

**BIODEGRADABILITY ASSESSMENT OF DIFFERENT
BULKING AGENTS FOR COMPOSTING THROUGH
RESPIROMETRIC TEST AND THERMAL PROFILE ANALYSIS**



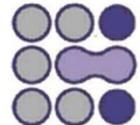
André M. Simões dos Santos

2014



ESCUELA POLITECNICA SUPERIOR DE ORIHUELA

**Máster Universitario de Investigación en
Gestión, Tratamiento y Valorización de Residuos Orgánicos**



BIODEGRADABILITY ASSESSMENT OF DIFFERENT BULKING AGENTS FOR COMPOSTING THROUGH RESPIRATION TEST AND THERMAL PROFILE ANALYSIS

André M. Simões dos Santos

2014



UNIVERSIDAD MIGUEL HERNÁNDEZ DE ELCHE

Se autoriza a la alumna **D. André Manuel Simões dos Santos**, a realizar el Trabajo Fin de Máster titulado: “Biodegradability assessment of different bulking agents for composting through respirometric test and thermal profile analysis”, bajo la dirección de D^a. Maria Pilar Bernal Calderón y la codirección de D. Raúl Moral Herrero, debiendo cumplir las normas establecidas para la redacción del mismo que están a su disposición en la página Web específica del Master.

Orihuela, 30 de enero de 2014

La Directora del Máster Universitario de Investigación en Gestión, Tratamiento y Valoración de Residuos Orgánicos



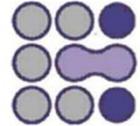
Fdo.: Concepción Paredes Gil

TRIBUNAL	
FECHA:	
PRESIDENTE:	FIRMA:
VOCAL:	FIRMA:
VOCAL:	FIRMA:



ESCUELA POLITECNICA SUPERIOR DE ORIHUELA

**Máster Universitario de Investigación en
Gestión, Tratamiento y Valorización de Residuos Orgánicos**



BIODEGRADABILITY ASSESSMENT OF DIFFERENT BULKING AGENTS FOR COMPOSTING THROUGH RESPIRATION TEST AND THERMAL PROFILE ANALYSIS

Vº Bº Director

Vº Bº Codirector

Dra. Mª Pilar Bernal Calderón

Dr. Raúl Moral Herrero

REFERENCIAS DEL TRABAJO FIN DE MASTER

Identificaciones:

Autor: André Manuel Simões dos Santos

Title: Biodegradability assessment of different bulking agents for composting through respiration test and thermal profile

Director/es del TFM: Dra. M^a Pilar Bernal Calderón, Dr. Raúl Moral Herrero

Año: 2014

Titulación: Máster de Investigación en Gestión, Tratamiento y Valorización de residuos

Tipo de proyecto: Experimental

Palabras claves: Compostaje, fracción sólida de purín de cerdo, perfil térmico, test respirométrico

Keywords: Composting, solid fraction of pig slurry, thermal profile, respiration test

Nº citas bibliográficas: 95

Nº de tablas: 12

Nº de figuras: 14

Resumen: El objetivo de este trabajo es estudiar el comportamiento de diferentes agentes estructurantes en el co-compostaje de la fracción sólida de purín de cerdo (SPS), en base al estudio de su degradabilidad, determinado mediante el CO₂ emitido (respiración), así como del perfil térmico desarrollado en un ensayo de auto-calentamiento. También se pretende estudiar las diferencias en el comportamiento de una fracción sólida fresca con otra almacenada. Para eso, la fracción sólida procedente de la granja y almacenada tres meses (SPS_i) se mezcló con cuatro agentes estructurantes distintos (cañote de maíz, paja de cebada, desmotado de algodón y residuo de poda de jardín) en proporciones adecuadas para el proceso de compostaje, teniendo en cuenta el contenido en humedad y relación C/N de las mezclas iniciales; otra SPS obtenida en el laboratorio por separación del purín fresco (SPS_f) se mezcló con el desmotado de algodón y la poda de jardín. Las pruebas de auto-calentamiento se hicieron en reactores discontinuos de 5 L, aislados térmicamente, donde se registró la temperatura dentro de cada reactor durante un periodo de 11-15 días. Las muestras obtenidas al inicio y al final del test de

auto-calentamiento se incubaron a 26°C durante 10 días para determinar su degradabilidad (respiración), como el CO₂ producido por los microorganismos.

Los perfiles térmicos demostraron una evolución rápida de la temperatura de las mezclas con el desmotado de algodón y con la poda de jardín, sin embargo, el cañote de maíz presentó los valores más bajos de temperatura. Las emisiones de CO₂ disminuyeron entre las muestras iniciales y finales del test de auto-calentamiento en las mezclas más activas (desmontado de algodón y poda de jardín), lo que indica que la materia orgánica fue fácilmente degradable. Sin embargo, el cañote de maíz produjo emisiones lentas y constantes de CO₂, indicando una lenta degradación que permitiría mantener una proporción de MO más alta en el compost, afectando positivamente a las emisiones de CO₂ y a la conservación del C en el sistema.

El almacenamiento de la SPS demostró ser un factor importante, pero no limitante, del proceso de compostaje, mostrando las mezclas con SPS fresca (SPS_i) un mejor desarrollo de la temperatura, lo que a su vez indica una mayor actividad microbiana, debido probablemente a su mayor concentración de NT y COT, que la SPS almacenada.

Abstract: The aim of this work is to study the implication of the bulking agent in the co-composting of the solid fraction of pig slurry, based on their degradability, determined as the CO₂ emissions, as well as the thermal profile developed by a self-heating test. The influence of the freshness of the solid fraction of pig slurry (SPS) was also determined by comparing two materials with different storage time. The SPS separated in the farm and stored for three months (SPS_f) was mixed with four different bulking agents (maize stalk, barley straw, cotton gin and garden pruning) in adequate proportions for composting, considering the moisture content and the C/N ratio of the initial mixtures. Other sample of SPS separated in the laboratory from freshly collected pig slurry (SPS_i) was mixed with cotton gin and garden pruning, at the same conditions. The self-heating test was set in insulated 5 L batch reactors where temperature evolution was measured during 11-15 days. Samples from the beginning and end of the self-heating experiment were incubated at 26°C for 10 days to determine their degradability as the CO₂ produced by microorganisms.

Thermal profiles showed a quick temperature development for the mixtures with cotton gin and garden pruning, with the lowest values with maize stalks. The CO₂ emissions (respiration) decreased from the initial mixtures to the end of the self-heating test in the most actively degraded mixtures (cotton gin and garden pruning), indicating that the organic matter was very easily degradable. However, maize straw produced slow and constant CO₂ emissions, showing a slow degradation process, which will allow maintaining high proportion of its OM in the compost, affecting positively the CO₂ emissions and C-conservation in the system.

