NH_4^+-N (mg kg^{-1})	34.8	689	466
NO_3^--N (mg kg^{-1})	44.7	8932	5740
Total P (g kg^{-1})	0.06*	15.2	10.8
Total K (g kg^{-1})	0.07*	22.1	21.9
Total Cu (mg kg^{-1})	3.2*	326	262
Total Zn (mg kg^{-1})	0.7*	947	719

*: Soil available P, K, Cu and Zn.

Six different treatments were considered:

- AD1 and BD1: compost A and compost B at dose 1, providing 360 mg TN pot^{-1}, equivalent to 5.14 g m^{-2} or 308 kg ha^{-1} yr^{-1}, respectively;
- AD2 and BD2: compost A and compost B at dose 2, adding double the amount of dose 1;
- F: mineral fertilizer (10:10:10) at a rate of 360 mg N pot^{-1} (as in dose 1 of compost) equivalent to 308 kg N ha^{-1} yr^{-1}; and
- C: control treatment without any fertilization.

The application rates of the composts and fertilizer were calculated based on the N requirements of the plants. The experiment was run in 10-L double-layer pots which allow leachate collection from the bottom. The composts were mixed with 9 kg of dry soil at the beginning of the experiment, and the inorganic fertilizer was divided in two applications: before sowing and after the first harvest. All treatments were replicated four times (total number of pots = 24). The moisture content of the soils was adjusted to 70% of the water holding capacity (WHC) with distilled water; then, 0.5 g of ryegrass seeds were added per pot. Watering, with distilled water, was on a gravimetric basis, maintaining the soil water content at 70% of the WHC. Any leachate produced after watering was collected from the bottom of the pot, quantified and frozen for further analysis. During the experiment, the plant material was harvested three times: 30, 60 and 120 days after emergence, by cutting the aerial parts 2 cm above the soil surface. Fresh and dry weights were determined before and after drying at 65 °C, respectively. Samples were milled for analysis.

The potential nitrate leaching risk in the soil was assessed after the first and second harvests. For this, a heavy rain event (equivalent to 24 mm) was simulated by adding 1.75 L of distilled water to the top of the pot. The leachates produced were quantified and frozen for further analysis.

At the end of the experiment, after the third harvest, the soil was separated from the roots, homogenized and sampled for analysis. The roots were cleaned, first by removing most of the soil particles with tap water, then two times with abundant distilled water and, finally, by ultrasound (5 minutes at 750 W), to eliminate any remaining soil particles adhering to the roots.

2.2 Physico-chemical and chemical analysis

The moisture content of the plant material was determined by drying the sample at 60 °C for 48 h in an oven with forced aeration. Then, chemical analyses were performed on the dry and ground samples: total nitrogen (TN), directly, by automatic microanalysis (EuroVector EuroEA 3000 elemental analyzer); after H_2O_2/HNO_3 microwave-assisted digestion, total P by a colorimetric method, K by atomic emission spectrophotometry (AES) (iCE 3000 series, Thermo Scientific) and Cu and Zn by atomic absorption spectroscopy (AAS) (iCE 3000 series, Thermo Scientific).

The soil samples were analyzed for: moisture content by oven-drying the samples at 105 °C for 12 h; total organic carbon (TOC) and total nitrogen (TN) by automatic microanalysis (EuroVector EuroEA 3000 elemental analyzer) (*Navarro* et al., 1991); NH_4^+-N by a colorimetric method based on Berthelot's reaction (*Sommer* et al., 1992), after 2 M KC1 1:20 (w/v) extraction; NO_3^--N with a selective electrode in a 1:20 water extract; available-P by a colorimetric method, after 0.5 M $NaHCO_3$ 1:10 (w/v) extraction (Olsen-P); available-K by EAS, after 1 M CH_3COONH_4 1:10 (w/v) extraction (*Kundsen* et al., 1982); water-soluble and exchangeable Cu and Zn by AAS, after 0.1 M $CaCl_2$ 1:10 (w/v) extraction. The leachates were analyzed for: water-soluble nitrogen (N_w), using an automatic analyzer for liquid samples (TOC-V CSN Analyzer, Shimadzu), and nitrate, by ionic chromatography (850 Professional IC, Metrohm, Herisau, Switzerland). All the analyses were performed at least in duplicate.

2.3 Statistical analysis

For statistical analysis, IBM SPSS Statistics 21.Ink software was used. The standard error of the means was calculated for the chemical and physico-chemical characteristics of the soils, and plant biomass and nutrients; one-way analysis of variance (ANOVA) and least significant difference (LSD) were used to determine changes in the parameters according to the treatments. Two-way ANOVA was used to determine changes in the plant parameters according to the harvest and treatment. The normality and homogeneity of the variances were checked using the Shapiro-Wilk and Levene tests, respectively, before ANOVA.

The plant N utilization efficiency was calculated on the basis of the Apparent Recovery Fraction (ARF) approach, as suggested by *Gunnarsson* et al. (2010), and was reported as cumulative according to the following equation:

$$ARF = \sum_{t=1}^{3} \frac{[N\ uptake\ treatment_{(tn)}] - [N\ uptake\ control_{(tn)}]}{TN_{added}} x\ 100$$

in which: N uptake $\text{treatment}_{(tn)}$ is the total N uptake (mg pot^{-1}) of a fertilizer treatment (AD1, AD2, BD1, BD2 and F) at time n (n = harvest 1, 2 and 3); N uptake $\text{control}_{(tn)}$ is the total N uptake (mg pot^{-1}) of the unfertilized control at time n (n = harvest 1, 2 and 3); TN_{added} is the total N added to each pot (mg pot^{-1}).

The relative agronomic efficiency (RAE) of N, P and K in the compost treatments was calculated from the nutrient uptake in the aboveground biomass of the compost treatment in comparison with the mineral fertilizer, taking into account the N input in the double-dose treatments (*Brod* et al., 2015).

3. Results and discussion

3.1 Biomass production of *L. multiflorum*.

The shoot biomass production of *L. multiflorum* increased in the compost treatments and with the compost application rate, in comparison with the control plants, at all harvests (Tables 2). Increases in the biomass production of maize (12-15 %) with the use of composted pig manure, in comparison with the fresh manure, were found by *Loecke* et al. (2004) during a two-year experiment; *Cordovil* et al. (2007) also found greater wheat production with composted pig manure than with pig slurry; and *Bedada* et al. (2014) observed an increase in crop production of 11 %, in comparison with the control treatment, when compost of cattle manure and agricultural wastes was applied. The pig manure composts had high inorganic N concentrations (Table 1), thus supplying adequate N for correct plant growth (*Cordovil* et al., 2007). The increases in biomass produced by the higher doses of the composts - treatments AD2 and BD2 - probably resulted, at least in part, from increased N availability to the plants (*Eghball and Power*, 1999). In this sense, a positive correlation ($r = 0.98$; $p < 0.001$) was found between the aerial biomass production (DM) and the TN supplied by the amendments, reflecting the dependence of growth on N supply.

At the first harvest, the plant growth was similar for the compost treatments at dose 1 and the mineral fertilizer (F), being lower than with compost at dose 2. But, this was not observed in the further harvests because the composts were applied only once, at the beginning of the experiment, while F was divided into two applications, at the beginning of the experiment and after the first harvest. As a consequence, the highest biomass production at the second and third harvests, as well as the greatest root production, was found in treatment F, due to the higher N availability.

Table 2 – Plant biomass production and nutrient concentrations in the aerial parts of *L. multiflorum* in the three harvests, according to the different treatments applied to the soil: AD1, compost A at dose 1; AD2, compost A at dose 2; BD1, compost B at dose 1; BD2, compost B at dose 2; F, mineral fertilizer; C, non-fertilized control.

Treatment	**Fresh Biomass (g/pot)**	**Dry Biomass (g/pot)**	**N (g kg^{-1})**	**P (g kg^{-1})**	**K (g kg^{-1})**	**Cu (mg kg^{-1})**	**Zn (mg kg^{-1})**
Harvest 1							
AD1	28.1±1.86 b	3.65±0.26 d	28.4±2.72 ab	0.96±0.05	37.7±2.4 a	9.6±0.53 ab	19±2.5 ab
AD2	46.5±2.27 a	5.98±0.17 a	32.0±1.50 ab	0.99±0.07	38.2±1.0 a	9.9±0.88 a	23±3.5 a
BD1	32.0±3.17 b	4.52±0.40 b	23.4±0.59 b	0.89±0.05	34.7±0.9 ab	8.1±0.38 bc	19±4.9 ab
BD2	48.2±5.07 a	6.07±0.53 a	35.4±8.80 a	0.93±0.12	38.0±0.9 a	10.0±1.1 a	19±1.6 ab
F	33.0±2.41 b	4.39±0.19 bc	32.8±1.78 a	0.88±0.15	34.7±3.0 ab	10.4±0.4 a	17±2.7 ab
C	9.9±0.93 c	1.50±0.34 d	23.6±2.29 b	0.82±0.06	33.3±0.3 b	7.4±0.35 c	15±0.9 b
ANOVA	***	***	**	n.s.	**	***	*
Harvest 2							
AD1	8.1±1.07 c	1.46±0.43 c	17.7±1.21 ab	1.22±0.05 a	28.3±1.3 ab	5.7±0.26	15±1.9
AD2	13.1±0.73 b	2.11±0.20 b	14.7±6.02 b	1.28±0.09 a	28.9±1.2 ab	5.8±1.88	17±4.0
BD1	8.2±0.40 c	1.41±0.12 c	17.1±1.77 ab	1.23±0.08 a	26.2±0.7 b	5.0±0.09	15±1.7
BD2	13.5±0.58 b	2.08±0.07 b	17.0±0.93 ab	1.28±0.07 a	28.0±0.8 ab	4.3±0.43	17±4.0
F	43.4±1.35 a	6.67±0.27 a	21.5±1.24 a	0.98±0.14 b	31.0±4.0 a	6.7±2.40	15±2.1
C	3.2±0.15 d	0.50±0.25 d	17.5±1.09 ab	1.13±0.08 ab	26.8±1.3 ab	4.5±0.64	16±1.0
ANOVA	***	***	*	**	*	n.s	n.s
Harvest 3							
AD1	9.8±0.73 c	2.85±0.24 cd	6.3±0.35	0.77±0.04 a	20.6±1.7 ab	2.3±0.16 a	16±2.8
AD2	11.4±0.32 b	3.58±0.10 b	6.9±0.29	0.86±0.03 a	21.4±1.3 ab	2.3±0.29 a	17±2.9
BD1	8.3±0.46 d	2.35±0.06 d	7.0±0.46	0.95±0.21 a	19.9±0.1 b	2.0±0.23 a	16±1.2
BD2	10.6±0.54 bc	3.25±0.30 bc	7.1±0.48	0.96±0.07 a	22.4±0.4 a	2.3±0.49 a	21±3.7
F	17.9±0.82 a	5.73±0.32 a	6.5±1.10	0.53±0.04 b	19.0±0.7 b	1.2±0.24 b	19±9.3
C	5.9±0.62 e	1.71±0.37 e	6.5±0.47	0.76±0.08 ab	19.4±1.5 b	1.4±0.19 b	15±0.8
ANOVA	***	***	n.s.	***	**	***	n.s.
ANOVA Harvest x Treatment	***	***	***	***	***	***	n.s.

Mean ± standard deviation (n=4); n.s.: not significant; *, **, ***: significant at $P<0.05$, 0.01, 0.001 respectively. For each parameter, values followed by the same letter do not differ significantly according to the Tukey test ($p<0.05$).

Considering the two types of compost used in this experiment, significant differences were found when the lower dose of compost was used. Compost A showed statistically-higher aerial biomass production than compost B at the last harvest, which can be related to the higher concentration of inorganic-N in compost A, as the application rates were adjusted according to the TN in the compost. These results indicate that the nutrients from compost A had a longerterm effect than those from compost B, suggesting that the degree of mineralization of organic-N forms was greater in compost A.

The biomass production of the roots was higher in all the treatments than in the control, but was greatest for treatment F (Table 3). However, the results did not show any significant differences between the types and doses of compost used.

Table 3 – Biomass production and concentration of nutrients in the roots of *L. multiflorum* at the end of the experiment.

Treatment	Fresh biomass (g/pot)	Dry biomass (g/pot)	N ($g\ kg^{-1}$)	P ($g\ kg^{-1}$)	K ($g\ kg^{-1}$)	Cu ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)
AD1	31.0±9.3 bc	2.64±1.25 bc	6.54±1.01	0.38±0.03	9.4±0.70 b	38.1±2.4 b	33.5±2.3 bc
AD2	36.7±6.1 b	3.20±0.22 b	6.59±0.61	0.45±0.07	11.6±0.58 ab	43.4±7.6 ab	34.6±3.6 abc
BD1	25.7±5.9 bc	2.45±0.73 bc	6.26±0.61	0.38±0.03	9.4±0.74 b	47.7±5.4 ab	38.4±4.4 ab
BD2	30.5±6.3 bc	3.08±0.71 bc	5.76±0.36	0.41±0.06	12.7±0.11ab	51.8±5.6 a	41.1±2.1 a
F	65.0±8.2 a	5.67±0.79 a	5.87±0.68	0.44±0.03	14.8±0.85 a	46.0±8.4 ab	29.6±2.3 c
C	19.8±1.5 c	1.48±0.29 c	7.34±1.29	0.38±0.03	9.9±0.64 b	51.7±2.1 a	32.8±2.5bc
ANOVA	***	***	n.s	n.s.	**	*	**

Mean ± standard deviation (n=4); n.s.: not significant; *, **, ***: significant at P<0.05, 0.01, 0.001, respectively. For each parameter, values followed by the same letter do not differ significantly according to the Tukey test (p<0.05).

3.2 Nutrient uptake and accumulation by *L. multiflorum*.

Compost application significantly increased the concentrations of the macronutrients N, P and K in the plants, compared with the control, at each harvest, without significant difference relative to treatment F for N and K (Table 2). Only treatment BD1, at the first harvest, reduced the N concentration in plants with respect to F; all compost treatments led to greater P concentrations in plants than treatment F at harvests 2 and 3, even if the amount of P applied was lower (composts at dose 1). These results confirm that both composts are good sources of nutrients, being able to substitute for mineral fertilizers and providing adequate concentrations of N, P and K for plants. Higher nutrient concentrations in the aerial parts of *L. multiflorum*, for plants grown in soils amended with composted livestock manure, in comparison with a mineral fertilizer, were also reported by *Lubis and Kumagai* (2007) when similar concentrations of both were applied. Also, the P concentration in the aerial parts of ryegrass has been found to rise with increasing rates of fertilizer, including animal manures – indicating that it existed in these manures in available forms (*Butler* et al., 2007; *Gaston* et al., 2003; *Szogi* et al., 2010).

Besides the significant, positive responses of the N, P and K concentrations in ryegrass to compost application, a significant decline in N with the harvesting cycle was observed, which may be due to the consumption of the easily-available N or to nutrient leaching after each "rain event". Despite the slightly-higher N concentration in plants from treatment D2, relative to D1, the values of the compost-based treatments did not differ significantly ($p<0.001$); however, they were higher than the control values, probably due to the mineralization of the organic-N. No significant differences ($p < 0.001$) in the root P and K concentrations were found between the compost treatments (Table 3). The root K concentration did differ significantly according to the treatment, the value for compost at dose 1 being similar to the control while compost at dose 2 had a value similar to that of treatment F.

Comparing the shoot N, P and K concentrations with the optimal values (30-42 g N kg^{-1} DM, 3.5-5g P kg^{-1} DM and 25-35 g K kg^{-1} DM) for Italian ryegrass growth (*Bergmann*, 1986), N and P might have limited the growth at the 2nd and 3rd harvests. The P concentration in the aboveground biomass was within the lower range found by *Ylivainio* et al. (2008), who suggested that a low P concentration can be due to a dilution effect caused by the enhanced growth of *L. multiflorum*. The N:P ratio in the aerial part of the plants can be used to indicate the nutrient that is restricting plant growth (*Güsewell*, 2004). The N:P ratio > 20 found at the first harvest, for all treatments, suggests that plant growth was initially restricted by P availability; while at harvest 3 the N/P ratio < 10 for the compost treatment indicates that N limited plant growth at the end of the experiment, except for the mineral fertilizer treatment (*Güsewell*, 2004). At the second harvest, for all treatments, the N:P ratio was adequate. These results indicate that high N from compost and F could be plant-available immediately after soil addition, but precipitation or fixation of P can occur shortly after addition to an alkaline soil (e.g. due to insoluble Ca-phosphate formation), being released later on during the growing session. Organic acids present in the soil, produced from root exudates, may compete for the same binding sites as

P, depressing the P sorption strength of the soil (*Ylivainio* et al., 2008). According to *Jorgensen* et al. (2010), composting of the separated solids from animal slurry does not alter the P-availability but P-precipitation as Ca or Mg phosphate may occur during composting due to the pH increase. *Ylivainio* et al. (2008) indicated that the high proportion of inorganic-P in manure compost makes it a convenient P fertilizer for *L. multiflorum* due to its high root-to-shoot ratio of P (as shown in the present experiment; Tables 2 and 3); these authors referred to it as a P-efficient species with relatively-low external P requirements.

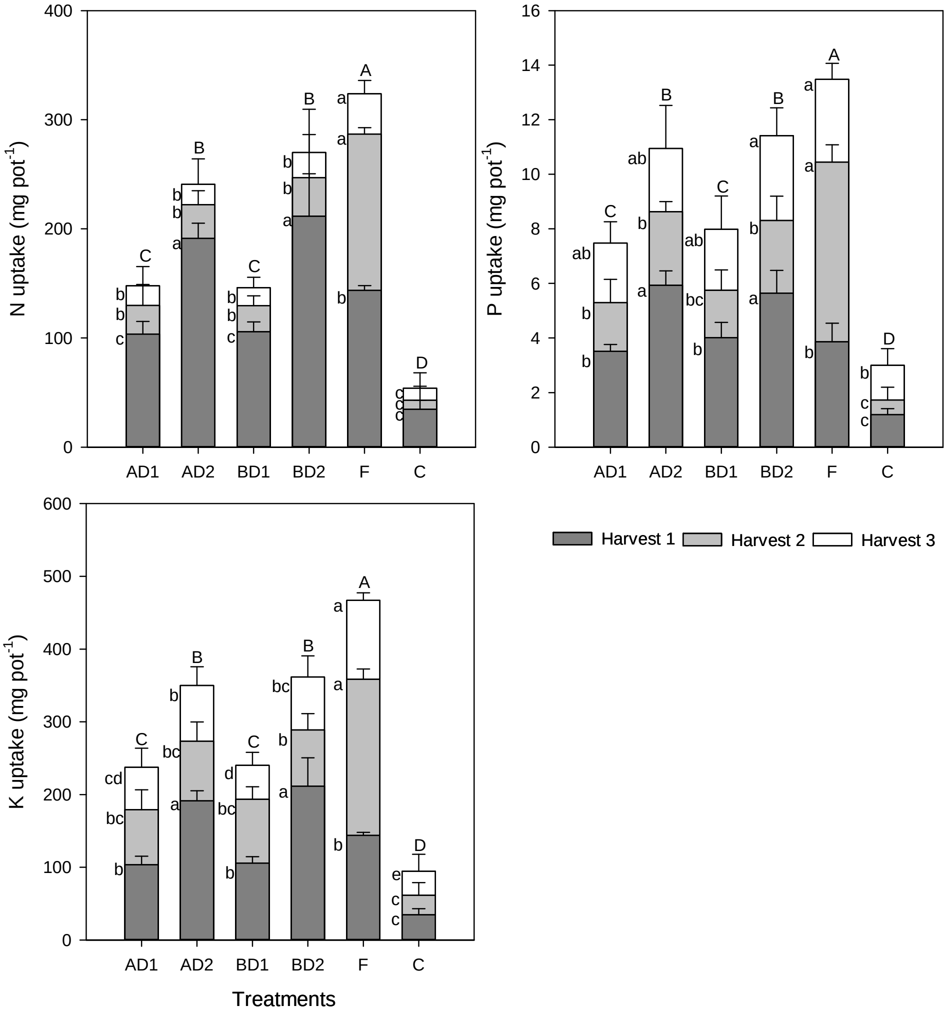

Figure 1. Nutrient uptake in the aerial parts of *L. multiflorum* in each harvest during the pot trial, according to the different treatments applied to the soil: AD1, compost A at dose 1; AD2, compost A at dose 2; BD1, compost B at dose 1; BD2, compost B at dose 2; F, mineral fertilizer; C, non-fertilized control. For each harvest, values (bars) with the same letter do not differ significantly according to the Tukey test ($p<0.05$). Capital letters refer to the accumulated values (sum of harvests 1+2+3) and the lower-case letters refer to each harvest.

The nutrient uptake by the aerial parts of *L. multiflorum* during the pot trial is shown in Figure 1, in relation to the fertilizing treatments. Compost application, particularly at the higher rate, significantly increased the N, P and K accumulation by the shoots, when compared with the control (Fig. 2). The uptake of N, P and K was greatest in treatment F (324, 13.5 and 467 mg pot^{-1}, respectively), with a considerable difference from BD2 (270, 11.4 and 362 mg pot^{-1}, respectively). Composts A and B did not show any significant differences at the same fertilizer rate; however, nutrient accumulation for AD2 and BD2 was higher than with AD1 and BD1. Similar behavior was found for the N uptake by ryegrass with pig manure compost in a pot experiment, the N uptake increasing with the compost application rate (*Cordovil* et al., 2006). Also, *Ylivainio* et al. (2008) reported higher P uptake by *L. multiflorum* when composted manure was applied at a double rate and even greater uptake at a quadruple dose, in all harvests.

The concentrations of Zn and Cu of the plants were determined in order to estimate the risk of their accumulation in plants, due to the use of these metal-rich composts (Table 1). The Spanish legislation for fertilizing products (*BOE*, 2013) set the limits of the total Cu and Zn concentrations in compost at 400 and 1000 mg kg^{-1}, respectively, for class C composts (limiting the use to 5 t ha^{-1} yr^{-1} on agricultural soil). By the time of the first harvest, the shoot Cu and Zn concentrations were generally higher in the compost treatments than in control plants, but without statistically-significant differences from treatment F. The concentrations of Zn measured in the aerial part of the plant can be considered normal for plant nutrition (27-150 mg kg^{-1}; *Kabata-Pendias*, 2001). The Cu concentration decreased in the following harvests; this may be due to the ability of Cu to form chelates with the stable and humified OM (*Bernal* et al., 2009b). Although the shoot Cu concentration remained higher in the compost treatment than in the control, the values cannot be considered toxic, as they are within the normal range for plants (5-30 mg kg^{-1}; *Kabata-Pendias*, 2001). So, the compost treatments did not affect negatively the shoot Cu and Zn concentrations. Higher concentrations of Cu and Zn were found in the roots than in the aerial parts; this is the usual response of metal-excluding, tolerant plant species (*Baker*, 1981) - which accumulate metals in the roots, restricting transport to shoots until the external concentration is extremely high.

3.3. Fertilizing efficiency.

The N fertilizing efficiency of the compost was estimated by the N Apparent Recovery Fraction (ARF), calculated according to Eq. 1. With respect to the control, the ARF of compost A was 26.5 % for both application rates and for compost B the values were 23.9 and 29 % for dose 1 and 2, respectively. Similar values (28 %) were found by *Thomsen and Kjellerup* (1997) for manure without litter (cattle feces), being 8-14 % for manure with litter (cattle feces + urine + straw), related to the inorganic-N concentration; lower values were found in winter, associated with N leaching. The mineral fertilizer treatment (F) reached an N ARF value of 74.5 %, because all the N was in inorganic forms, whereas composts A and B had 27.4 % and 17.8 % of the TN as inorganic forms, respectively (Table 1). This indicates that the inorganic-N present in compost A was assimilated by the plants, but partial mineralization of the organic-N of compost B may have occurred, rendering it available to the plants.

Compared with the efficiency of the mineral fertilizer, the relative agronomic efficiency (RAE) reached 47.6 and 37.8 % for compost A at doses 1 and 2, respectively; being 42.6 and 38.1% for compost B at doses 1 and 2, respectively. These results confirm that mineralization of organic-N in the mature composts occurred in the soil during the crop development, accounting for at least 10 % of the TN in compost A and 20 % in compost B; up to 20 % of TN was accounted for in well-matured compost in the work of *Bernal* et al. (1998).

The apparent recovery fraction (ARF) of P was low in all treatments, with the highest value in treatment F (6.6 %). This implies that this nutrient was applied in excess of crop requirements and accumulated in the soil. According to *Ylivainio* et al. (2008), the ARF of P for ryegrass in the first growing year was 20-26 % for manure compost applied at different rates, with similar values in the treatments with mineral fertilizer (21.7-26.8 %). The RAE of P in compost B (74.6 and 52.7 % in doses 1 and 2) was greater than in compost A (56.1 and 40.0% in doses 1 and 2), due to the lower concentration of P in compost B, giving a greater efficiency of P uptake by the plants. *Brod* et al. (2015) determined the P-RAE of different organic waste materials for ryegrass: the greatest values occurred for dairy manure, with greater efficiency than the mineral fertilizer ($Ca(H_2PO_4)_2$), followed by liquid digestate and chicken manure (72-78 %), with lower values for fish sludge and solid digestate (47-70%), for one or up to four harvests in a soil of pH 6.9. These values were well predicted using the $NaHCO_3$-extractable P (Olsen P).

Very different behavior occurred with respect to K, where 100 % of the K added to the soil with F was assimilated by the plants, the ARF reaching very-high values for compost A (64.5 and 57.6 % in doses 1 and 2) and compost B (60.0 and 55.0 % in doses 1 and 2). This is due to the highly-available forms of K present in the composts, mainly soluble forms; the fraction not taken up by plants can be retained in the soil as exchangeable and soluble forms, but can also be lost by leaching. The high EC of the leachates of the compost treatments (up to 630 µS cm^{-1} in the first rain event, and up to 263 µS cm^{-1} in the second), with respect to the control and treatment F (116-127 and 219-170 µS cm^{-1}), may indicate the leaching of soluble salts, including K.

3.4. Nitrogen leaching and residual soil nutrients availability.

Losses of N during the experiment could have occurred by leaching or denitrification (*Burgos* et al. 2006; *Hoffman and Van Cleemput*, 2004). For leaching to occur, N must be in a water-soluble, mobile form and the rainfall must be abundant enough to transport N through the soil. Although urea and nitrite are mobile, neither exists in significant concentrations in soil. Nitrate is the N form most susceptible to leaching, since ammonium-N can be retained in the soil cation exchange capacity. In this sense, water-soluble TN (N_w) present in the leachate from the first rain event occurred as nitrate (data not shown); then, only N_w was measured in the following leachates.

All the amendment treatments had higher N losses than the control during the experiment (1.7- to 2.1-times greater), without significant differences between treatments or rain periods (Figure 2). Such losses were low and accounted for 0.18, 0.09, 0.10, 0.06 and 0.13 % of added-N for treatments AD1, AD2, BD1, BD2 and F, respectively. These results indicate that, although a similar amount of N was leached for all fertilizer treatments, the proportion lost was lowest when compost was applied at a higher rate. The water holding capacity of the composts may have had a strong influence on N-leaching (*Fulekar*, 2010), considering that compost B, prepared with a greater amount of cotton gin waste than compost A, produced a slightly-lower volume of leachate than compost A, especially at dose 2 (2100 ± 395 and 1695 ± 380 ml pot^{-1} in AD2 and BD2, respectively). The two-phase fertilization applied in treatment F seemed to be effective in reducing the N loss by leaching and did not compromise the biomass production, considering that all the N in treatment F was readily available and was susceptible to loss during the first rain event.

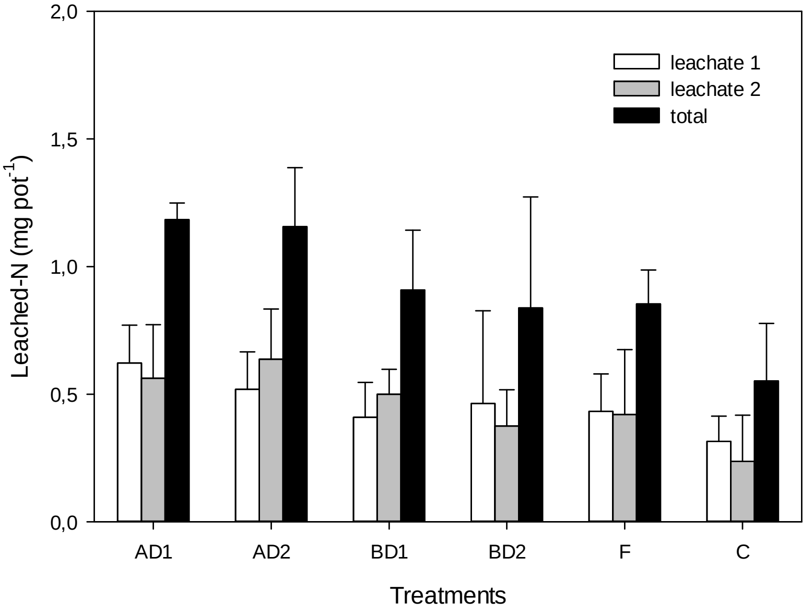

Figure 2. Nitrogen leached during each rain event simulated during the pot trial. No significant differences were found between the treatments.

In terms of the doses applied, no significant differences were found when comparing the amount of N in the leachates (compost A: 1.18-1.20 mg N pot^{-1}; compost B: 0.95-1.03 mg N pot^{-1}, doses 1 and 2, respectively). Higher nitrate-N application implies higher N leaching risks, but the lack of a significant increase in N loss by leaching (or nitrate accumulation in the soil, Table 4) indicates that the extra NO_3^--N was used by the plant. *Burgos* et al. (2006) pointed out that N losses by leaching tend to be higher when poorly-stabilized organic materials rich in N are applied, but also stated that nitrate losses by leaching from compost-amended soils are usually very low.

The chemical properties of the amended and control soils at the end of the experiment are shown in Table 4. The TOC in the soil showed small but significant differences between the treatments with compost A and the control. Similar results were found in soils amended with compost at low doses (*Evanylo* et al., 2008), indicating that a relevant proportion of the OM from the compost may have been mineralized during the experiment. All the treatments were able to increase TN in the soil, at the end of the experiment, with respect to the control soil. Increases in TN in the soil after application of composts produced from livestock manure or from municipal solid wastes have been found in pot studies (*Evanylo* et al., 2008; *Karami* et al., 2011; *Soumaré* et al., 2003), indicating that the use of N-rich composts increased the soil fertility, as part of the N from the composts was in organic forms, unavailable for plant uptake. However, the concentrations of available P, K, Cu and Zn in the soil of treatment AD1 were similar to or significantly lower (Cu) than those in the control. The fact that these nutrients in the composts are easily available to plants, together with the higher biomass production, when compared to the control, may have led to low available concentrations in the soil at the end of the experiment.