The storage time or freshness of the SPS proved to be an important but not limiting factor of the composting process, showing mixtures with SPS freshly separated a quick temperature development, reaching higher temperatures and higher microbial activity than the aged SPS, probably due to its higher concentrations of TN and TOC.

Acknowledgements

First of all, I would like to thank Dra. M^a Pilar Bernal for making it possible to me, to participate in such a magnificent project, for sharing her knowledge and wisdom and for all the comments and suggestions made to improve the work here presented. Also want to thank Dr. Raúl Moral for all the ideas and help given, during the elaboration of this work.

In the elaboration of these experiences, the support and knowledge shared by my co-workers was very important to me, and for that, I am really thankful to them, to the entire *PhytoRec* group.

Last, but not the least, a special thank to all my friends and family, for supporting me in my decisions, for keeping in touch and making the distance shorter and for my Spanish friends, for making me feel like home.

This research is included in the ReUseWaste project and has been funded by the People Program (Marie Curie Actions) of the European Union's Seventh Framework Program FP7/2007-2013/ under REA grant agreement n° 289887 and the results and conclusions achieved reflect only the author's view and the Union is not liable for any use that may be made of the information contained therein.

INDEX

1 - Introduction	5
1.1 - Pig slurry production and management: the current situation.....	7
1.1.1 - Pig slurry production	7
1.1.2 - Pig slurry management	8
1.1.2.1 - Storage.....	9
1.1.2.2 - Soil application.....	10
1.1.2.3 - Treatment	12
1.1.2.4 - Transport	14
1.2 - Pig slurry characterisation and environmental impact	15
1.3 - Composting process.....	17
1.4 - Requirements for pig slurry composting	24
2 - Objectives	27
3 - Materials and Methods	30
3.1 - Characterisation of the input materials	33
3.2 - Experimental design	36
3.2.1 - Self-heating test	36
3.2.1 - Respiration test	38
3.2.3 - Thermodynamic evaluation	39
3.3 - Statistical analysis	41
4 - Results and Discussion	43
4.1 - Properties of the input materials and of the mixtures before and after the self-heating test	45
4.1.1 - Input materials.....	45
4.1.2 - Mixtures with solid pig slurry from the farm (SPSf).....	46
4.2 - Thermal profile and respiration test	50
4.3 - Energetic evaluation	57
4.4 - Comparison of the behaviour of the different solid fraction of pig slurry (SPSf vs. SPSI).....	59
4.5 - Implication of the bulking agent on soil conservation C	62
5 - Conclusions	63
6 - Bibliography	67
7 - Annexes	80

INDEX OF FIGURES

Figure 1 - Animal production in Spain (A) and in Murcia (B) (2012), based on the livestock census	7
Figure 2 - Nitrate vulnerable zones in EU-27 and in the Region of Murcia.	10
Figure 3 - Schematic overview of possible animal manure treatments	13
Figure 4 - Thermal profile curve model of the composting process.	19
Figure 5 - a: SPS _f ; b: SPS _i separation process.	33
Figure 6 - a: Maize stalks before being chopped; b: garden pruning mixture already chopped.	34
Figure 7 - Schematic of the different filling phases of the self-heating reactors.	37
Figure 8 - a: Mixture inside the reactor; b: Final disposition of the reactors. ...	37
Figure 9 - a: Aspect of the mixture after being taken from the reactor; b: hermetic jars with sample and CO ₂ traps.	39
Figure 10 - a: Experimental setup to determine C _{ps} ; b: Compost bags.	40
Figure 11 - Thermal profiles of the mixtures with SPS _f and corresponding external temperature. The arrow indicates the turning. A: mixtures with maize stalks and garden pruning; B: mixtures with cotton gin and barley straw.	51
Figure 12 - Thermal profiles of the mixtures with SPS _i and corresponding external temperature.	55
Figure 13 - Accumulative values of energy production from the mixtures with SPS _f during the self-heating test.	57
Figure 14 - Accumulative values of energy production from the mixtures with SPS _i during the self-heating test.	58

INDEX OF TABLES

Table 1 - Pig slurry production and excreted nitrogen in the different type of animal.....	16
Table 2 - Benefits and drawbacks of composting. (Rynk, 1992).	20
Table 3 - Recommended conditions for composting of solid manure.....	21
Table 4 - Limits for potentially-toxic elements in compost I EU-27 and in Spain (mg/kg dm).	25
Table 5 - Chemical and physico-chemical characteristics of the input material.	35
Table 6 - Physical characteristics of the mixtures inside the batch reactors. ...	38
Table 7 - Chemical and physico-chemical characteristics of the mixtures of SPS with different bulking agents at the beginning and at the end of the 15-d self-heating tests in 5L batch reactors.....	49
Table 8 - CO ₂ -C emission values (accumulated during 10 days) from microbial activity of the mixtures with SPS _f at the beginning and at the end of self-heating tests (mg CO ₂ -C/g DM in 10-d). Mean ± Standard deviation (n=3).	52
Table 9 - CO ₂ -C emission values (accumulated during 10 days) from microbial activity of the mixtures with SPS _i at the beginning and at the end of self-heating tests (mg CO ₂ -C/g DM in 10-d). Mean ± Standard deviation (n=3).	56
Table 10 - Univariate general linear model comparison between the chemical and physico-chemical parameters from the mixtures of cotton gin and garden pruning with different SPS.	59
Table 11 - Pearson's correlation coefficient (r) and significance (P) between CO ₂ -C emissions and all the chemical and physico-chemical parameters from all the mixtures at the beginning and the end of the self-heating test (n=24). ..	60
Table 12 - Chemical and physico-chemical characteristics of the mixtures of cotton gin and garden pruning with different SPS at the beginning and at the end of the 15-d self-heating tests in 5L batch reactors.....	61

1. INTRODUCTION

1.1 Pig slurry production and management: the current situation

1.1.1 Pig slurry production

The pig production system in Europe has changed in the last years, passing from small farm production system to intensive production system, concentrating the activity in certain areas (Burton and Turner, 2003). This is explained by the biophysical conditions in different regions of Europe, pushing farmers in countries with short vegetation period or insufficient rain to more intensive production, while wet lowlands in mild climate or mountainous regions intensify animal raising (Leip et al, 2010). In such intensive system, on-farm manure recycling may not a feasible option, since that, normally, there is not enough agricultural land to dispose all the residues produced from the animals.

In European Union, pigs are one of the most produced livestock animal with over 152 million livestock units (LSU), producing more than 300 million tonnes of pig slurry annually (Cunault et al., 2010), while Spain represents 17 % of the total pig LSU produced in EU-27, with 25 million LSU (FAOSTAT, 2010). In Spain, pigs represents the major livestock animal produced, being the pig production of about 50 % of the total national LSU produced (Figure 1A), having increased by 6.7% between 2000 and 2010 (MAGRAMA, 2012).

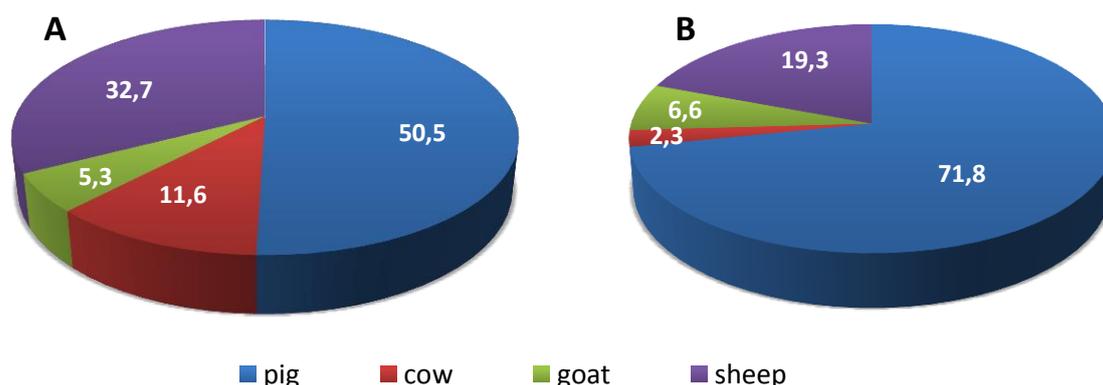


Figure 1 - Animal production in Spain (A) and in Murcia (B) (2012), based on the livestock census (MARM,2012).

Nowadays, the Spanish pig production is concentrated in the regions of Cataluña, Aragon and Castilla y Leon, representing more than 60% of the total

pig production, with 6.8, 6 and 3 million pigs, respectively, where fattening pigs represented more than 10 million units, followed by piglets and grower pigs, with 7 and 5 million pigs (MAGRAMA, 2012).

The Region of Murcia is ranked as the fifth major Spanish region in terms of livestock production, where pigs represented more than 71% of the total livestock production (Figure 1B). In Murcia it was produced around 2 million pigs in 2012 (more than one pig per person) where over 1 million were fattening pigs, generating over 6.5 million m³ of slurry per year.

The national agricultural database showed a reduction in the number of pig farms with an increase in production of LSU for the period of 1999-2009. With this decrease in pig farms number and the intensification of the production system, Murcia's pig production is now concentrated in two main areas, Guadalentín and Campo de Cartagena-Oeste, where 54% of the pig slurry produced is found in the Guadalentín area. Many of the farms, from both areas, are located in a zone where pig slurry application as fertiliser is restricted, as the areas are considered vulnerable to nitrate pollution (MANEV, 2012a).

With the great amounts of pig slurry generated, concentration of production in restricted areas and the rules that pig farmers are obliged to follow, a proper managing system have to be design in order to treat the surplus of pig slurry generated.

1.1.2 Pig slurry management

Pig slurry management includes a series of technological operations, that have as objective optimise nutrient retention and utilisation with minimum land, labour or money requirement and reduce environmental problems associated with piggery industries. In order to achieve this goal, a "Code of Good Agricultural Practice" was created to help farmers, growers and land managers protect the environment in which they operate. The Code describes key actions to take, in order to protect and enhance the quality of water, soil and air; achieve cost savings and meet legal obligations.

Pig slurry management can include operations such as storage, land application, treatment and/or transport.

1.1.2.1 Storage

Pig manure can be handled as a solid or semi-solid, a slurry, or a liquid and each different stage, requires different operating measures. Climate conditions, farming traditions, type of farm holding and volume of slurry produced are key-factor to define the managing system to use (Burton and Turner, 2003).

The most common pig slurry storage facilities in EU-27 are concrete insulated tanks. The tanks are design taking into account the number of pigs in the holding facility and the quantity of slurry that can be produced. This operation intent to group the great amounts of pig slurry produced daily in the holding facility in one insulated place and can be seen as mode of treatment, since it enhances the timeliness and convenience of disposal. Burton and Turner (2003) found that phosphorous, nitrogen, dry matter and biological oxygen demand (BOD) is reduced during storage through sedimentation and microbial transformations and that multiple store units connected in series could also reduce BOD and pathogens.

Storage also allows manure application to match crop nutrient requirement, since storage time can vary from 3-6 months in regions were crop may be planted and harvested during the year or where crop growing season is long, and about 9 months in the northern countries, where crop growing season is short (Burton and Turner, 2003). Manure can also be stored for several years (lagoons).

Slurry open-air lagoons and lined ponds are a relatively uncommon option for manure storage in most Europe, being especially reported from Mediterranean countries, where climatic conditions (high temperatures and low rainfall) promote the volume reduction by water evaporation, concentrating the nutrients in the sludge (EUROSTAT, 2013). The highest proportion of holdings with this storage facility is found in Spain (31 %) and in Netherlands (40 %). In fact, it is reported that in Murcia, the conditions for storage and agricultural use are established by the regional Government (Code of good agricultural practices, BORM 2003) and that drying in open-air lagoons (insulated at the bottom) is a common treatment strategy, where most of the small-medium farms have quite efficient evaporation ponds for pig slurry storage and drying,

but with a high environmental impact due to gases and odours emissions (MANEV, 2012a).

1.1.2.2 Soil application

Back in the days, soils were seen as a depurating system to treat animal manures. Since then, slurry application to the soil is considered as one of the oldest management practices for pig slurry. The excessive application of slurry and mineral fertilisers to the soil during those years, made it necessary to denominate as vulnerable zones for nitrate contamination the areas where the drinking water exceeded or were at risk of exceeding 50 mg NO₃/l (Figure 2). So, in those areas, closed periods of application were defined and a limit of application of 170 kg of N per hectare and per year (250 kg/ha/yr for crops with high N needs) was imposed to avoid N and P leaching or runoff to the waters (EEC 91/676). Most of the vulnerable zones for nitrate contamination in EU-27 are located in the northern and central part.