The lack of significant differences in the soil NH_4^+-N concentration among the treatments indicates the complete nitrification of the fertilizer and the retention of this cation in the exchange complex of the soil, in similar proportions in all treatments. Low concentrations of NO_3^--N were observed in the soils amended with compost A (lower than the control) and no statistically-significant differences occurred for the rest of the treatments, suggesting that the inorganic-N supplied by the amendments may have been used by the plants or lost from the soil. The low N losses by leaching during the two rain events (Fig. 2) indicate that the N applied was used by the plants, accumulated in the soil or was lost by denitrification. According to *Estavillo* et al. (1996), N losses by denitrification from mineral fertilizers can be 9-17 % during spring/autumn, reaching 2 % from mature composts (*Cambardella* et al., 2003). In fact, the soil TN concentration was significantly higher in the compost and mineral fertilizer treatments than in the control. Towards the end of the experiment, the lower temperatures that occurred (winter time) could have slowed down the organic-N mineralization in the compost-treated soils, limiting the plant-available N.

Table 4 – Total organic carbon (TOC), total-N (TN), inorganic-N, available P and K and the soluble and exchangeable fraction of Cu and Zn ($CaCl_2$-extractable) of the amended soils at the end of the experiment.

Treatments	TOC (g kg^{-1})	TN (g kg^{-1})	NH$_4^+$-N (mg kg^{-1})	NO$_3^-$-N (mg kg^{-1})	P$_{avail}$ (mg kg^{-1})	K$_{avail}$ (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
AD1	4.0±0.14	0.43±0.02 a	17.5±1.86	9.58±0. 53 b	63.2±2.96 c	48.4±2.49 e	2.97±0.10 b	0.65±0.01 c
AD2	4.8±0.38	0.45±0.02 a	13.7±3.58	9.71±1.18 b	81.5±4.77 b	64.9±1.84 c	3.32±0.15 a	1.07±0.18 b
BD1	4.8±0.21	0.44±0.03 a	17.6±2.19	11.0±0.80 ab	98.6±5.46 a	74.0±1.27 b	3.48±0.11 a	1.53±0.16 a
BD2	4.3±0.22	0.42±0.03 a	16.8±1.04	11.3±0.32 ab	82.1±6.97 b	64.7±1.33 c	3.40±0.14 a	1.17±0.13 b
F	4.9±0.36	0.44±0.04 a	15.9±0.72	12.1±1.29 a	97.3±2.19 a	79.0±3.65 a	3.42±0.18 a	1.54±0.03 a
C	3.8±0.16	0.37±0.01 b	18.3±3.41	11.6±0.34 ab	63.2±3.48 c	56.0±1.44 d	3.40±0.16 a	0.76±0.15 c
ANOVA	n.s.	**	n.s.	**	***	***	**	***

Mean ± standard deviation (n=4); n.s.: not significant; *, **, ***: significant at $P<0.05$, 0.01, 0.001, respectively. For each parameter, values followed by the same letter do not differ significantly according to the Tukey test ($p<0.05$).

Copper and Zn are micronutrients essential for plant growth, but the use of materials with high concentrations of these elements may have an accumulative effect in soils. The available Cu concentration found in the amended soils was similar to that of the control soil (Table 4). But, the available Zn concentration in the soils amended with compost A or B at the higher dose was significantly higher than in the control; although the values were low, they indicate a pollution risk due to accumulation resulting from repeated applications over a long-term period. However, toxic effects on plants were not observed (Tables 2 and 3).

4. Conclusions

Both composts can be considered adequate organic fertilizer products, since they efficiently increased the biomass yield of *L. multiflorum*, especially when a higher dose was applied. Also, their provision of nutrients for plant growth was adequate, although differences in the timing of the supply of N and P to plants were detected. This lack of synchronization between the plant availability of N and P could lead to plant growth restriction due to N or P deficiency in the early stages or later on during the growing period.

The fertilizer efficiency of the N from the composts was lower than from the mineral fertilizer, as part of the N supplied by the composts was organic-N. However, the relative agronomic efficiency (RAE) reached 47.6 %, indicating that partial mineralization of the compost N may have occurred during the experiment, supplying inorganic-N to plants. Low fertilizer efficiency of P was found for all treatments, but the P-RAE percentages reached 56 and 75 % in composts A and B, respectively. Also, high RAE values occurred for compost K due to the high solubility of this nutrient in compost.

Despite the high concentrations of Cu and Zn in the composts used, their levels in *L. multiflorum* biomass (aerial and root) and in the soil at the end of the experiment did not produce any toxic effects on plants or constitute an immediate threat of soil contamination.

The use of both composts as soil amendments did not pose any threat in terms of nitrate leaching, even after a heavy rain event, and the use of a double dose of compost did not increase the amount of nitrate leached.

In an agronomic scenario, a combination of mineral and organic fertilizers during the growth season might be recommended, using composts as a base fertilization before sowing and complementing with mineral fertilizer during the growing season to supply the nutrients required for efficient crop production.

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5. References

Abram, A. and Forster, D.L. (2005): A Primer on Ammonia, Nitrogen Fertilizers, and Natural Gas Markets. Department of Agricultural, Environmental, and Development Economics, Ohio State University: 38.

Baker, A.J.M. (1981): Accumulators and excluders – strategies in the response of plants to heavy metals. J. Plant Nut. 3, 643-654.

Bedada, W., Karltun, E., Lemenih, M, Tolera, M. (2014): Long-term addition of compost and NP fertilizer increases crop yield and improves soil quality in experiments on smallholder farms. Agric. Ecosyst. Environ. 195, 193-201.

Bergmann, W. (1986) Bemerkungen und Tabellen zur analytischen Pflanzendiagnose der Pflanzenoder Blattanalyse. Farbatlas Ermährngsstörungen bei Kulturpflanzen und Analytische Diagnose. VEG Gustav-Fischer-Verlag, Jena.

Bernal, M.P., Navarro, A.F., Sánchez-Monedero, M.A., Roig, A., Cegarra, J. (1998): Influence of sewage sludge compost stability and maturity on carbon and nitrogen mineralization in soil. Soil Biol. Biochem. 30, 305-313.

Bernal, M.P., Alburquerque, J.A., Moral, R. (2009^{a}): Composting of animal manures and chemical criteria for compost maturity assessment. A review. Bioresour. Technol. 100, 5444–5453.

Bernal, M.P., Clemente, R., Walker, D.J. (2009b): Interactions of heavy metals with soil organic matter in relation to phytoremediation. In: J.P. Navarro-Aviñó (Ed.) Phytoremediation: the Green Salvation of the World. Research Signpost, Kerala, India, pp. 109-129.

Biau, A., Santiveri, F., Mijangos, I., Lloveras, J. (2012): The impact of organic and inorganic fertilizers on soil quality parameters and productivity of irrigated maize crops in semiarid regions. Eur. J. Soil Biol. 53, 56-61.

BOE (2013). Real Decreto 506/2013, de 28 de junio, sobre productos fertilizantes. Boletín Oficial del Estado 164: 51119-51207.

Brod, E., Øgaard, A.F., Haraldsen, T.K., Krogstad, T. (2015): Waste products as alternative phosphorus fertilizers part II: predicting P fertilisation effects by chemical extraction. Nutr. Cycl. Agroecosyst. 103, 187-199.

Burgos, P., Madejón, E., Cabrera, F. (2006): Nitrogen mineralization and nitrate leaching of a Sandy soil amended with different organic wastes. Waste Manage. Res. 24, 175-182.

Butler, T.J., Muir J.P., Provin, T.L. (2007): Phosphorus fertilization of annual ryegrass and comparison of soil phosphorus extractants. J. Plant Nutr. 30, 9–20.

Cambardella, C.A., Richard, T.L., Russell, A., 2003. Compost mineralization in soil as function of composting process conditions. Eur. J. Soil Biol. 39, 117-127.

Cavanagh, A., Gasser, M.O., Labrecque, M. (2011): Pig slurry as fertilizer on willow plantation. Biomass Bioenerg. 35, 4165-4173.

Cordovil, C.M.d.S., Cabral, F., Coutinho, J., Goss, M. (2006): Nitrogen uptake by ryegrass from organic wastes applied to a sandy loam soil. Soil Use Manage. 22, 320–322.

Cordovil, C.M.d.S, Cabral, F., Coutinho, J. (2007): Potential mineralization of nitrogen from organic wastes to ryegrass and wheat crops. Bioresour. Technol. 98, 3265-3268.

Corrêa, R.S., White, R.E., Weatherley, A.J. (2005): Modelling the risk of nitrate leaching from two soils amended with five different biosolids. Rev. Bras. Ciênc. Solo 29, 619-626.

Eghball, B., Power, J.F. (1999): Phosphorus and nitrogen-based manure and compost applications: corn production and soil phosphorus. Soil Sci. Am. J. 63, 895–901.

Egodawatta, W.C.P., Sangakkara, U.R., Stamp, P. (2012): Impact of green manure and mineral fertilizer inputs on soil organic matter and crop productivity in a sloping landscape of Sri Lanka. Field Crop Res. 129, 21-27.

Estavillo, J.M., Rodriguez, M., Gonzalez-Murua, C. (1996): Nitrogen losses by denitrification and leaching in grassland: The effect of cow slurry application. Fert. Res. 43, 197-201.

Evanylo, G., Sherony, C., Spargo, J., Starner, D., Brosius, M., Hearing, K. (2008): Soil and water environmental effects of fertilizer-, manure-, and compost-based fertility in an organic vegetable cropping system. Agric. Ecosyst. Environ. 127, 50-58.

Food and Agriculture Organization of the United Nations (FAO) (2015): FAOSTAT database. http://faostat.fao.org. (visited 21.11.2015)

Fertilizers Europe (2008): Energy efficiency and greenhouse gas emissions in European nitrogen fertilizer production and use. http://www.fertilizerseurope.com/ fileadmin/user_upload/publications/agriculture_publications/Energy_Efficiency__V9.pdf (visited 10.12.2015)

Fertilizers Europe (2015): Forecast of food, farming and fertilizer use in European Union 2012-2022. http://www.fertilizerseurope.com/fileadmin/user_upload/ publications/agriculture_publications/Forecast_2012-final.pdf (visited 10.12.2015)

Fulekar, M.H. (2010): Environmental Biotechnology: chemical benefits of compost. CRC Press LLC, Boca Raton, Florida.

Gaston, L.A., Eilers, T.L., Kovar, J.L., Cooper, D., Robinson, D.L. (2003): Greenhouse and field studies on hay harvest to remediate high phosphorus soil. Commun. Soil Sci. Plant Anal. 34, 2085–2097.

Gräber, I., Hansen, J.F., Olesen, S.E., Petersen, J., Østergaard, H.S., Krogh, L. (2005): Accumulation of copper and zinc in Danish agricultural soils in intensive pig production areas. Danish J. Geogr. 105, 15–22.

Güsewell, S. (2004): N:P ratios in terrestrial plants: variation and functional significance. New Phytol. 164, 243-266.

Gunnarsson, A., Bengtsson, F., Caspersen, S. (2010): Use efficiency of nitrogen from biodigested plant material by ryegrass. J. Plant Nutr. Soil Sci. 173, 113–119.

He, Z.L., Alva, A.K., Yan, P., Li, Y.C., Calvert, D.V., Stoffella, P.J., Banks, D.J. (2000): Nitrogen mineralization and transformation from composts and biosolids during field incubation in a sandy soil. Soil Sci. 165, 161–169.

Hoffman, G., Van Cleemput, O. (2004): Soil and plant nitrogen. International Fertilizer Industry Association (IFA), Paris, France, p.48.

Jorge-Mardomingo, I., Jiménez-Hernández, M.E., Moreno, L., de la Losa, A., de la Cruz, M.T., Casermeiro, M.A. (2015): Application of high doses of organic amendments in Mediterranean agricultural soil: An approach for assessing the risk of groundwater contamination. Catena 131, 74-83.

Jorgensen, K., Magid, J., Luxhoi, J., Jensen, L.S. (2010): Phosphorus distribution in untreated and composted solid fractions from pig slurry separation. J. Environ. Qual. 39, 393-401.

Kabata-Pendias, A. (2001): Trace elements in soils and plants, third ed. CRC Press LLC, Boca Raton, Florida.

Karami, N., Clemente, R., Moreno-Jiménez, E., Lepp, N.W., Beesley, L. (2011): Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. J. Hazard. Mat. 191, 41-48.

Keener, H.M., Dick., W.A., Hoitink, H.A.J. (2000): Composting and beneficial utilization of composted by-product materials. In: W.A. Dick (ed.) Land Application of Agricultural, Industrial, and Municipal By-Products. Nº 6 Soil Science Society of America Book Series. SSSA Inc, Wisconsin, pp. 315-341.

Kundsen, D., Peterson, G.A., Pratt, P.F. (1982): Lithium, sodium and potassium. In: Page, A.L., Miller, R.H., Keeney, D.H. (eds.) Methods of soil analysis. Part 2, 2nd edn. Agronomy Monograph 9. ASA and SSSA, Madison, Wisconsin, pp. 225-246.

Legros, S., Chaurand, P., Rose, J., Masion, A., Briois, V., Ferrasse, J.H., Macary, H.S., Bottero, J.Y., Doelsch, E. (2010): Investigation of copper speciation in pig slurry by a multitechnique approach. Environ. Sci. Technol. 44, 6926-6932.

Loecke, T.D., Liebman, M., Cambardella, C.A., Richard, T.L. (2004): Corn growth responses to composted and fresh solid swine manures. Crop Sci. 44, 177-184.

Lubis, A.D, Kumagai, H. (2007): Effects of cattle barnyard compost and nitrogen fertilizer application on yield and chemical composition of maize (*Zea mays* L.) and Italian ryegrass (*Lolium multiflorum* Lam.) in double cropping system. J. Int. Dev. Coop. 13, 109-117.

Moral, R., Paredes C., Bustamante M.A., Marhuenda-Egea F., Bernal M.P., (2009): Utilisation of manure composts by high-value crops: safety and environmental challenges. Bioresour. Technol. 100, 5454-5460.

Navarro, A.F., Cegarra, J., Roig, A., Bernal, M.P. (1991): An automatic microanalysis method for the determination of organic carbon in wastes. Commun. Soil Sci. Plant Anal. 22, 2137-2144.

Santos, A., Bustamante, M.A., Tortosa, G., Moral, R., Bernal, M.P. (2016): Gaseous emissions and process development during composting of pig slurry: the influence of the proportion of cotton gin waste. J. Clean. Prod. 112, 81-90.

Sommer, S.G., Kjellerup, V., Kristjansen, O. (1992): Determination of total ammonium nitrogen in pig and cattle slurry: sample preparation and analysis. Acta Agric. Scand., Sect. B, Soil Plant Sci. 42, 146-151.

Soumaré, F.M., Tack, F.M.G., Verloo, M.G. (2003): Ryegrass response to mineral fertilization and organic amendment with municipal solid waste compost in two tropical agricultural soils of Mali. J. Plant Nutr. 26, 1169-1188.

Szogi, A.A., Bauer, P.J., Vanotti, M.B. (2010): Fertilizer effectiveness of phosphorus recovered from broiler litter. Agron. J. 102, 723–727.