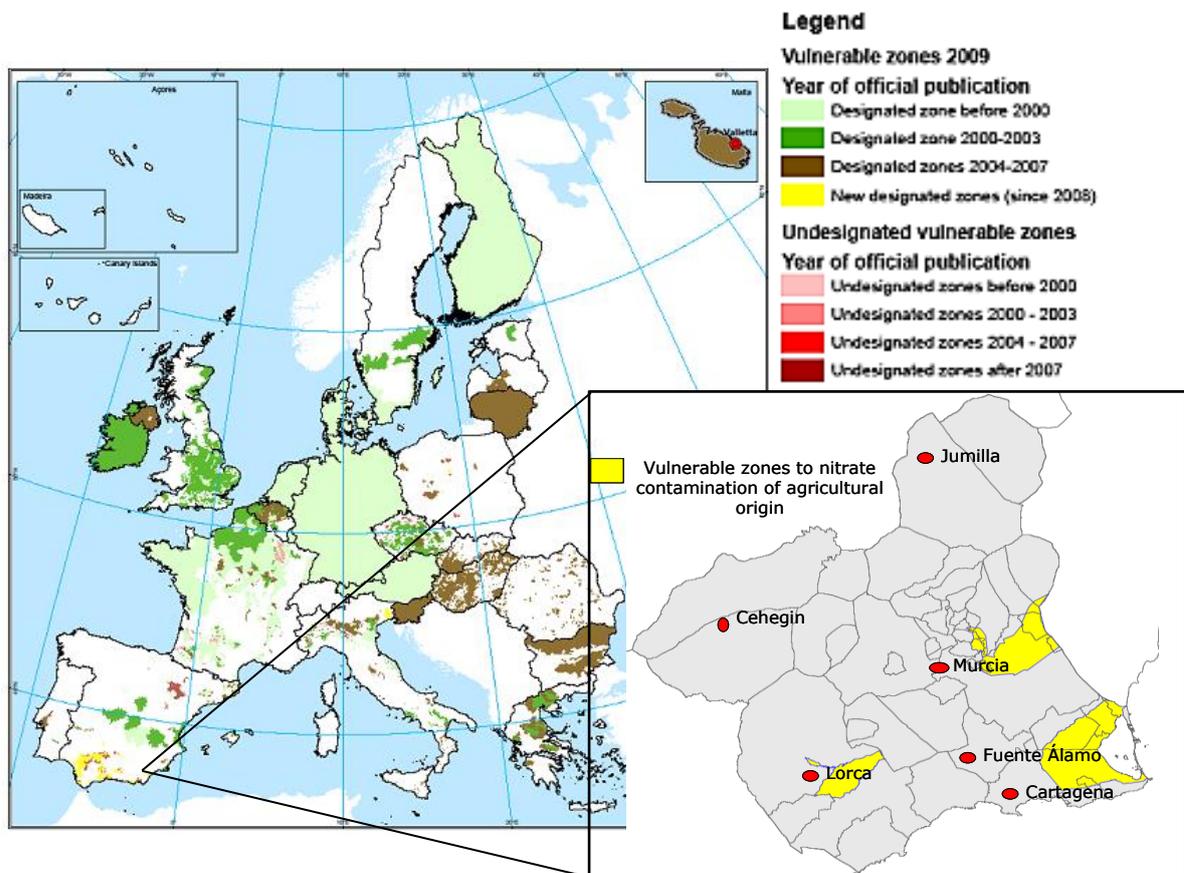


Figure 2 - Nitrate vulnerable zones in EU-27 and in the Region of Murcia. (EUROSTAT, 2013; MANEV, 2012a).

One of the most common methods of slurry/liquid manure application to the soil used in Europe is the broad-spreading with a splash plate inclined slightly toward the soil, being one of the fastest and cheapest methods for slurry and liquid manure application. However, this method is being phase out in many countries, in order to reduce NH₃ and odour emissions, being substituted by techniques that inject the slurry into the soil (Sorensen et al., 2013).

The most common use of pig slurry in Murcia is the agricultural application to soils as a fertiliser, after the adequate storage in tanks. However, the pig production is concentrated in two main areas, where there are many small-medium farms and many of the pig farms are located within the vulnerable zone to nitrate contamination. According to data collected by MANEV (2012a) the average pig slurry which can be used in agriculture is for horticultural crops (40%).

There are some strict restrictions in the application of pig slurry to horticultural crops, due to the relatively proximity of the crops to the soil; and there is a maximum amount, as well time of application to the soil of nitrogen, settled by local and communitarian laws (Royal Decree 261/1996, 91/676/EEC), to 170kg per year, in vulnerable zones, which means that there is a great amount of pig slurry needing carefully management strategies. The combination of those factors makes the direct use of pig slurry as a fertiliser difficult.

A recent study (MANEV, 2012a) showed that more than 50% of the slurry produced in Lorca, the most populated area in terms of pig production, could be applied to the soil, considering the nutrient requirement of the crops, the restrictions of pig slurry application on certain crops, time of application and limit of N allowed to apply in that area. Almost 20 % of the pig slurry produced can be used for 5 different crops: broccoli, artichoke, oat, lettuce and barley. The most significant woody crops for pig slurry application are almond and olive trees, with almost 27 % of the total pig slurry production in Lorca. The remain percentage of pig slurry that it is not allowed to apply to the soil, can be managed differently, where transport to areas where nutrients are scarce or composting of the solid fraction are one of the possible solutions given (MANEV, 2012b).

1.1.2.3 Treatment

Several management options and treatment are nowadays available in order to reduce the environmental impact of the pig slurry, reducing pollution risk. In Figure 3 is presented some treatment options to minimize those risks.

Nowadays, solid/liquid separation is common in the pig farms, allowing treating the solids and the liquids separately. It can be done by techniques like a screw-press, centrifugation, decantation, using belt-filters. The application of chemical pre-treatments is a common procedure, enhancing the volume of solids separated. Usually, the liquid part is used for irrigation and the solid part can be used directly in soil application or composting, anaerobic digestion or incineration (Raven and Gregersen, 2007) and transported back to the farm for land spreading, after the treatment (Sorensen et al., 2013). Solid/liquid separations concentrates great amount of the nutrients in the solid part, making more effective and easier the handling and the nutrient transportation between areas with a surplus of nutrients to areas were nutrients are scarce. In Murcia, solid-liquid separation can be found in certain farms in order to manage the solids and the liquid separately. The liquid is usually used for irrigation, mainly in fruit trees, allowing the farmers to safe irrigation water and fertilisers. The solid is frequently sold as a solid manure (MANEV, 2012a).

Biogas production via anaerobic digestion is a more common procedure used in northern European countries to treat pig manure. There are private or cooperating organisations that own biogas plants to treat the pig solids generated in their farms. The end product of the biogas plant is a hygienised sludge, which can be applied to the soil as a fertiliser. The electricity used in the plant and sometimes, in the immediate villages, comes from the conversion of the biogas produced into energy. There are some biogas plants that also use the heat generated in the plant to warm the immediate villages. According to Amon et al. (2006) anaerobic digestion is a feasible technology to reduce methane emissions to the atmosphere from animal manure.