Tejada, M., Gonzales, J.L. (2006): Crushed cotton gin compost on soil biological properties and rice yield. Eur. J. Agron. 25, 22-29.

Thomsen, I.K., Kjellerup, V. (1997): Yields and N uptake of barley and ryegrass from soils with added animal manure differing in straw and urine content. Eur. J. Agron. 7, 285-292.

Tiquia, S.M., Richard, T.L., Honeyman, M.S. (2002): Carbon, nutrient, and mass loss during composting. Nutr. Cycl. Agroecosyst. 62, 15-24.

Ylivainio, K., Uusitalo, R., Turtola, E. (2008): Meat bone meal and fox manure as P sources for ryegrass (*Lolium multiflorum*) grown on a limed soil. Nutr. Cycl. Agrosyst. 81, 267-278.

4. Resumen de las publicaciones

CARBON CONSERVATION STRATEGY FOR THE MANAGEMENT OF PIG SLURRY COMPOSTING: INITIAL STUDY OF THE BULKING AGENT INFLUENCE.

ESTRATEGIAS DE CONSERVACIÓN DE CARBONO PARA LA GESTIÓN DEL PURÍN DE CERDO MEDIANTE COMPOSTAJE: ESTUDIO INICIAL DE LA INFLUENCIA DEL AGENTE ESTRUTURANTE.

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Mitigation and Adaptation Strategies for Global Change, DOI 10.1007/s11027-014-9593-0

El objetivo principal de este estudio fue evaluar la influencia del tipo de agente estructurante usado en la reducción de las emisiones de CO_2, y por lo tanto en la promoción de la conservación del C, durante la gestión del purín de cerdo mediante compostaje.

Para ello se realizaron estudios de laboratorio en reactores para determinar la capacidad de autocalentamiento de cada mezcla, y estudios de incubación aeróbica para determinar la degradación de las mezclas mediante la determinación del CO_2 desprendido. Se prepararon cuatro mezclas (M1, M2, M3 y M4), utilizando la fracción sólida del purín de cerdo (SPS) con diferentes agentes estructurantes: caña de maíz (MS), paja de cebada (BS), residuo del desmotado de algodón (CW) y poda de jardín (mezcla 1:1 de morera (*Morus alba*) y jacaranda (*Jacaranda mimosifolia*)) (GP). El SPS se recogió de una granja de cerdas y lechones en Guazamara (Almería, España), después de una separación sólido-líquido utilizando un tornillo prensa. De los materiales estructurantes, BS fue proporcionada por la misma granja que el SPS, el CW procedió de una desmotadora de algodón situada en Sevilla, MS fue suministrada por la empresa Gestcompost (Zaragoza) y la mezcla de residuos de poda de jardín procedió de una empresa responsable del mantenimiento de jardines públicos en Murcia.

Antes de su uso en las mezclas, el SPS se homogeneizó; los agentes estructurantes se cortaron a un tamaño de partícula inferior a 5 cm, excepto el CW (que sólo fue homogeneizado). Las proporciones de las mezclas, en base a peso fresco, fueron las siguientes: M1: 83% de SPS + 17% MSF CW; M2: 92% de SPS + 8% MS; M3: 94% de SPS + 6% BS; M4: 87% de SPS + 13% PW.

Las proporciones de las mezclas se ajustaron con el fin de utilizar la cantidad máxima de SPS, teniendo en cuenta una relación inicial C/N de 20-25 y un contenido de humedad de 55-80%, adecuada para el compostaje. A continuación, la SPS se mezcló con el agente estructurante, y las mezclas obtenidas se colocaron en los respectivos reactores de 5 L (por duplicado para cada mezcla). Los reactores eran cilindros de 14 cm de diámetro interno y 40 cm de altura con aislamiento térmico. Las sondas de temperatura se colocaron en el centro de los reactores y se conectaron a un registrador de datos, que permitió el registro de la temperatura de forma automática. La temperatura externa también se registró automáticamente. Se determinó el peso inicial, la altura y la densidad de las diferentes mezclas dentro de los reactores. Sólo las mezclas elaboradas con PW y MS se voltearon en el día 7, debido a la disminución de la temperatura de estas mezclas, con la finalidad de mejorar la homogeneidad y la porosidad de las mezclas. El volteo se llevó a cabo vaciando completamente el reactor, mezclando fuera cada mezcla. El experimento se consideró terminado cuando la temperatura de las mezclas era cerca a la del ambiente y no se produjo re-calentamiento, durando aproximadamente 15 días.

Se tomaron muestras representativas de cada mezcla al inicio y al final de cada experimento. Cada muestra representativa se dividió en tres fracciones en el laboratorio: uno de ellas para determinar el contenido de humedad y para la realización de los ensayos de incubación, la segunda para la determinación de nitrógeno de amonio (NH_4^+-N) y la tercera para el resto de las determinaciones analíticas tras su congelación, liofilización y trituración. Se calculó también la energía producida por los microorganismos, responsables del aumento de la temperatura en los reactores.

El ensayo de incubación consistió en colocar 5 g de las muestras iniciales y finales del ensayo de autocalientamiento junto con un vial con 10 mL de NaOH 0,5 M dentro de frascos herméticos para atrapar el CO_2 producido por la respiración microbiana. Los frascos se mantuvieron dentro de un incubador a 26 ºC durante 10 días, y los viales se cambiaron a cada 2-3 días.

La producción de CO_2 se determinó mediante y la valoración del exceso de disolución de NaOH con ácido clorhídrico (HCl) 0,5 M. Todos los análisis se realizaron al menos por duplicado.

Los **análisis físico-químicos** realizados consistieron en: conductividad eléctrica (CE), pH, materia orgánica (OM), carbono orgánico total (TOC), nitrógeno total (TN), carbono orgánico soluble en agua (C_w) y nitrógeno en forma de amonio ($N\text{-}NH_4^+$). El CO_2 producido en el experimento de incubación se determinó mediante valoración del exceso de NaOH con HCl en presencia de $BaCl_2$ y fenolftaleína como indicador. Para el **análisis estadístico**, se utilizó el análisis de la varianza de un factor (ANOVA) para evaluar las diferencias significativas entre los valores de cada parámetro estudiado durante el compostaje, mientras que la prueba de Tukey a $P < 0{,}05$ se utilizó para determinar las diferencias estadísticamente significativas en los parámetros estudiados entre las mezclas al principio y al final del experimento. La normalidad y la homogeneidad de las varianzas fueron comprobadas mediante la prueba de Kolmogorov-Smirnov y Levene, respectivamente, antes de aplicar ANOVA. También se determinó el error estándar de los valores medios. Además, se obtuvo el coeficiente de correlación de Pearson entre la energía producida, la concentración de C_w y las emisiones de CO_2-C para todas las mezclas y los dos muestreos ($n = 8$). El análisis de datos se realizó utilizando el software estadístico SPSS v.19.0.

Los resultados obtenidos respecto al perfil térmico, se pudo observar que los residuos del desmotado de algodón y la poda de jardín fueron materiales fácilmente degradables, produciendo las temperaturas más elevadas, alrededor de 24-26 ºC, y un desarrollo rápido de la temperatura, lo que indica una alta actividad microbiana. Esta observación está apoyada reducción en la producción de C-CO_2 en las muestras analizadas al final del experimento, respecto a las muestras iniciales. La reducción de la emisión de CO_2 fue más significativa en la mezcla con poda de jardín, con una reducción de 57%, lo que indica que la actividad microbiana de la mezcla con residuos del desmotado de algodón todavía seguía activa al final del experimento de autocalentamiento en los reactores.

Como se observó en los valores de C-CO_2, las mezclas de residuos de desmotado de algodón y de poda de jardín tenían los valores más altos de las emisiones de CO_2-C en comparación con la paja de cebada o caña de maíz, que tenían los valores más bajos. Los resultados están de acuerdo con el perfil de temperatura. Los valores de aumento de la producción de C-CO_2 en las mezclas de maíz y cebada después de 15 días de compostaje pueden indicar que estas mezclas son más difíciles de degradar. Quizás, la parte interna de las partículas no puede ser accesible para el ataque microbiano, y los 15 días de compostaje habrán actuado como un pre-tratamiento para romper la superficie de las partículas.

Se **concluyó** que el análisis del perfil térmico de los materiales de compostaje a escala de laboratorio, con la degradación microbiana medida por las emisiones de CO_2 medidas en incubaciones de 10 días son parámetros adecuados para definir las mezclas factibles de usar en el compostaje de la fracción solida del purín de cerdo a nivel de laboratorio. Se puede concluir que la poda de jardín o los residuos del desmotado de algodón pueden ser considerados agentes estructurantes adecuados para el compostaje de la fracción sólida del purín de cerdo. Sin embargo, el uso de caña de maíz o paja de cebada como agentes estructurantes, garantizan una mayor conservación del C y más bajas emisiones de CO_2, siendo mejores agentes estructurantes para la mitigación de las emisiones de gases con efecto invernadero.

GASEOUS EMISSIONS AND PROCESS DEVELOPMENT DURING COMPOSTING OF PIG SLURRY: INFLUENCE OF THE PROPORTION OF COTTON GIN WASTE.

EMISIONES GASEOSAS Y DESARROLLO DEL PROCESO DURANTE EL COMPOSTAJE DEL PURÍN DE CERDO: INFLUENCIA DE LA PROPORCIÓN DE DESMOTADO DE ALGODÓN.

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El objetivo principal de este ensayo fue evaluar la influencia de la proporción de residuo de desmotado de algodón como agente estructurante en el compostaje de la fracción sólida de purín de cerdo mediante la evaluación del perfil térmico y la evolución de los parámetros físico-químicos del compostaje, y sus implicaciones medioambientales mediante las emisiones de gases de efecto invernadero.

Se prepararon dos mezclas (M1 y M2) de la fracción sólida del purín de cerdo (SPS) con los residuos del desmotado de algodón (CGW), teniendo en cuenta el contenido de humedad y la relación C/N de ambos materiales: M1, con una proporción de 4:3 (SFP:CGW; v/v) ; y M2, con una relación de 3:4 (SPS:CGW). La SPS se obtuvo de una granja de cerdos de engorde después de una separación sólido-líquido con un tornillo prensa y el CGW de una desmotadora de algodón de Sevilla. El experimento se llevó a cabo en una planta de compostaje a escala piloto mediante el sistema de pila estática con ventilación forzada a demanda de temperatura (máxima 65 ºC). Las mezclas se establecieron en pilas trapezoidales de 2000 kg cada una, con una base de 2,7 x 3,7 metros y una altura de 1 y 1,2 m, para M1 y M2, respectivamente. La aireación fue programada de manera que se activara cada 120 minutos durante: 1 min si T < 55 ºC; 2 min si 55 ºC < T < 60 ºC; 3 min si 60 ºC < T < 65 ºC; y continuamente si T > 65 ºC, hasta que T ≤ 60 ºC. La demanda de ventilación se calculó como el tiempo (horas por día) de ventilación continua de la bomba (T > 65 ºC). Las pilas se voltearon dos veces durante todo el proceso, cuando la temperatura comenzó a disminuir, con el fin de mejorar tanto la homogeneidad de los materiales y como del proceso de compostaje. La humedad de las pilas se controló semanalmente mediante la adición de la cantidad de agua necesaria para mantener el contenido de humedad superior al 40%. La evolución de la temperatura se controló usando dos sondas de temperatura en cada pila, instaladas en diferentes lugares de la pila. La fase biooxidativa del compostaje se consideró finalizada cuando la temperatura dentro de la pila era cercana a la temperatura exterior y no se produjo recalentamiento después del volteo. A continuación, la ventilación se apagó y los compost se dejaron madurar durante un periodo de dos meses.

Durante los 167 días que duró el proceso de compostaje, se tomaron diez muestras para evaluar la evolución de las mezclas. Las muestras se tomaron mediante la mezcla de siete sub-muestras de siete sitios representativos de la pila, de todo el perfil (desde la parte superior a la parte inferior de la pila). Cada muestra representativa se dividió en tres fracciones en el laboratorio: una para determinar el contenido de humedad, otra para la determinación del nitrógeno de amonio ($N-NH_4^+$) y el tercero para el resto de las determinaciones analíticas, la cual se congeló, liofilizó y trituró.

Respecto a los **análisis químicos y físico-químicos**, los materias iniciales y las muestras obtenidas durante el compostaje se analizaron respecto a la conductividad eléctrica (EC), el pH, la materia orgánica (MO), el carbono orgánico total (COT), el nitrógeno total (NT), el carbono orgánico soluble en agua (C_w), el carbono extraíble (C_{ext}), el carbono de los ácidos fúlvicos (C_{FA}) y húmicos (C_{HA}), el nitrógeno en forma de amonio ($N-NH_4^+$) el nitrógeno en forma de nitrato ($N-NO_3^-$), la capacidad de cambio catiónico (CCC), los macro y micronutrientes y el índice de germinación (IG). El flujo de emisión de los gases de efecto invernadero (dióxido de carbono - CO_2, metano - CH_4 y óxido nitroso - N_2O) se midió en la superficie de las pilas, utilizando el sistema de cámara estática cerrada durante la fase termófila. Se calculó también la energía producida por la actividad microbiana durante el proceso de compostaje. Para el **análisis estadístico**, se calculó el error estándar de las medias de los parámetros químicos y físico-químicos de las muestras; se realizó un análisis de la varianza de un factor (ANOVA) y las menores diferencias significativas (LSD) se utilizaron para determinar los cambios de los parámetros durante el compostaje. La normalidad y homogeneidad de las varianzas se comprobó mediante el test de Shapiro-Wilk y Levene, antes del ANOVA. Se utilizó el paquete de software v.19 IBM SPSS Statistics para el análisis estadístico. La mineralización de la MO se calculó ajustando los datos a un modelo cinético de primer orden, mediante el ajuste no lineal por mínimos cuadrados, utilizando el Software SigmaPlot v.12.0 Systat Inc.

Como **resultados**, se observó en ambas pilas un aumento de temperatura durante la primera semana del proceso, alcanzando temperaturas superiores a 60 ºC. Dichas temperaturas se mantuvieron durante más de 35 días, indicando una buena actividad microbiana y biodegradabilidad de los materiales y garantizando una buena higienización del compost. M2 presentó una fase termófila más larga que M1, debido al uso de una mayor proporción de agente estructurante rico en COT. Las características térmicas del agente estructurante demostraron ser el factor determinante en las temperaturas máximas de compostaje así como en la ventilación extra necesaria. Tras los volteos, la temperatura se reactivó en ambas pilas, verificando que las mezclas seguían microbiológicamente activas. La fase biooxidativa del proceso de compostaje duró 103 días, cuando las temperaturas de las pilas alcanzaron valores estables cercanos a la temperatura ambiente.

Se observó una mineralización más intensa en M1 durante los 5 primeros días, lo que puede estar relacionado con la mayor cantidad de SPSusada, que proporciona una forma de C más fácilmente degradable por los microorganismos. Sin embargo, la mayor cantidad de materiales recalcitrantes de M2 proporcionaron una mineralización más lenta de la MO. Ambas pilas demuestran una alta estabilidad de la mineralización al final del proceso.

La concentración de COT y C_w disminuyo al largo del proceso, verificándose un rápido descenso entre la fase inicial y la fase termófila, indicando una fuerte actividad microbiana, traducida por las elevadas temperaturas verificadas durante esta fase. La concentración de COT disminuyó el 15% y el 24% para M1 y M2, respectivamente. Al final del proceso, la concentración de C_w representaba el 2,3 y 2,5% del COT en M1 y M2, respectivamente.

Analizando la evolución de las formas de nitrógeno, se observó un aumento en la concentración de NT, debido a un efecto de concentración por la reducción del volumen de las pilas. La concentración de $N\text{-}NH_4^+$ sufrió una disminución más acentuada en M1 que en M2 en la etapa inicial del proceso, que está relacionada con la mayor intensidad microbiana detectada en esta pila, por las elevadas temperaturas observadas en la fase termófila. La concentración de $N\text{-}NO_3^-$ aumentó durante el proceso, siendo este más acentuado cuando la temperatura de las pilas empezó a disminuir de valores termófilos. M1 presentó concentraciones más elevadas de $N\text{-}NO_3^-$, lo que indica que el proceso de nitrificación fue más intenso.

Las menores emisiones de gases de efecto invernadero (CO_2, CH_4 y N_2O) ocurrieron en M2, debido al menor contenido en SPS y a la mayor demanda de ventilación extra para mantener la temperatura inferior de 65 ºC. Se verifico que las emisiones de gases de efecto invernadero dependen de la intensidad de la mineralización de la MO.

Según los valores límite considerados por varios autores para compost maduros, los compost obtenidos presentaron un adecuado grado de madurez, con valores de IG > 50%, $C_{AF} < 12{,}5$ g kg^{-1}, relación C/N < 12, relación $N\text{-}NH_4^+/N\text{-}NO_3^- < 0{,}16$ y CCC > 67 meq 100 g^{-1} MO. También la materia orgánica alcanzó un buen grado de humificación, donde el C_{AH} representó el 2,9 y 1,6% del COT para M1 y M2, respectivamente. La mayoría de los parámetros de calidad se adecuan a los valores considerados en la legislación nacional, pero ambos compost se clasifican como clase C, debido a su elevado contenido en Cu y Zn proveniente de la FSP.

Se **concluyó** que el residuo del desmotado de algodón presenta buenas características para controlar la humedad excesiva de la SPS, siendo un material adecuado como agente estructurante en el proceso compostaje, y los compost obtenidos presentan un buen grado de madurez. Al aumentar la proporción de agente estructurante, la fase termófila del proceso se alarga, extendiendo así el tiempo necesario para la fase activa del compostaje, y produciendo un compost con menores concentraciones de C, N y sustancias húmicas. Así, el uso de una proporción 4:3 de SFP:CGW (v/v) es adecuada para el compostaje de la SFP, obteniéndose un compost con buena calidad y con alto grado de madurez. Sin embargo, para garantizar su calidad es preciso controlar las concentraciones de Cu y Zn en la SPS.

SUSTAINABLE MANAGEMENT OF PIG SLURRY USING DIFFERENT COMPOSTING SCENARIOS: ASSESSMENT OF THE ORGANIC MATTER CHANGES.

GESTIÓN SOSTENIBLE DEL PURÍN DE CERDO USANDO DIFERENTES ESCENARIOS DE COMPOSTAJE: EVALUACIÓN DE LOS CAMBIOS EN LA MATERIA ORGÁNICA.

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El **objetivo** de este trabajo ha sido evaluar los cambios producidos en la materia orgánica durante el proceso de compostaje, utilizando técnicas espectroscópicas. Los compost se prepararon a partir de la fracción solida del purín de cerdo y residuo de desmotado de algodón en diferentes proporciones, escenarios y sistemas de compostaje. La utilización de técnicas termogravimétricas se implementan con los resultados obtenidos por la utilización de CP ^{13}C RMN para estado sólido y FT-IR, con el fin de aumentar el conocimiento sobre las transformaciones de la materia orgánica presente en las muestras de compost a lo largo del proceso.

En cuanto a los **materiales** utilizados, se prepararon tres pilas (P1, P2 y P3) utilizando la fracción sólida de purín de cerdo (SPS) y el residuo de una desmotadora de algodón (CW). La fracción sólida se obtuvo mediante una separación sólido-líquido utilizando un tornillo prensa. Las pilas P1, P2 y P3 se elaboraron en las proporciones SFP:CW: 4:3, 3:4 y 3:7,5 v/v; las dos primeras (P1 y P2) se prepararon en una planta piloto de 2 toneladas de peso fresco, mediante el sistema de pila estática Rutgers, con aireación forzada a demanda de temperatura, con una temperatura máxima de 65 °C. En P1 y P2 la fase biooxidativa duró 103 días y se voltearon dos veces al disminuir la temperatura. La pila P3 se preparó en una granja de porcino, utilizando el sistema de volteo con un volumen inicial de 19,2 m^3. En esta pila, las temperaturas termófilas se prolongaron durante 70 días, alcanzando valores superiores a 60 ºC; y la fase biooxidativa duró 146 días, durante los cuales la pila se volteó cinco veces. Se consideró que el proceso de compostaje había terminado cuando la temperatura era estable y cercana a la ambiental. Se dejaron madurar dos meses. La humedad se controló semanalmente y se adicionó agua necesaria para mantener la humedad al 40 %. Las muestras se obtuvieron de siete zonas diferentes de las pilas y se tomaron en el día 0 (muestra inicial-I), dos durante la fase termófila (comienzo- BT y avanzada- T), al final de la fase biooxidativa (EB) y después del periodo de maduración (M).

En cuanto al **análisis químico de las muestras**, se determinó el carbono orgánico total (COT), el nitrógeno total (NT), la materia orgánica (MO), el carbono orgánico soluble (C_w), la fracción húmica (carbono orgánico extraíble; C_{EX}), carbono de ácido fúlvico (C_{FA}) y carbono de ácido húmico (C_{HA}), la relación de humificación (HR), el índice de humificación (HI), el porcentaje de carbono de tipo ácido húmico (P_{HA}) y el índice de polimerización (P_I) .Todos los parámetros fueron determinados por triplicado.

Los **análisis térmicos** se llevaron a cabo realizando una combustión con una mezcla de Oxígeno/Helio (20/80 %) en un rango de temperaturas de 25 a 650 ^{0}C. La **RMN de CP MAS ^{13}C** se llevó a cabo operando a 125,75 MHz para ^{13}C, calculándose la integración de la señal para siete regiones: carbonilo (210-165 ppm), O-aromático (165-145 ppm), aromático (145- 110 ppm), O_2-alquilo (110-95 ppm), O-alquilo (95-60 ppm), N-alquil/metoxi(60-45 ppm) y alquilo (45-10 ppm). Los espectros **FT-IR** utilizaron un rango de operación de 400-4000 cm^{-1}. El **análisis estadístico** para evaluar las diferencias significativas entre los valores de los parámetros estudiados durante el compostaje se llevó a cabo mediante el test ANOVA y la prueba de LSD ($P< 0,05$). Para evaluar las diferencias significativas entre los resultados del análisis térmico (T50 y R1) se utilizó el test ANOVA de dos factores y la prueba de Tukey HSD ($P<0,05$). Para controlar la normalidad y homogeneidad de la varianza se utilizaron los test de Shapiro-Wilk y de Levene, previo a realizar el ANOVA. Se llevó a cabo el análisis de regresión de Pearson entre R1 y los parámetros químicos (MO, COT, Cw, NT y COT/NT). Los datos se analizaron mediante el paquete de software estadístico SPSS v. 19.0.

Durante el proceso de compostaje todas las pilas mostraron el perfil típico de temperaturas: Para P1 y P2, la fase termófila fue más larga alcanzando la temperatura máxima antes que P3, pudiendo deberse a las diferencias entre las muestras de fracción sólida de purín utilizadas en P3 respecto a P1 y P2. La concentración de MO disminuyó por la degradación microbiana de compuestos orgánicos lábiles. En una segunda fase se dio una menor pérdida de MO, que indicaba compuestos más resistentes a la actividad microbiana, polímeros como ligninas, que se mantuvieron en el producto, sugiriendo que el contenido en MO se estabilizó. El COT y C_w disminuyeron en el proceso, debido a la mineralización de la MO. El NT aumentó en todas las pilas pudiendo deberse al efecto de concentración causado por la reducción de la masa de compost y/o los procesos de N-inmovilización, disminuyendo la relación COT/NT hasta valores menores a 12, que indican un aceptable grado de madurez. En cuanto a los parámetros que indican las **fracciones de C**, los compost obtenidos a partir de P1 y P3 mostraron mayores valores de C_{HA} que el de P2, mientras que P1 y P2 mostraron mayores valores de C_{FA} que P3. Para valores de **índices de humificación** (HR, HI, P_{HA} P_I)**,** los valores más elevados se mostraron en los compost de mayor proporción de SFP, P1 y P3, pero sus valores son para todos los compost, superiores a los referidos por diferentes autores, como indicativos de la madurez del compost.

Las **curvas de TG** mostraron el comportamiento típico de la materia orgánica en un compost entre 25 y 600^0 C, mostrando un aumento del porcentaje de la fracción residual inorgánica relacionada al tiempo de compostaje, a la vez que disminuía la MO. El aumento de la fracción inorgánica (compost maduro frente a las muestras iniciales) fue mayor en P1 que en P2 y P3. En las curvas **DTG** se observaron tres regiones, la primera se dio entre los 25 y 105 ºC atribuida a la pérdida de agua, la segunda entre 200 y 430 ºC que se puede corresponder a la combustión de materia orgánica lábil (hidratos de carbono, lípidos simples y aminoácidos) y una tercera entre 430 y 580 ºC que se relaciona con la combustión de materia orgánica más estable (como por ejemplo compuestos aromáticos y polifenoles). Se estudió el efecto catalítico de las sales solubles inorgánicas y se observó que estas no influían en el área del pico obtenido en DTG, ya que se obtenían datos similares tanto para las muestras originales como para las que se había extraído el agua. Con estas áreas se calculó el índice de termoestabilidad **R1**. Este índice aumentó para los tres tipos de pilas, mostrando valores estables en la etapa de maduración. El análisis de ANOVA mostró que no existían diferencias significativas en las muestras termófilas y en la etapa final de la fase de maduración, mostrando también, que no existían diferencias significativas en los valores de R1 antes y después de haber extraído el agua. En cuanto al índice **T50** aumentó para todas las pilas durante el proceso de compostaje. El análisis de regresión de Pearson entre R1 y los parámetros químicos (MO, COT, C_w y COT/NT), mostraron correlaciones inversas altamente significativas ($p<0.001$), indicando que la materia orgánica recalcitrante estaba relacionada con los valores más elevados de R1. Los picos endo- y exotérmicos mostrados en las curvas **DTA** se asociaron a los mostrados en DTG. El pico endotérmico alrededor de 98 ºC correspondía al proceso de deshidratación. El pico exotérmico entre 200 y 400 ºC se vincularon a la degradación térmica de carbohidratos y otras moléculas lábiles, que fue mayor en las muestras iniciales, disminuyendo a lo largo del proceso coincidiendo con la disminución del porcentaje O-alquilo C. La región entre 430 y 580 ºC se asoció a la combustión de los compuestos más recalcitrantes que confirmaban el aumento del porcentaje de C alquilo.

Los espectros de **CPMAS ^{13}C NMR** mostraron picos alrededor de la zona de 73 ppm atribuidos a la presencia de carbohidratos (celulosa y hemicelulosa). La región correspondiente a O-alquilo (95 a 60 ppm) disminuyó a lo largo del proceso de compostaje sugiriendo la degradación de carbohidratos en el proceso. El incremento de los tipos de C en otras regiones del espectro se debía al efecto de concentración. El aumento de la intensidad relativa en la región de C-alquilo (45 a 10 ppm) coincide con el enriquecimiento de las muestras en compuestos recalcitrantes detectado en el análisis térmico. La proporción entre las fracciones de C más estable de la región alquilo y las fracciones de C lábiles asociadas a la región O-alquilo, disminuyó en las pilas P1 y P2, mostrando un comportamiento errático en la pila P3 que indicaba diferentes patrones de biotransformación, probablemente debido a los volteos. El distinto comportamiento de P3 puede deberse al proceso utilizado en el sistema de compostaje (volteo de la pila). Se observa una menor intensidad en P3 en las señales de las regiones carbonilo (210-165 ppm), O-aromático (165-145 ppm) y aromática (145-110 ppm).

En cuanto a los espectros obtenidos de **FT-IR**, se observó un incremento en la banda de 1384 cm^{-1} asignado a nitratos, y un decrecimiento en las bandas 2920 cm^{-1} y 1050 cm^{-1} asignados a vibraciones C-H alifático y polisacárido, respectivamente. Los cambios en la banda de 2920 cm^{-1} se pueden utilizar como referencia para evaluar la biotransformación de la materia orgánica durante el proceso de compostaje. De hecho, se ha verificado una intensa correlación directa entre la concentración de MO y la banda 2920 cm^{-1} ($p < 0,01$). La relación entre la intensidad de las bandas de polisacáridos (1050 cm^{-1}) y de nitratos (1384 cm^{-1}) disminuyó para todas las pilas con el tiempo de compostaje, correlacionándose directamente con la relación C/N e inversamente con la concentración de MO ($p < 0,01$). El comportamiento en P3 fue diferente al mostrado en P1 y P2, probablemente debido a diferencias en la transformación de la materia orgánica, en concordancia con lo observado en los espectros de CPMAS ^{13}C NMR.

Como **conclusiones** se puede decir que las técnicas termogravimétricas como las clásicas de análisis se correlacionaban de forma significativa entre R1 y los parámetros de C. Las técnicas de RMN y FT-IR se mostraron más eficaces para entender la evolución de C durante el compostaje, especialmente cuando se comparan los C recalcitrantes frente a los C lábiles. FT-IR se mostró más eficaz en el seguimiento de la biotransformación de la materia orgánica que los métodos clásicos de análisis, utilizando los polisacáridos y los nitratos como compuestos “señalizadores”. Estos cambios detectados en la transformación de la materia orgánica en las técnicas instrumentales, pueden ser utilizados para determinar la calidad en compost maduros.

FERTILISER VALUE AND POTENTIAL NITRATE LEACHING RISKS OF PIG SLURRY COMPOSTS.

VALOR FERTILIZANTE Y RIEGO POTENCIAL DE LIXIVIACIÓN DE NITRATOS DE COMPOST DE PURÍN DE CERDO.

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El **objetivo** de este estudio fue evaluar el potencial fertilizante de los dos compost producidos de la fracción solida del purín de cerdo y el residuo del desmotado de algodón, así como el riesgo potencial de lixiviación de nitratos tras su aplicación al suelo como fertilizantes orgánicos.

Se realizó un ensayo en macetas de cuatro meses de duración con raigrás (*Lolium multiflorum* L.) como planta testigo bajo condiciones de invernadero. Se utilizó un suelo agrícola, franco arenoso recogido de la capa arable de suelo (0-15 cm) de un campo agrícola situado en las instalaciones de UTAD (Universidade de Trás-os-Montes e Alto Douro), Vila Real, Portugal. El suelo se secó al aire se tamizó a 4 mm para el experimento en macetas y a 2 mm para su análisis. Se utilizaron dos compost (A y B), obtenidos a partir de dos mezclas de fracción sólida de purín de cerdo y residuo de desmotado de algodón en dos proporciones (4:3 y 3:4 v/v). La descripción del sistema de compostaje y de los compost se pueden obtener en Santos et al. (2016) (capítulo 3.2 de la presente memoria). Los compost se aplicaron en dos dosis distintas y se compararon con un fertilizante mineral NPK (10:10:10). Se consideraron seis tratamientos diferentes: AD1 y BD1: compost A y compost B a dosis 1 (proporcionando 360 mg NT por maceta, equivalente a 308 kg ha^{-1} año^{-1}); AD2 y BD2: compost A y compost B a dosis 2 (doble de la dosis 1); F: fertilizante mineral (10:10:10) a razón de 360 mg NT por maceta (equivalente a 308 kg de NT ha^{-1} año^{-1} - dosis 1 de compost); y C: suelo control sin ningún tipo de fertilización.