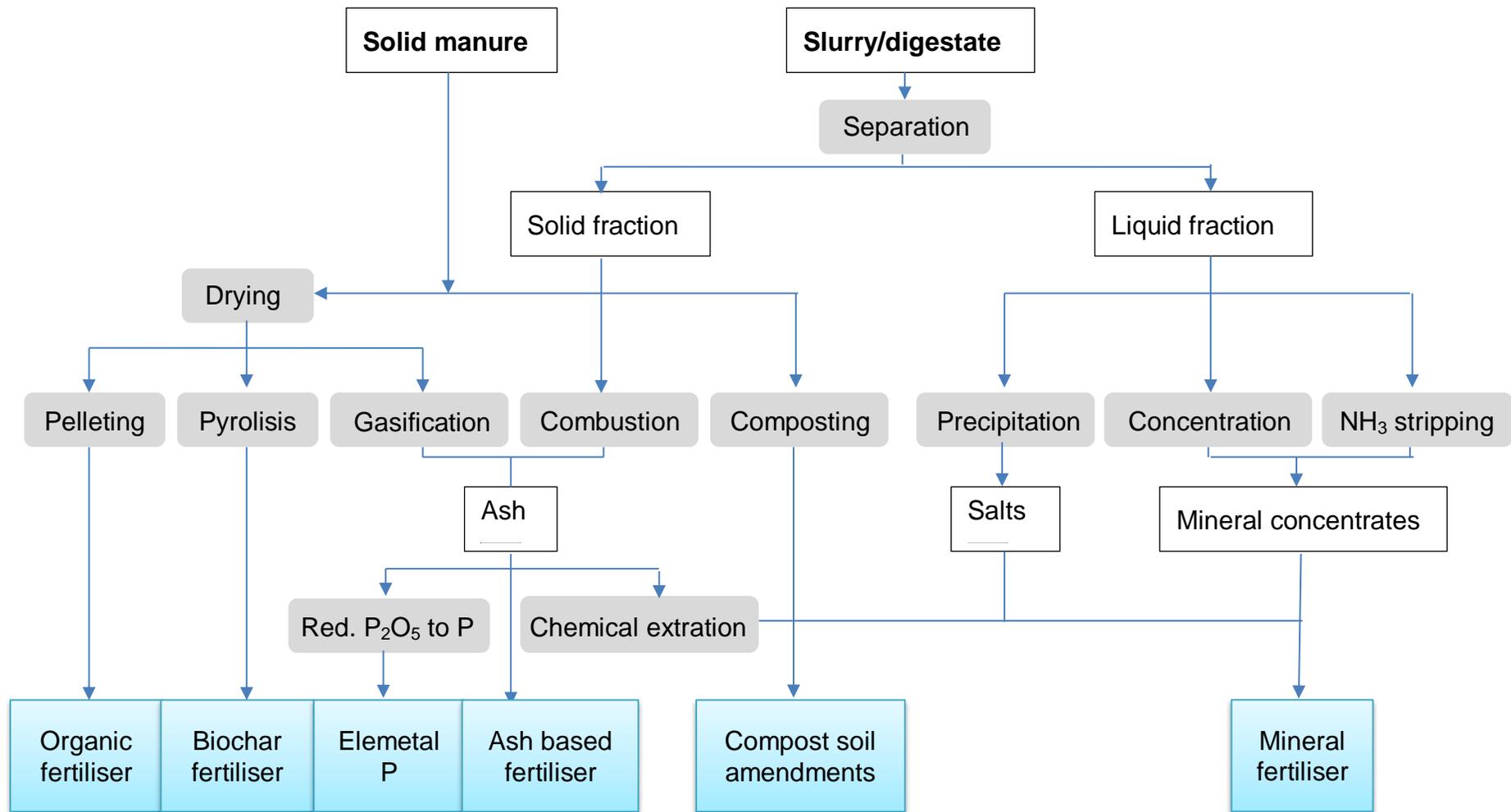


Figure 1 - Schematic overview of possible animal manure treatments (© University of Copenhagen).

In Murcia, only the big farms associated to meat industries are capable to use more sophisticated treatments, such as anaerobic digestion for biogas production and use by the farm and the industrial processes (MANEV, 2012a), since it is a technology that requires high investment and operating/maintenance costs. However, in Murcia there are big enterprises willing to improve pig farms, in order to make them more efficient.

Pig slurry pelletising is a new trend in the slurry management. The dehydration of the slurry and its compaction (90% DM), concentrates the N and P, reduces odour and creates a more stable product, allowing to be used as fertiliser. Along with this option, the pellets or just the dried solids can also be used as fuel in the incinerator to produce heat or energy. However, this procedure requires high energy and promotes ammonia losses (Jensen, 2013).

Another option to treat pig slurry is through composting, after a solid/liquid separation, where the solids can be mixed with other residues generated from agricultural activities. Composting of pig slurry and manure has been traditionally carried out by the farmers after manure collection (for better handling, transport and management), without the proper control of the process conditions (aeration, temperature, ammonia loss, etc.) and with rudimentary methodology. The cost of composting of animal manures can be considerably higher than the direct utilisation of raw manures and along with the process, ammonia losses can be observed, as well as other GHG (Jensen, 2013). This process can be seen as a feasible option to treat the surplus of pig slurry that cannot be applied directly in the soils. The final product obtained in the composting process, is a hygienised and stabilised compost, with considerable humic-like substances that can be applied to the soil as organic fertiliser (Jensen, 2013).

1.1.2.4 Transport

Pig slurry is normally transported through channels from the holding facility to the storage tank or lagoons. During transport, precipitation of the solids may occur. It is advised to pre-treat the slurry, to transport the solids and the liquids separately or increase flow rate to avoid phenomena like this (Sorensen et al., 2013). Other transportation system applied is the transport of

slurry by pumps, from different locations in the farm or from the storage facility to the application area. Pumping low dry matter slurries is easier than the high dry matter ones, allowing transporting the slurries for longer distances with lower costs associated. In that sense, diluting the slurries can be seen as a measure to increase transport efficiency. Fermentation of the slurries in the biogas digesters have the same result, since reduces the viscosity of the slurry. (Sorensen et al., 2013).

Another common operation in slurry transportation is the transport of the solid fraction or the liquid fraction of pig slurry to areas where the nutrient are scarce. In Murcia, most of the solid fraction is given to other farmers to apply in their fields free of charge. Sometimes, farmers have to pay to get free of such residue (MANEV, 2012a).

1.2 Pig slurry characterisation and environmental impact

Pig slurry composition varies widely with the pig race, sex, reproductive state, and feed (sows in a closed cycle, sows with piglets and weaners are the ones that produce more slurry and excrete more N) (Table 1) and is mainly a composition of the undigested components in the form of faeces and urine excreted by the animal, along with wash water and bedding material from the management of the holding facilities. The high quantity of wash water used during management contributes to the high moisture and low dry matter (DM) content (<12%), normally found in this residue (Christensen and Sommer, 2013).