Las dosis de aplicación de los compost y fertilizante, se calculó en base al N requerido por la planta. El experimento se realizó en macetas de 10L de capacidad con doble fondo, que permitió recoger los lixiviados por la parte inferior. Los compost se mezclaron con 9 kg de suelo seco al comienzo del experimento, y el fertilizante inorgánico se dividió en dos aplicaciones: antes de sembrar y después de la primera cosecha. Se utilizaron 4 repeticiones por tratamiento (número total de macetas: 24). El contenido de humedad de los suelos se ajustó al 70% de la capacidad de retención hídrica (WHC) utilizando agua destilada y, a continuación, se añadieron 0,5 g de semillas de raigrás (*Lolium multiflorum* L.) por maceta. El riego se realizó de modo gravimétrico con agua destilada, manteniendo el 70% de WHC. Los lixiviados producidos después del riego se recogieron en el fondo de la maceta, se cuantificaron y se congelaron para su posterior análisis. Durante el experimento, el raigrás se cosechó tres veces, tras 30, 60 y 120 días de su emergencia, mediante el corte de la parte aérea 2 cm por encima de la superficie del suelo. El peso fresco y seco se determinó antes y después de secar a 65 ºC, respectivamente. Las muestras se molieron para el análisis.

El riesgo potencial de lixiviación de los nitratos en el suelo se evaluó después de la primera y segunda cosechas. Para ello, un evento de lluvia fuerte (equivalente a 24 mm) se simuló mediante la adición de 1,75 L de agua destilada a la parte superior de la maceta. Los lixiviados producidos se cuantificaron y se congelaron para su posterior análisis.

Al final del experimento, después de la tercera cosecha, el suelo se separó de las raíces, se homogeneizó y se tomaron muestras para el análisis. Las raíces se limpiaron, en primer lugar mediante la eliminación de la mayor parte de las partículas del suelo con agua, luego dos veces con abundante agua destilada y finalmente, por ultrasonidos (5 minutos a 750 W), para eliminar cualquier partícula de suelo adherida a las raíces.

Los **análisis físico-químicos** de plantas consistieron en: materia seca, nitrógeno total (NT), fósforo total (P), potasio (K), cobre (Cu) y zinc (Zn). Además, las muestras de suelo se analizaron respecto a: contenido de humedad, carbono orgánico total (COT), NT, nitrógeno amónico (NH_4^+-N), nitrógeno de nitratos (NO_3^--N), P disponible, K disponible, fracción soluble e intercambiable de Cu y Zn. Los lixiviados se analizaron en cuanto a nitrógeno soluble en agua (N_W) y nitratos. Todos los análisis se realizaron al menos por duplicado.

Para el **análisis estadístico**, se calculó el error estándar de la medias para las características químicas y físico-químicas de los suelos, la biomasa vegetal y nutrientes; se efectuó un análisis de la varianza de un factor (ANOVA) y se calculó las menores diferencias significativa (LSD) para determinar los cambios de los parámetros de acuerdo con los tratamientos. El ANOVA de dos vías se utilizó para determinar los cambios de los parámetros de la planta según los dos factores: la cosecha y el tratamiento. La normalidad y la homogeneidad de las varianzas se comprobaron mediante el test de Shapiro-Wilk y Levene, respectivamente, antes de ANOVA. Se calculó también la fracción de recuperación aparente (ARF) de N, P y K por la planta, así como la eficiencia agronómica relativa (RAE) de N, P, y K para los tratamientos con compost. El análisis de datos se realizó utilizando el paquete de software estadístico SPSS v.19.0.

En los **resultados**, se verificó que el uso de compost como fertilizante fue capaz de aumentar la producción de biomasa y la fertilidad del suelo con respecto al control, siendo los incrementos más relevantes en la dosis de compost más elevada. Sin embargo, después del primer corte, el crecimiento de las plantas en los tratamientos con compost fue inferior al logrado con el fertilizante mineral, debido a los diferentes tiempos de aplicación de cada uno de ellos. Las altas concentraciones de Cu y Zn que se encuentran en los compost no afectaron negativamente el desarrollo de las plantas, ya que actuaron como micronutrientes esenciales para el crecimiento de la planta, sin mostrar gran acumulación en el suelo. Las pérdidas de N por lixiviación fueron muy bajas en todos los tratamientos, y el uso de dosis más elevada de agente estructurante no supuso un incremento de las pérdidas de nitratos por lixiviación. Los resultados sugieren que la capacidad de retención de agua del compost pudo afectar al riesgo de lixiviación. En comparación con el fertilizante mineral, la eficiencia agronómica relativa (RAE) del N del compost alcanzó un 47,6 %, indicando una mineralización parcial del N-orgánico del compost. Respecto al P, la RAE alcanzó 56 y 75 % para los compost A y B, respectivamente, siendo superior en el compost con menor concentración de éste elemento. La alta solubilidad del K en el compost produjo unos valores altos de RAE, lo que demuestra el valor fertilizante de los nutrientes del compost preparado a partir de la fracción solida del purín de cerdo.

Se **concluyó** que los dos compost se pueden considerar como eficientes fertilizantes orgánicos, ya que aumentaron la producción de biomasa de *L. multiflorum*, especialmente cuando se aplicó en la dosis superior y se pueden utilizar como sustituto parcial de los fertilizantes minerales sin un riesgo de lixiviación de nitratos o acumulación de Cu y Zn a corto plazo en el suelo. Sin embargo, el uso continuado de compost como enmiendas, podría llevar a una contaminación por metales pesados por acumulación en el suelo. Es necesario considerar las eficiencias agronómicas de los nutrientes del compost a la hora de calcular la dosis de fertilización.

En un escenario agronómico, se propone una combinación de fertilización orgánica y mineral durante el periodo de cultivo, utilizando el compost como fertilizante de fondo antes de la siembra y ajustando la fertilización mediante fertilizantes minerales durante el periodo de crecimiento en función de la demanda de los nutrientes para una producción eficiente del cultivo.

5. General discussion

5.1 Composting the solid fraction of pig slurry.

The solid fraction of pig slurry (SFP) is an N-rich solid material with some inadequate characteristics for a proper development of the composting process. The low carbon to nitrogen ratio (C/N) provides a limited organic-C source for microorganisms, then during composting the organic-N mineralisation led to inorganic-N production that can be lost by ammonia volatilisation or by nitrate leaching from the composting mass. The high moisture content may promote the formation of anaerobic microsites, increasing the formation of CH_4 and N_2O, due to the lack of aeration of the composting mass (Bernal et al., 2009; Georgacakis et al., 1996; Nolan et al., 2011). Ros et al. (2006) and Nolan et al. (2011), found that during composting the SFP without bulking agent, low temperatures were reached, reflecting the low microbial activity and consequent low microbial respiration, due to both, the low C concentration in the SFP and maybe the scarce aerobic conditions in the composting mass. Ros et al. (2006) also found that the poor conditions of the process produced a scarcely sanitised compost with certain pathogenic microorganisms and high nitrate-N concentration subject to be lost by leaching, concluding that the use of a bulking agent was required for a good development of the composting process.

In this sense, the selection of the correct bulking agent is an essential step for composting the solid fraction of pig slurry. The bulking agent can not only improve the physical and chemical characteristics of the mixture and speed-up the process, but also define the quality of the end-product, when the objective is the treatment of wastes with the production of organic fertilisers. Ros et al. (2006) observed that mixing wood shavings with the SFP increased the temperature during composting, indicating that the bulking agent favoured aeration and hence, the rapid establishment of microbial activities in the composting pile, by the increase of C and the improvement of the pile structure. In the case of the SFP in the present study, a bulking agent able to control the excessive moisture and provide a good structure, with high TOC concentration in order to achieve an adequate initial C/N ratio for composting to avoid excessive N losses was required.

For selecting the bulking agent self-heating tests in isolated reactors at laboratory scale, and incubation experiments to assess the biodegradability of the different mixtures of SFP and bulking agents were run. The thermal profiles developed during the self-heating test and the CO_2 emissions from microbial respiration during the incubation test were evaluated.

The thermal profiles of the mixtures showed higher temperatures when cotton gin waste (CGW) and garden prunings (GP) were used, in comparison with maize stalks (MS) or barley straw (BS). According to Holman (2002) and Labance et al. (2006), the increase in temperature can be related to the high water holding capacity of CGW and GP, considering that the thermal conductivity and volumetric heat capacity of water are greater than those of air, allowing the materials with higher water holding capacity to increase quicker the temperature of the mass. Also, the moisture content is directly related to the specific heat capacity (Ahn et al., 2009), which indicates that SFP would have a higher specific heat capacity than any of the tested bulking agents, and the higher the proportion of SFP in the mixture the greater the energy necessary to increase its temperature. The specific heat capacity may also explain the delay in reaching thermophilic temperatures when composting SFP with certain lignocellulosic materials (Ros et al., 2006), considering that higher energy is required to increase the temperature of these materials and therefore, thermophilic temperatures are reached later than for materials with low specific heat capacity.

The microbial respiration assessed in the incubation test, indicated that the mixtures elaborated with CGW and GP had greater degradability than the mixtures with MS and BS, reaching higher stability after the self-heating test, as the CO_2 emissions were greatly reduced at the end of the test. These results were in accordance with Paredes et al. (1996) who also reported higher microbial respiration (higher microbial activity) in the mixtures elaborated with the olive-mill wastewater sludge and CGW than with MS.

However, from the point-of-view of C-conservation strategies, MS and BS should be the most adequate materials for co-composting SFP, due to the high concentration in recalcitrant compounds, such as lignin, that provide a slow C-release. However, the use of these materials as bulking agents would imply a poorer development of the composting process. Bernal et al. (1997) found that when MS were used as bulking agent, the composts produced presented lower maturation degree than those compost prepared with CGW, concluding that the higher concentration of recalcitrant compounds of maize stalks and the higher particle size were the main obstacles for a good development of the composting process.

Then, cotton gin waste was chosen as the best bulking agent to be used in the co-composting of the SFP at pilot-scale due to several factors: i) its capacity to control the excessive moisture content and to adjust the C/N ratio of the SFP; ii) its thermal properties that allow to achieve high temperatures during the self-heating test, which could guarantee the hygienic conditions of the composts; and iii) the high biodegradability which could provide a quick composting process. Paredes et al. (1996) also found effective the use of CGW in the control of the excessive moisture content of olive-mill wastewater sludge during composting; at the end of the process, the compost elaborated with CGW presented higher concentration in humic substances.

In the pilot-scale composting, two proportions of SFP:bulking agent were tested: M1 was built with the highest SPF proportion, in order to recycle the maximum amount of SFP; and in M2, higher CGW proportion was used to obtain the best initial conditions for the composting process, in terms of C/N ratio and moisture content.

The CGW is a material with good thermal properties, with a calorific value of 14.7 MJ kg^{-1} (Zabaniotou et al., 2007), higher than wood chips (12.2 MJ kg^{-1}; Francescato et al., 2008); with a specific heat capacity of 1.34 kJ kg^{-1} K^{-1}, similar to those of several kinds of wood and other biomasses (soybean straw or corn stalks). However, the specific heat capacity of CGW is lower than those of wheat straw, silage, oat straw, alfalfa hay and leaves and wood shavings (Ahn et al., 2009) – frequently used as bulking agents for animal manure composting (Bernal et al., 2009; Ros et al., 2006) – requiring less energy for its temperature to increase.

During the pilot-scale composting, the thermal profiles of the piles reflected the results of the self-heating test run with CGW, which proves the effectiveness of the use of such tests to predict the behaviour of the mixtures at pilot-scale composting. The quick increase of temperature observed at the beginning of the process indicated the great biodegradability of the materials, due to the presence of easily degradable organic-C for microbial consumption (Bernal et al., 2009). Also, the thermal properties of CGW helped to raise the temperatures above 55 ºC for more than 35 d ensuring, as predicted, the hygienic conditions required for compost (Saveyn and Eder, 2014). However, the thermophilic phase was longer in M2 (with greater proportion of CGW) than in M1. The differences observed in the thermal profiles were mostly related with the thermal properties of the CGW (low specific heat capacity) than with the organic matter (OM) mineralisation, as longer thermophilic phase in M2 with similar OM degradation during composting in both piles occurred. Similar results were found by Yañes et al. (2009) during composting of sewage sludge with garden prunings, where mixtures with a greater proportion of bulking agent showed higher temperatures for a longer period of time.

However, OM mineralisation (and reductions of TOC and C_w concentrations) was well related with the GHG emissions measured during the bioactive phase of the pilot-scale composting process. Higher emissions of CO_2, CH_4 and N_2O were found in M1– due to the higher proportion of SFP – than in M2, indicating that the GHG emissions did not depend exclusively on temperature, but on OM mineralisation rate. Aldo, the emissions in both piles were lower than those found by other author when composting animal manures with or without bulking agents (Hao et al., 2004; Sánchez-Monedero et al., 2010; Pampuro et al., 2014). A possible option to reduce the GHG emissions during composting is to provide the correct proportion of bulking agent, in order to improve the pile structure and to avoid anaerobic microsites. Also, in the Rutgers composting system, aeration can be controlled in critical moments, such as intense microbial activity and high ammonia concentration, adjusting the ventilation program to the required O_2 concentration for reducing CH_4 emissions at the beginning of the process as well as N-volatilisation; such system reduces considerably the need of turnings during the process. Most of GHG are released at the time of the turnings, when the internal air is in contact to the atmosphere; then limiting the number of turnings by using the static pile could restrict the GHG emissions. Maeda et al. (2013) found that the addition of dried grass to cattle manure could reduce the CH_4 and N_2O emissions up to 74.3 and 62.8 %, respectively. Sánchez-Monedero et al. (2010) also found that limiting the N input in the composting system was a viable solution to avoid ammonia and nitrous oxide emissions during the composting of animal manures and olive mill wastewater with different bulking agents. Szanto et al. (2007)

found that preforming monthly turnings during the passively aerated composting of straw-rich pig manure could reduce GHG emissions.

The quality of the compost was evaluated according to several physico-chemical parameters, considering that there is no a single parameter able to define the quality of the composts (Bernal et al., 2009). According to the limit values stablished by several authors, the composts produced presented an acceptable quality in terms of maturity degree: NH_4^+-N/NO_3^--N ratio < 0.16, C_w concentration < 10 g kg^1, C_w/TN ratio < 0.7, water-soluble C/N < 16, CEC > 67 meq 100 g^1 OM, CEC/TOC ratio > 1.7 and GI > 50% (Bernal et al., 1998, 2009; Itavaara et al., 2002; Benito et al., 2003; Chang and Chen, 2010). Also, the OM of both compost (HR, HI, PHA and PI) demonstrated the high degree of humification, similar to those found by Bustamante et al. (2008) when composting distillery wastes with animal manures, except for the higher HR in M1. The agronomic quality of the composts was evaluated in terms of nutrient and TOC concentrations. The composts obtained presented pH values close to neutrality, relatively-high concentrations of TOC and TN and high concentrations of macro and micronutrients, providing the essential elements for plant nutrition. Similar results were found for other composts produced from manures (Zhu et al., 2004; Huang et al., 2004) and sewage sludge (Paredes et al., 2001; Fels et al., 2014). However, the concentrations of Cu and Zn of the mature composts allow their classification as class C, according to the Spanish legislation for fertiliser products (BOE, 2013), which restricts their use in agriculture to 5 t ha^{-1} $year^{-1}$. The concentration of these elements in both composts was lower than the results found by Bustamante el al. (2013) in the mature compost produced from the solid phase of anaerobically-digested pig slurry, and by Tiquia et al. (1996) for compost prepared with pig slurry and sawdust. These is because the pig slurry used in the present work came from fattening pigs, and the use of Cu ($CuSO_4$) and Zn (ZnO) as feed additives occurs especially during the pregnancy of sows and in the post-weaning phase, to avoid certain digestive pathologies and improve growth (Carlson et al., 1999; Woodworth et al., 1999).