Table 1 - Pig slurry production and excreted nitrogen in the different type of animal (BORM, 2011).

Age/weight	Slurry production (m ³ / animal place/ year)	N produced (kg N/animal place/year)
Sows closed cycle	17.75	67.17
Sows with suckling piglets (0-6 kg)	5.1	15.28
Sows with piglets (0-20kg)	6.12	18.9
Sows	2.5	8.5
Piglet (0-6 kg)	0.41	1.8
Fattening pig (20-50 kg)	1.8	6.31
Fattening pig (50-100 kg)	2.5	8.05
Fattening pig (20-100 kg)	2.15	7.25
Weaners	5.11	15.93

Pig slurry is also characterised as a material with a considerable amount of organic matter (OM) and beneficial nutrients to plants, mainly in nitrogen (N) and phosphorus (P), and poor in total organic carbon (TOC). The high concentration of N and P are related with the feed (high organic N content and it is given a surplus of P to cover their needs) and age/weight of the pig (Table 1). Therefore, pig slurry also presents several negative characteristics, such as pathogens, high heavy metals content and unpleasant odours, among others, that make necessary a suitable management.

The intensification in terms of production, the lack of agricultural land for its disposal and the legislation applied to pig slurry, mentioned before, along with their characteristics, can create serious environmental problems, due to slurry accumulation if amounts, methods, and times of disposal are not properly monitored, such as greenhouse gases emissions (GHG) (ammonia, methane, and nitrous oxide), leaching to groundwater and/or runoff to surface waters of organic matter and nutrients (mainly N and P), eutrophication of surface waters, and the spread of unpleasant odours and pathogens in the environment (Burton and Turner, 2003).

Most of the environmental risks enumerated are associated with the managing of pig slurry occurred during storage, transport and/or soil application.

In EU-27, 16% of the GHG emissions from 2003-2005 came from the piggery industry (Lesschen et al., 2011), while in Spain, GHG emissions from animal residues comes majorly from pig slurry (51%) and are due to its storage and land application without treatment or inefficient management (FAOSTAT, 2010; Hansen et al., 2006).

The main emissions from storage are due to gaseous emissions to the atmosphere in the form of NH_3 , N_2 , N_2O , CO_2 and CH_4 (Sommer and Christensen, 2013). Most of methane (CH_4) emitted from pig slurry is due to the anaerobic conditions created during storage, estimated in 470 Mt $\text{CO}_{2\text{eq}}/\text{yr}$ in 2010 with an expected 11% increase by 2020 (Montes et al., 2013). However, short-term storage in animal houses and removing manure reduces the risks of disease spread and ammonia odour and GHG emissions (Sorensen et al., 2013)

In 2011, nitrous oxide emissions from manure application to the soil were responsible for 25 Mt $\text{CO}_{2\text{eq}}/\text{yr}$ in EU-27 and 1.5 Mt $\text{CO}_{2\text{eq}}/\text{yr}$ emitted in Spain, being the major contributor to total GHG emissions from agriculture (FAOSTAT 2010; Davidson, 2009) with animal waste representing 30 to 50% of the global agricultural N_2O emissions (Oenema et al., 2005). Since Spain is a Mediterranean country, climatic conditions favour nitrous oxide (N_2O) and ammonia (NH_3) volatilisation to the atmosphere when animal residues are applied to the soils as fertiliser.

Transportation may be responsible for the spread of animal diseases, GHG and malodours emissions, since slurry is not hygienised and presents high amounts of N in ammonia form and hydrogen sulphide (H_2S), while landfill application of slurries is responsible for ground waters and surface waters contamination by leaching and runoff and GHG emissions as well.

1.3 Composting process

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 can be seen as a feasible treatment method to manage pig slurry, reducing 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 CH₄ emissions when manure is stored under anaerobic conditions, allowing to reduce 99% of CH₄ emissions and 75% of N₂O 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). Concerning soil application, the use 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 O₂ demand, promoting increases in N₂O and NO soil emissions following application (Vallejo et al., 2006). Then, Kariyapperuma et al. (2012) observed a 57% decrease in soil N₂O emissions with composted vs. liquid pig manure.

During the composting process, several aspects are usually considered to study the development of the composting process, such as the evolution of different physical, chemical and biological parameters (Bernal et al., 2009).

In general, the composting process is constituted by different phases (Figure 4), indicated by the development of the temperature profile.

So, according to Keener et al. (2000), the bio-oxidative phase is developed in three steps:

- 1) Mesophilic phase, lasting 1-3 days, where mesophilic bacteria and fungi degrade simple compounds such as sugars, amino acids, proteins, etc., increasing quickly the temperature;
- 2) Thermophilic phase, where thermophilic microorganisms 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;
- 3) Curing phase, characterised by a decrease of the temperature into temperatures near external temperatures, due to the reduction of the microbial activity associated with the depletion of degradable organic

substrates, the composting mass is re-colonised by mesophilic microorganisms which are able to degrade the remaining sugars, cellulose and hemicellulose.

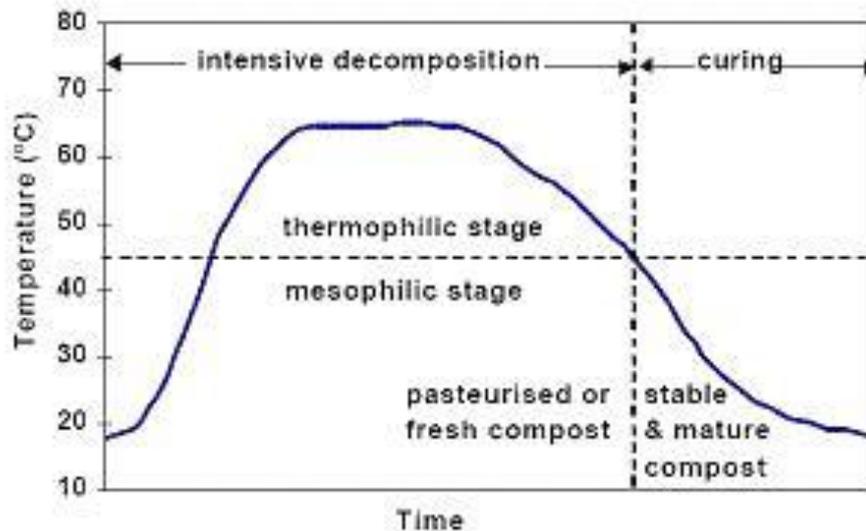


Figure 4 - Thermal profile curve model of the composting process.

The high temperatures are developed by the biological activity of microorganisms that decompose and stabilise organic matter. Then, as the microorganisms gradually deplete the food sources, their metabolic activity declines, and so does the temperature of the mix (Vanotti et al., 2006).