5.2 Organic matter transformations during composting.

Understanding the OM transformations throughout the composting process is a key aspect to indicate the good performance of the process and to predict the compost stability and maturity. In this sense, the use of advanced analytical techniques such as thermal analysis, FT-IR and CP MAS 13C NMR spectroscopy can be useful tools to identify the OM transformations during the composting process (Hsu and Lo, 1999; Jouraiphy et al., 2005; Marhuenda-Egea et al., 2007).

The thermal analysis are based on a programmed heating of the sample in controlled atmosphere which provide qualitative and quantitative information regarding different organic and inorganic compounds content of the samples tested; Fourier transform infrared (FT-IR) spectroscopy is based on the interaction of infrared light with matter and sensitive to the presence of different chemical functional groups; and solid-state ^{13}C nuclear resonance spectroscopy with cross polarisation and magic angle spinning (CP MAS NMR) has a great strength to provide information about the carbon molecules in a complex sample without any chemical or physical fractionation.

The OM transformations were assessed in three piles, elaborated with different proportions of SFP and CGW, and using two composting systems (static Rutgers system and turned pile) and composting scales (pilot plant and farm scale). The M1 and M2 piles (static Rutgers system at pilot scale) described before were compared with a pile elaborated at farm-scale by turning system (P3, with 3:7.5 proportion of SFP:CGW, v/v).

The differential thermal analysis (DTA) curves from thermal analysis showed two main peaks in all composts, where the first represents the easily degradable OM and the second the more stable compounds. The second peak in the samples from the beginning of the process was smaller in piles M1 than M2 (P1 and P2 in the paper) and P3, indicating lower concentration of recalcitrant materials in the pile with lower proportion of bulking material. In addition, the integration of the solid-state ^{13}C NMR spectrum, showed the highest relative intensity of the peaks referent to alkyl C-forms – more recalcitrant compounds – in the initial samples of P2 and P3, due to the higher proportion of CGW used. This observations were also well related with the faster OM mineralisation rate found in P1 than in P2 or P3, at the beginning of the process (4.53, 1.35, 0.98 % OM d^{-1}, respectively) and related to the lower proportion of CGW used in the mixture M1. The analysis of these results indicated that the higher relative intensity of O-alkyl C-forms and lower relative intensity of alkyl C-forms of pile with greater SFP:CGW explains the quicker OM mineralisation, related also with the TOC and C_w decrease observed at the beginning of the process. These observations were well related with strong correlations found between the C_w and the 2920, 1510, 1450 and 1384 cm^{-1} bands and 1050/1384 ratio obtained from the FT-IR spectra (0.784, -0.814, 0.822, -0.782, and 0.874, respectively; $p < 0.01$), indicating the decomposition of easily degradable compounds and the synthesis of more stable compounds. Marhuenda-Egea et al. (2007) also observed that the compost elaborated with lower proportion of recalcitrant materials presented a lower area for the second peak of the DTA curves in the initial samples, when composting the winery and distillery residues. During composting of sewage sludge and palm tree waste at different proportions, Fels et al. (2014) also observed a close relationship between the decrease of TOC and the quick decrease of the O-alkyl C-forms at the beginning of the process; the increase of bulking agent also increased the concentration of recalcitrant materials and slightly reduced the OM mineralisation rate (from 1.18 to 1.13 % OM d^{-1}).

During the maturation phase of the composting process a stabilisation the OM mineralisation was observed (based on weight loss of the piles). The thermal analysis of the samples from the beginning and the end of the composting process showed a decrease of the labile organic compounds – associated with the first peak of the DTA curves – coinciding with the decrease of O-alkyl C, aliphatic C-H, amino and polysaccharides percentages during the process, observed in the NMR and FT-IR spectrum. Also, the 1050/1384 ratio – comparable to the C/N ratio – from the FT-IR spectra, showed a small decrease and the 1450 cm^{-1} band (referent to lignin) remained stable during this phase, which can be related with the fact that easily degradable C was scarce, remaining the C forms with more recalcitrant character. Because the organic compounds concentration decreased during decomposition, the relative increase of inorganic components, such as nitrates, caused a rise of this band again (1384 cm^{-1}). The correlation of the chemical parameters with the relative absorbance obtained from the FT-IR spectra revealed strong direct correlation

($p < 0.01$) between the OM and the 2920 cm^{-1} band (aliphatic C-H vibrations of aliphatic methyl and methylene groups) and 1050/1384 ratio (0.751 and 0.843, respectively; $p < 0.01$). Also a strong inverse correlation between the OM concentration and 1510 cm^{-1} and 1384 cm^{-1} bands (-0.872 and -0.722, respectively; $p < 0.01$), indicated the consumption of easily degradable compounds during OM mineralisation – associated with the 2920 cm^{-1} and 1050 cm^{-1} decrease – and the formation of amine II and aromatic C=C compounds along the process (during humification), represented by the 1510 cm^{-1} region. During SFP composting, Hsu and Lo, (1999) found that most peaks in the aliphatic, amino, and polysaccharide regions levelled off during the composting process, indicating that pig manure material had become more uniform and stable with the attainment of compost maturity.

The increase of alkyl C percentage observed in the mature composts coincides with the enrichment in recalcitrant compounds detected with the thermal analysis and can be related with the humification process. The polymerisation of OM, and HA formation, was observed during the composting process, indicating the stabilisation of the organic matter. Huang et al. (2006) also found similar changes in FT-IR spectra, indicating that easily degradable organic matter constituents such as short aliphatic chains, polysaccharides and alcohols were chemically or biologically oxidised, leading to increased aromatic structures of high stability.

5.3 Effects of bulking agent proportion on plants and environment

As previously indicated, the composts produced at pilot-scale (M1 or compost A and M2 or compost B in the paper) presented a good quality and maturation degree, were rich in OM, organic- and inorganic-N and other beneficial nutrients for plant growth, which indicates that were adequate materials to be used as organic fertilisers.

Testing the agronomic value of the composts produced is necessary to determine the plant available fraction of nutrients in compost for an adequate agricultural use as organic fertilisers, as in the composts, N is present in both, inorganic and organic forms, the former are directly available to plants. Then, the fertiliser value of the composts was compared with a mineral fertiliser in a pot experiment with ryegrass.

In this experiment, compost was applied at a rate which provided the same amount of TN as with the mineral fertiliser (D1) and a double-dose (D2), considering that not all the N of compost was plant available.

During the pot trial, the use of both composts as organic fertilising products, revealed to be effective in increasing the biomass production of ryegrass and in improving the soil fertility (independently of their bulking proportion), when compared with the unamended soil. Thomsen and Kjellerup (1997) indicated that the compost with high and low proportion of bulking agent had similar biomass production and N uptake. Even if compost with greater SFP:CGW proportion (A) showed the best process development and highest OM humification degree, the effect of the proportion of bulking agent used in the compost was not statistically significant when these were used in soil. Maybe the characteristics of the composts were homogenised during the composting process. Differences were only found when increasing the application rate (D2), providing the highest amount of available N for plants. Cordovil et al. (2006) also found that increasing dose of compost increases the uptake by the plant.

The apparent recovery efficiency (ARF) was calculated to evaluate the nutrient utilisation from the amendments by the plant in comparison with the control treatment (Gunnarsson et al., 2010), and in the relative agronomic efficiency (RAE) the plant uptake from the compost-amended treatments was evaluated by comparing with the mineral fertiliser (Brod et al., 2015). As observed in the N apparent recovery efficiency (N-ARF), both composts presented similar N-efficiencies, but compost A presented higher N relative agronomic efficiency (N-RAE) in D1 (47.6 %) than compost B (42.6 %), due to the higher concentration of inorganic-N (27.4 and 17.8 % of TN in compost A and B, respectively). The N-RAE values indicated that not all the TN of the composts was plant available and organic-N mineralisation may have occurred during the experiment. In fact, TN mineralisation of at least 10 % in compost A and 20 % in compost B was estimated, comparable to the values found by Bernal et al. (1998) during an incubation experiment with soil amended with a mature compost.

Composts B presented higher P-efficiency (P-RAE) than compost A (74.6 and 52.7 % in doses 1 and 2 for compost B; 56.1 and 40.0 % in doses 1 and 2 for compost A), indicating lower proportion of available P. The highest efficiency was obtained from the compost with the lowest P concentration. According to Brod et al. (2015), the P-RAE of different organic waste materials for ryegrass decreased in the order: dairy manure (with greater efficiency than the mineral fertilizer), liquid digestate and chicken manure (72-78 %), with lowest values for fish sludge and solid digestate (47-70%); these indicating their plant available P. According to Jorgensen et al. (2010), P-precipitation as Ca or Mg phosphate may occur during composting of the separated solids from animal slurry due to the pH increase. The P-ARF by ryegrass found by Ylivainio et al. (2008) in soils amended with manure compost was higher than those found in the present composts, and similar to that of the mineral fertiliser treatment. The higher concentration of P in the manure compost (25.7 g kg^{-1}) found by Ylivainio et al. (2008), in comparison with the composts used in the present experiment (15.2 and 10.8 g kg^{-1} in compost A and B, respectively) may have been the main reason for the higher P-ARF.

Such values of ARF and RAE for N and P may reflect the differences N:P ratio in the aerial part of the plants, which can indicate the nutrient restricting plant growth (Güsewell, 2004). The N:P ratio > 20 found at the first harvest, suggests that plant growth was initially restricted by P availability; while at harvest 3 the N/P ratio < 10 for the compost treatment indicates that N limited plant growth at the end of the experiment, except for the mineral fertilizer treatment. Then, high N from compost could be plant-available immediately after soil addition, due to the high proportion of TN as nitrates; but precipitation or fixation of P can occur shortly after addition to an alkaline soil (e.g. due to insoluble Ca-phosphate formation), being released later on during the growing session. Also, during the growing period, organic acids produced from root exudates in the soil, may compete for the same binding sites as P, depressing the P sorption strength of the soil (Ylivainio et al., 2008), improving P availability. These results indicated a lack of synchronization between the plant availability of N and P from compost, which could lead to plant growth restriction due to N or P deficiency in the early stages or later on during the growing period.

The F treatment gave 100 % for K-ARF, indicating that all the K assimilated by the plants. The ARF values for compost A (64.5 and 57.6 % in doses 1 and 2) and compost B (60.0 and 55.0 % in doses 1 and 2) where very high and were related to the highly-available forms of K present in the composts, mainly soluble forms.

One of the risks associated with the use of compost can be due to nitrate leaching, as inorganic-N is mainly found as nitrates in mature compost, considered a maturity index (Bernal et al., 2009). No significant differences were found between composts in terms of nitrate leaching risk, although the use of compost B seemed to reduce the volume of leachate. Compost B was elaborated with the greatest proportion of cotton gin waste which could give high water holding capacity. Contrarily of what expected, increasing the compost application rate did not favour the N-leaching. The inorganic-N provided by the composts seemed to be absorbed by the plants, since no accumulation on the soil neither increased N-losses by leaching were verified. Both composts produced lower N-leaching than the N-losses observed by Daudén et al. (2004) from pig slurry application to the soil, indicating that composting can be considered as a preferable option for agricultural fertilisation, in order to minimise nitrate leaching into surface and ground waters.

The composts presented high concentrations of Cu and Zn that could cause negative effects on the plants and on the environment. However, the use of both composts as fertilisers did not pose any threat to plants, being the concentration in plant below the toxic levels considered for ryegrass (5 - 30 mg Cu kg^{-1} and 27 - 150 mg Zn kg^{-1}; Kabata-Pendias, 2001). Aldo, higher concentration of these elements was found on roots, due to a defence mechanism that restricts the transport of these to the aerial part of the plant, under toxic or non-toxic environments. The compost treatments did not show any significant differences in available Cu concentration in soil with the control treatment. However, available Zn concentration in soil was higher than control when the composts were used at the highest rate. Therefore, as no significant metal accumulation was observed in the soil in a short-term, the continued use of composts as amendment may impose a risk of pollution as accumulation in a long-term period.

5.4 References

Ahm, H.K., Sauer, T.J., Richard, T.L., Glanville, T.D. 2009. Determination of thermal properties of composting bulking agents. Bioresource Technology, 100: 3974-3981.

Benito, M., Masaguer, A., Moliner, A., Arrigo, N., Palma, R.M. 2003. Chemical and microbiological parameters for the characterisation of the stability and maturity of pruning waste compost. Biology Fertility Soils, 37: 184-189.

Bernal, M.P., Paredes, C., Sánchez-Monedero, M.A., Cegarra, J. 1997. Maturity and stability parameters of composts prepared with wide range of organic wastes. Bioresource Technology, 63: 91-99.

Bernal, M.P., Navarro, A.F., Sánchez-Monedero, M.A., Roig, A., Cegarra, J. 1998. Influence of sewage sludge compost stability and maturity on carbon and nitrogen mineralization in soil. Soil Biology and Biochemistry, 30: 305-313.

Bernal, M.P., Alburquerque, J.A., Moral, R. 2009. Composting of animal manures and chemical criteria for compost maturity assessment. A review. Bioresource Technology, 100: 5444–5453.

BOE, 2013. Real Decreto 506/2013, de 28 de junio, sobre productos fertilizantes. Boletín Oficial del Estado 164: 51119-51207.

Brod, E., Øgaard, A.F., Haraldsen, T.K., Krogstad, T. 2015. Waste products alternative phosphorus fertilisers part II: predicting P fertilisation effects by chemical extraction. Nutrient Recycling Agroecosystems, 103: 187-199.

Bustamante, M.A., Paredes, C., Marhuenda-Egea, F.C., Pérez-Espinosa, A., Bernal, M.P., Moral, R. 2008. Co-composting distillery wastes with animal manure: carbon and nitrogen transformations and evaluation of compost stability. Chemosphere, 72: 551-557.

Bustamante, M.A., Restrepo, A.P., Alburquerque, A., Pérez-Murcia, M.D., Paredes, C., Moral, R., Bernal, M.P. 2013. Recycling of anaerobic digestates by composting: effect of the bulking agent used. Journal of Cleaner Production, 47: 61-69.

Carlson, M.S., Hill, G.M. & Link, J.E. 1999. Early- and traditionally weaned nursery pigs benefit from phase-feeding pharmacological concentrations of zinc oxide: Effect on metallothionein and mineral concentrations. Journal of Animal Science, 77: 1199-1207.

Chang, J.I., Chen, Y.J. 2010. Effects of bulking agent on food waste composting. Bioresource Technology, 101: 5917-5924.

Cordovil, C.M.d.S., Cabral, F., Coutinho, J., Goss, M. 2006. Nitrogen uptake by ryegrass from organic wastes applied to a sandy loam soil. Soil Use and Management, 22: 320–322.