Composting of pig slurry not only allows its recycling and the production of an organic material with good fertilising properties, but also implies the volume reduction of the waste, the elimination of weed seeds and of pathogenic microorganisms (Bernal et al. 2009) (Table 2).

Therefore, it can also be seen as a mitigation process to reduce GHG emissions from animal manure. The heat generated and the regular aeration by turning of the pile during the early stages of composting favour ammonia losses, which are generally greater than for the piled manure (Amon et al., 2001; Gibbs et al., 2002). Such NH_3 losses are low after subsequent soil application of the compost, because the remaining N is mainly in organically bound forms and thus concentrations of inorganic N are very low (Sommer and Hutchings, 2001; Amon et al., 2001; McNeill et al., 2005).

Table 2 - Benefits and drawbacks of composting. (Rynk, 1992; MANEV, 2012c).

<i>Benefits of composting</i>	<i>Drawbacks of composting</i>
Destroys weed seeds and pathogens.	Emissions of ammonia, carbon dioxide, methane and nitrous oxide, especially in the early stages.
Decreases bulk of raw inputs (volume reduction of 50-70%).	Runoff from compost piles must be controlled to prevent movement of nutrients into ground and surface waters.
Finished compost has a consistent soil-like quality that makes it easier to handle and apply.	Aeration and moisture must be managed throughout the composting process.
Stabilises nutrients as organic compounds.	Time, money, equipment and space are required.
Ease of storage, transport and use.	Requirement for a bulking agent. Necessity of pre-treatments or conditioners.
Stable organic nutrients release more slowly, providing plants with a more sustainable source of nutrients for growth.	Some additional fertiliser may be needed to meet crop requirements.
Results in an odourless, marketable product.	

However, pig slurry usually shows several characteristics that are not adequate for composting and could limit the efficiency of the process, such as excess of moisture, low porosity, high N concentration for the organic-C, which gives a low C/N ratio, and in some cases high pH values (Bernal et al., 2009). Other factors like particle size, temperature of the process, O₂ concentration and aeration can also affect the composting process (MANEV, 2012c). In table 3 are shown the recommended conditions for composting of solid manure.

Table 3 - Recommended conditions for composting of solid manure (Rynk, 1992).

<i>Condition</i>	<i>Reasonable Range</i>	<i>Preferred Range</i>
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 (°C)	43 – 66	54 – 60

The adequate C/N ratio for composting is in the range 25-30, because it is considered that the microorganisms require 30 parts of C per unit of N (Bishop and Godfrey, 1983). High C/N ratios make the process slower as there is an excess of degradable substrate for the microorganisms. But with a low C/N ratio, as it occurs in the composting of pig slurry, there is an excess of N per degradable C and inorganic N is produced in excess, promoting ammonia volatilisation.

Low C/N ratios can be corrected by adding a bulking agent to provide degradable organic-C. The selection criteria of the bulking agents are usually based on the availability of the materials, their efficiency during the composting process and the possibility of testing new materials. The materials mostly used as bulking agent for the co-composting of the solid fraction of pig slurry are 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). 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).

Lignocellulosic materials are frequently used for the co-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. Lignocellulosic materials are rich in lignin, they are 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 C/N ratio decreases during composting due to the degradation of the OM, releasing CO₂ and reducing the dry weight of the pile, which leads to an increase in N concentration due to the concentrating effect (Bernal et al., 1998).

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 controls 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). During composting, the pH increases during the bio-oxidative phase due to the degradation of OM of acidic character. However, during maturation it tends to decrease, owing to the nitrification of the NH₃-N, which is an acidifying process.

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.

Substrate porosity is directly related with the air distribution that must be maintained during the process. 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%.

Proper aeration controls the temperature, removes excess of moisture and CO₂ and provides O₂ for the biological processes, while insufficient aeration can lead to anaerobic conditions, and the proliferation of anaerobic microorganisms and odours. The optimum O₂ concentration is between 15 and 20% (Miller, 1992). Excessive ventilation can cool down the mass, reducing the metabolic activity of the microorganisms (Kulcu and Yaldiz, 2004). Controlled aeration should maintain temperatures below 60-65°C, which ensures that enough O₂ is supplied (Finstein and Miller, 1985).

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 O₂ and the gases resulting from the OM degradation. When the moisture content exceeds 60%, O₂ movement is inhibited and the process tends to become anaerobic (Das and Keener, 1997). During composting a large quantity of water can evaporate. In order to control temperature and maintain the decomposition rate by the microbial activity, rewetting may be applied.

Since pig manure is collected in liquid form, its moisture content is very high (moisture > 90%) for composting (Yagüe et al., 2012). The solid-liquid separation of pig slurry is required for its adequate composting but also a low-moisture bulking materials, such as sawdust or straw, should be used to reduce the potential excess of moisture of the mechanically separated solid fraction of pig slurry and provide adequate porosity in the compost heap (Imbeah, 1998).

The temperature pattern indicates the intensity of microbial activity and the occurrence of the composting process. Optimum temperatures for composting are considered in a range of 40-65°C (de Bertoldi et al., 1983), temperatures above 55°C are required to a correct sanitation of the compost and if temperature reach values higher than 63°C, microbial activity starts to decline rapidly as the optimum for various thermophiles is surpassed, with activity approaching low values at 72°C. The range of 52-60°C 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).

1.4 Requirements for pig slurry composting

In order to meet the requirements established by legislation (EC, 2001; BOE 2013, IPTS-JCR, 2012) for the composting process, to ensure a sufficient level of sanitisation of the compost, some operational conditions are required in terms of temperature achieved, presence of pathogens and concentration of heavy-metals and organic pollutants.

Temperature should be higher than 55 °C for 2 weeks and 5 turning should be made or temperature should be kept higher than 65 °C for at least 1 week, with a minimum of 2 turnings for windrow composting; In in-vessel composting, temperatures higher than 60 °C for 1 week should be observed.

Another requirement is the presence of pathogens in the compost, being the compost considered as sanitised when *Salmonella* spp. are absent in 25 g of compost E. coli lower than 1000 CFU/g and *Clostridium perfringens* is absent in 1 g of compost.

The quality of compost is based on the concentrations of heavy metals and organic pollutants, with impurities (> 2mm) limited to < 0.5 % and gravel and stones (> 5 mm) to < 5 %, all normalised to an OM content of 30 %, with the lowest limits for class 1 and the highest limits for class 2 (Table 4). The following parameters should also be indicated: dry matter, OM, bulk density, electrical conductivity, pH, P, K, Ca, Mg, B, Mo and C/N.

Table 4 - Limits for potentially-toxic elements in compost I EU-27 and in Spain (mg/kg dm).