Daudén, A., Quílez, D., Vera, M.V. 2004. Pig slurry application and irrigation effects on nitrate leaching in Mediterranean soil lysimeters. Journal of Environmental Quality, 33: 2290-2295.

Fels, L., Zamama, M., Asli, A., Hafidi, M. 2014. Assessment of biotransformation of organic matter during co-composting of sewage sludge-lignocellulosic waste by chemical, FTIR analyses, and phytotoxicity tests. International Biodeterioration and Biodegradation, 87: 128-137.

Francescato, V., Antonini, E., Ziccoli, L. 2008. Wood Fuel Handbook. Production, Quality Requirements, Trading. AIEL- Italian Agroforestry Energy Association. Legnano, Italy.

Georgacakis, D., Tsavdaris, A., Bakouli, J., Symeonidis, S. 1996. Composting solid swine manure and lignite mixtures with selected plant residues. Bioresource Technology, 56: 195-200.

Güsewell, S. 2004. N:P ratios in terrestrial plants: variation and functional significance. New Phytology, 164: 243-266.

Hao, X., Chang, C., Larney, F.J. 2004. Carbon, nitrogen balances and greenhouse gas emission during cattle feedlot manure composting. Journal of Environmental Quality, 33: 37–44.

Holman, J.P. 2002. Heat Transfer, ninth ed. MacGraw-Hill, New York.

Hsu, J.H., Lo, S.L. 1999. Chemical and spectroscopic analysis of organic matter transformations during composting of pig manure. Environmental Pollution, 104: 189-196.

Huang, G.F., Wong, J.W.C, Wu, Q.T., Nagar, B.B. 2004. Effect of C/N on composting of pig manure with sawdust. Waste Management, 24: 805–813.

Huang, G.F., Wu, Q.T., Wong, J.W.C., Nagar, B.B. 2006. Transformation of organic matter during co-composting of pig manure with sawdust. Bioresource Technology, 97: 1834-1842.

Itavaara, M., Venelampi, O., Vikman, M., Kapanen, A. 2002. Compost maturity – Problems associated with testing, in: Insam, H., Riddech, N., Klammer, S. (Eds.), Microbiology of Composting. Springer, Heidelberg, pp. 373-382.

Jorgensen, K., Magid, J., Luxhoi, J, Jensen, L.S. 2010. Phosphorus distribution in untreated and composted solid fractions from pig slurry separation. Journal of Environmental Quality, 39: 393-401.

Jouraphy, A., Amir, S., Gharous, M., Revel, J.C., Hafidi, M. 2005. Chemical and spectroscopic analysis of organic matter transformations during composting of sewage sludge and green plant waste. International Biodeterioration and Biodegradation, 56: 101-108.

Kabata-Pendias, A. 2001. Trace elements in soil and plants, third ed. CRC Press LLC, Boca Raton, Florida.

Labance, S.E., Heinemann, P.H., Graves, R.E., Beyer, D.M. 2006. Evaluation of the effects of forced aeration during phase 1 mushroom substrate preparation: Part 1. Model development. Transactions of the ASABE 49, 167–174.

Maeda, K., Hanajima, D., Morioka, R., Toyoda, S., Yoshida, N., Osada, T. 2013. Mitigation of greenhouse gas emission from cattle manure composting process by use of a bulking agent. Soil Science and Plant Nutrition, 59: 96-106.

Marhuenda-Egea, F.C., Martínez-Sabater, E., Jordá, J., Sánchez-Sánchez, A., Moral, R., Bustamante, M.A., Paredes, C., Pérez-Murcia, M.D. 2007. Evaluation of the aerobic composting process of winery and distillery residues by thermal methods. Thermochimica Acta, 454: 135-143.

Nolan, T., Troy, S.M., Healy, M.G., Kwapinski, W., Leahy, J.J., Lawlor, P.G. 2011. Characterization of compost produced from separated pig manure and a variety of bulking agents at low initial C/N ratios. Bioresource Technology, 102: 7131-7138.

Pampuro, N., Dinuccio, E., Balsari, P., Cavallo, E. 2014. Gaseous emissions and nutrient dynamics during composting of swine solid fraction for pellet production. Applied Mathematical Science, 129: 6459-6468.

Paredes, C., Bernal, M.P., Roig, A., Cegarra, J., Sánchez-Monedero, M.A. 1996. Influence of bulking agent on the degradation of olive-mill wastewater sludge during composting. International Biodeterioration and Biodegradation, 38: 205-210.

Paredes, C, Bernal, M.P., Roig, A., Cegarra, J. 2001. Effects of olive mill wastewater addition in composting of agroindustrial and urban wastes. Biodegradation, 12: 225-234.

Ros, M., Garcia, C., Hernández, T. 2006. A full-scale study of treatment of pig slurry by composting: Kinetic changes in chemical and microbial properties. Waste Management, 26: 1108-1118.

Sánchez-Monedero, M.A., Serramiá, N., Civantos, C.G., Fernández-Hernández, A, Roig, A. 2010. Greenhouse gas emissions during composting of two-phase olive mill wastes with different agroindustrial by-products. Chemosphere, 81: 18-25.

Saveyn, H., Eder, P. 2014. End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals. European Commission, Joint Research Centre, Institute for Prospective Technological Studies. Luxembourg: Publications Office of the European Union.

Szanto, G.L., Hamelers, H.V.M., Rulkens, W.H., Veeken, A.H.M. 2007. NH_3, N_2O and CH_4 emissions during passively aerated composting of straw-rich pig manure. Bioresource Technology, 98: 2659-2670.

Thomsen, I.K., Kjellerup, V. 1997. Yields and uptake of barley and ryegrass from soils with added animal manure differing in straw and urine content. European Journal of Agronomy, 7: 285-292.

Tiquia, S.M., Tam, N.F.Y., Hodgkiss, I.J. 1996. Effects of composting on phytotoxicity of spent pig-manure sawdust litter. Environmental Pollution, 93: 249-256.

Woodworth, J.C., Tokach, M.D., Nelssen, R.D., Goodband, P. R., O'Quinn & Fakler, T.M. 1999. The effects of added zinc from an organic zinc complex or inorganic sources on weaning pig growth performance. Journal of Animal Science, 77 (supplement 1): 61.

Yañes, R., Alonso, J.L., Díaz, M.J. 2009. Influence of bulking agent on sewage sludge composting process. Bioresource Technology, 100: 5827-5833.

Ylivainio, K., Uusitalo, R., Turtola, E. 2008. Meat bone meal and fox manure as P sources for ryegrass (*Lolium multiflorum*) grown on a limed soil. Nutrient Cycling in Agrosystems, 81: 267-278.

Zabaniotou, A.A., Skoulou, V.K., Koufodimos, G.S., Samaras, Z.C. 2007. Investigation study for technological application of alternative methods for the energy exploitation of biomass/agricultural residues in Northern Greece. Thermal Sciences, 11: 125-134.

Zhu, N., Deng, C., Xiong, Y., Qian, H. 2004. Performance characteristics of three aeration systems in the swine manure composting. Bioresource Technology, 95: 319–326.

6. Conclusions

The thermal profile of composting materials at the laboratory scale and the microbial degradation measured by CO_2-C emissions are adequate parameters to define the degradability of the materials and, especially, to predict the behaviour of the mixtures and the potential C conservation during composting process at pilot-scale.

The mixtures of solid fraction of pig slurry with garden pruning waste and cotton gin waste showed a quick temperature development and high degradability, indicating that these materials can be adequate for composting, guaranteeing a good and quick process development. However their fast organic matter degradation significantly increased the CO_2 release into the atmosphere. The use of maize stalks as bulking agent produced a thermal profile with low temperature development, but also implied a low impact on the environment, due to its slow degradation, helping to promote C conservation while significantly reducing CO_2 emissions.

The temperature evolution during the SFP composting process has been shown to rely on the thermal properties of the bulking agent, while the gaseous emissions were very well related to the OM degradation process. The use of cotton gin waste as bulking agent improved the less adequate parameters of the SFP, favouring good development of the composting process, as shown by the thermal profiles. An increase of cotton gin waste proportion led to higher total-N losses by ammonia emissions, due to the high aeration demand for maintaining adequate aerobic conditions in the composting mass. But increasing bulking agent proportion reduced the gaseous emissions during composting, especially of CO_2, CH_4 and N_2O.

Based on the process performance, the 4:3 proportion of SFP:bulking agent (v/v) was the most adequate for composting the SFP, giving a compost with high OM humification and nutrient concentrations.

The thermogravimetric methods and classical analytical approaches were very synergic obtaining good correlations between thermostability index (R1) and C related parameters. NMR and FT-IR showed more powerful capacities to understand the evolution of C pools especially when recalcitrant C vs. labile C pools are compared. The composting system produced differences in the OM changes only detected by instrumental analysis, which can be also used to discriminate quality aspects in mature composts.

The production of quality compost at the industrial or farm level will be conditioned by the concentration of Cu and Zn in the pig slurry. Increasing the proportion of bulking agent has a dilution effect on such elements in the compost, but the process will have a greater energy cost for aeration of the composting mass. The use of SFP with low Cu and Zn concentrations will be the best way to ensure the production of high-quality compost appropriate for commercial use.

Composts from solid fraction of pig slurry can be considered adequate organic fertiliser products, efficiently increasing biomass yield of *L. multiflorum*, with greater biomass production when increasing the rate of soil application.

The fertiliser efficiency of the N from the compost was lower than from the mineral fertiliser, as part of the N supplied by composts was as organic-N. However, the relative agronomic efficiency (RAE) reached up to 47.6 %, indicating that partial N-mineralisation from the compost may have occurred during the experiment for supplying inorganic-N to plants. Low fertiliser efficiency of P was found for all treatments, but the P-RAE percentages reached 56 and 75 % in compost A (with greater proportion of pig slurry) and B (with lower proportion of pig slurry). Also high RAE values occurred for compost K due to the high solubility of this nutrient in compost.

Despite the high concentrations of Cu and Zn in the composts used, their levels in *L. multiflorum* biomass (shoots and roots) and in the soil at the end of the experiment, did not demonstrate any toxic effects on plants or constitute an immediate threat of soil contamination.

The use of both composts as soil amendments did not pose any risk, in terms of nitrate leaching, even after a heavy raining event and the use of a double dose of compost reduced the amount of nitrates leached.

In an agronomical scenario, a combination of mineral and organic fertilisers during the growth season might be recommended, using composts as basal fertilisation before sowing and complementing with mineral fertiliser during the growing season, to ensure adequate production and supplying the required nutrients for an efficient crop production.

El perfil térmico de los materiales a compostar a escala de laboratorio y la degradación microbiana medida por la emisión de C-CO_2 son parámetros adecuados para definir la capacidad de descomposición de los residuos y, especialmente, para predecir el comportamiento de las mezclas y la conservación potencial del C durante el proceso de compostaje en escala piloto.

Las mezclas de la fracción sólida de purín con los residuos de poda de jardín y desmotado de algodón mostraron un desarrollo rápido de la temperatura y una elevada degradabilidad, lo que indica que estos materiales serian adecuados para su compostaje a escala piloto, garantizando un buen y rápido desarrollo del proceso. Sin embargo, la rápida degradación de su materia orgánica aumentó significativamente las emisiones de CO_2 a la atmósfera. El uso de caña de maíz como agente estructurante produjo un perfil térmico con un desarrollo de bajas temperaturas, pero también implicó un bajo impacto en el medio ambiente, debido a su lenta degradación, lo que ayuda a promover la conservación del C, a la vez que reduce significativamente las emisiones de CO_2.

La evolución de la temperatura durante el proceso de compostaje de la fracción solida de purín (FSP) demostró depender de las propiedades térmicas del agente estructurante, mientras que las emisiones gaseosas se relacionaron muy bien con el proceso de degradación de la MO. El uso del residuo de desmotado de algodón como agente estructurante mejoró los parámetros poco adecuados de la FSP para su compostaje, favoreciendo el buen desarrollo del proceso, como demostraron los perfiles térmicos. Un aumento de la proporción del residuo de desmotado de algodón implicó mayores pérdidas de N-total por emisiones de amoníaco, debido a la alta demanda de aireación para mantener las condiciones aeróbicas del proceso. Pero el aumento en la proporción del agente estructurante redujo las emisiones gaseosas durante el compostaje, especialmente de CO_2, CH_4 y N_2O.

Para el desarrollo del proceso, la proporción 4:3 de FSP:agente estructurante (v/v) fue la más adecuada para el compostaje de la FSP, produciendo un compost con elevada humificación de la MO y concentración de nutrientes.

Los métodos termogravimétricos y las técnicas analíticas clásicas resultaron muy sinérgicas, obteniendo buenas correlaciones entre el índice de termo-estabilidad (R1) y los parámetros relacionados con el C orgánico. RMN y FT-IR mostraron mejores capacidades para explicar la evolución de las fracciones de C, especialmente cuando se comparan formas recalcitrantes de C con las fracciones lábiles. El sistema de compostaje produjo diferencias en los cambios de la MO, solamente detectadas por análisis instrumental, que se pueden también utilizar para discriminar los aspectos de calidad en compost maduros.

Sin embargo, la producción de compost de calidad a nivel industrial o de granja estará condicionada por la concentración de Cu y Zn en el purín de cerdo. El aumento de la proporción de agente estructurante tiene un efecto de dilución sobre tales elementos en el compost, pero el proceso tendrá un coste energético más grande debido a la aireación de la masa de compostaje. El uso de la fracción sólida de purín con bajas concentraciones de Cu y Zn será la mejor opción de garantizar la adecuada producción de compost de alta calidad para uso comercial.

Ambos compost pueden considerarse productos fertilizantes orgánicos adecuados, ya que aumentaron eficazmente el rendimiento de biomasa de *L. multiflorum*, mostrando una mayor producción de biomasa cuando se aplicó una dosis más alta.

La eficiencia fertilizante en N de los compost fue inferior a la correspondiente del fertilizante mineral, ya que parte del N suministrado por los compost se encontraba en forma orgánica. Sin embargo, la eficiencia agronómica relativa (EAR) alcanzó el 47,6 %, lo que indica que debió ocurrir una mineralización parcial del N orgánico de los compost durante el experimento, para poder suministrar N-inorgánico a las plantas. Se encontró una baja eficiencia fertilizante en P para todos los tratamientos, pero los porcentajes P-EAR alcanzaron el 56 y el 75% en el compost A y B. Además los altos valores de K-EAR en los tratamientos con compost se debieron a la alta solubilidad de este nutriente en el compost.

A pesar de las altas concentraciones de Cu y Zn en los compost usados, sus niveles en la biomasa de *L. multiflorum* (parte aérea y raíces) y en el suelo al final del experimento, no demostraron ningún efecto tóxico en las plantas o constituyeron una amenaza inmediata de contaminación del suelo.

El uso de ambos compost como enmienda de suelo no representó ningún riesgo en términos de la lixiviación de nitratos, incluso después de un evento de lluvia fuerte, y el aumento de la dosis de compost aplicada redujo la cantidad de nitratos lixiviados.

En un escenario agronómico, se recomienda la combinación de fertilizantes minerales y orgánicos durante el periodo de crecimiento del cultivo, mediante la aplicación del compost como un fertilizante de fondo antes de la siembra y complementar con fertilizantes minerales durante el periodo de crecimiento para asegurar una producción adecuada y el suministro de los nutrientes necesarios para una eficiente producción del cultivo.