Trace elements	EU		Spain		
	(EC, 2001)		(BOE, 2011)		
	Class 1	Class 2	Class A	Class B	Class C
Cd	0.7	1.5	0.7	2	3
Cr	100	150	70	250	300
Cr (VI)	n.d.	n.d.	n.d.	n.d.	n.d.
Cu	100	150	70	300	400
Hg	0.5	1.0	0.4	1.5	2.5
Ni	50	75	25	90	100
Pb	100	150	45	150	200
Se	NS	NS	NS	NS	NS
Zn	200	400	200	500	1000

n.d.: Not detectable.

The most limiting heavy-metal elements, in terms of compost quality, found during 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) are a little bit more harsh when it comes to regulating the characteristics of fertilisers made from organic wastes, setting 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 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 3 quality products, A, B and C (Table 4); 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, (2008) and Bernal et al. (2009), compost quality should also be based in other 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.

Maturity is not defined by one single parameter, but by a group of parameters. According to Bernal et al. (2009), maturity can be assessed using at least two parameters that can be: physical, chemical and biological.

Physical: Temperature, colour, odour, particle size distribution, moisture and air content;

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.;

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, etc.

Self-heating tests are commonly used to assess compost maturity rate (Brinton et al. 1995), relating the temperature increase of the material with the degree of maturity of the material. Self-heating tests can be seen as simulators of the initial phase of the composting process and can be also used to determine how biodegradable a material is. Higher temperatures development during the self-heating tests indicates higher microbial activity and so, an easily degradable material. Also, respiration tests based on CO_2 -C production or oxygen (O_2) consumption are common procedures for determining compost stability (Hue and Liu, 1995, Barrena-Gómez et al. 2006, Iannotti et al. 1994). 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.

2. OBJECTIVES

The main aim of this study was to test different bulking agents for the co-composting of solid phase of pig slurry after solid/liquid separation (SPS) by study the temperature development during a self-heating test and their degradability as CO₂ production.

The partial objectives are:

- Analyse the composition and specific characteristics of the bulking agents and the solid phase of pig slurry;
- Select the most adequate bulking agent for SPS composting based on degradability and thermal profile;
- Assess the influence of the storage time of the SPS on the temperature development.

3. MATERIALS AND METHODS

3.1 Characterisation of the input materials

The samples used in this experiment as bulking materials were: maize stalks, barley straw, cotton gin and garden pruning; two solid fraction of pig slurry from piglets and sows were tested: A separated in the farm with almost 3 months old (SPS_f) (Figure 5a) and a fresh solid fraction of pig slurry separated on the laboratory (200 µm sieve) from freshly collected pig slurry from the same farm (SPS_i) (Figure 5b).

Barley straw and the slurries came from a pig farm located in Guazamara, Almeria (Spain); maize stalks came from a farm located in Zaragoza (Spain); cotton gin came from a cotton industry located in Seville (Spain) and the garden pruning came from a local company responsible for the maintenance of Murcia's urban gardens.

Barley straw and maize stalks were chopped into small pieces with diameter around 5 cm (Figure 6a); the garden pruning mixture was elaborated from a 1:1 ratio of jacaranda (*Jacaranda mimosifolia*) and white mulberry (*Morus alba*) pruning where the branches were separated from the leaves and grounded in a mill, reducing its size into 5 mm diameter particles (Figure 6b); cotton gin did not suffer any pretreatment.



Figure 5 - a: SPS_f; b: SPS_i separation process.

The solid fraction of pig slurry collected in the farm was stored, part at -4°C to be used promptly, along with the bulking agent materials, and other part was froze at -18°C, to be used in future experiments, along with the solid fraction separated in the laboratory.



Figure 6 - a: Maize stalks before being chopped; **b:** garden pruning mixture already chopped.

For the chemical and physico-chemical analysis of the input materials, part of the bulking agent materials was milled into a thin powder and part of the two solid fractions was freeze-dried and grounded.

Chemical and physico-chemical analyses consisted in the determination of electrical conductivity (EC), pH, moisture content, organic matter content (OM), total organic carbon (TOC), total nitrogen (TN) and macro and micronutrients for all the input materials. However, lignin was determined just for the bulking agent materials and water-soluble organic carbon (C_w) and nitrogen from ammonia ($N-NH_4^+$) was determined in the solid fractions. All the analyses were done in duplicates and the results are resumed in Table 5.

Table 5 - Chemical and physico-chemical characteristics of the input material (in dry weight).

		Cotton gin	Maize stalks	Barley straw	Garden pruning	SPS_f	SPS_i
pH		6.97	6.31	7.47	6.50	7.35	8.24
EC	dS/m	7.15	4.81	3.89	3.40	1.26	2.80
Moisture	(%)*	14	8.83	9.52	53.76	76.51	83.64
OM	(%)	87.9	91.7	93.1	92.7	69.4	79.5
TOC	(g/kg)	411	462	471	462	335	385
C_w	(g/kg)	n.d	n.d	n.d	n.d	7.7	33.9
TN	(g/kg)	5.1	7.4	7.8	12.6	31	38
N-NH₄⁺	(g/kg)	n.d	n.d	n.d	n.d	12	16
C/N		81.6	62.4	60.4	36.7	10.8	10.2
Lignin	%	49.92	50.25	52.66	47.54	n.d	n.d
Ca	(g/kg)	22	6.69	5.26	5.54	19	13
K	(g/kg)	15	10.88	7.14	5.26	5.39	8.57
Mg	(g/kg)	3.28	1.84	1.16	0.93	7.41	4.47
Na	(g/kg)	0.70	0.90	0.42	0.35	2.11	2.91
P	(g/kg)	1.56	2.19	0.82	0.78	15	10.7
Cd	(mg/kg)	<0.1	<0.1	<0.1	<0.1	0.30	0.21
Cr	(mg/kg)	30	25	6.22	0.62	6.40	4.51
Cu	(mg/kg)	8.9	6.76	5.80	6.45	359	131
Fe	(mg/kg)	875	673	259	100	1488	713
Mn	(mg/kg)	76	46	38	26	431	273
Pb	(mg/kg)	5.1	5.97	1.70	1.35	2.18	0.98
Zn	(mg/kg)	68	81	36	24	4888	1616

* - calculated based on fresh weight; n.d.: not determined

3.2 Experimental design

The experiment consisted in two tests: thermal profile developed inside a self-heating reactor; and the respiration test by measuring the CO₂ emitted during 10 days by each mixture of bulking and solid fraction tested, using samples taken at the beginning and at the end of self-heating test.

This experiment had two phases: in phase number one, the four bulking agents with the solid fraction separated in the farm were tested; and in the second phase, the two best bulking agents from the 1st experiment were used with the solid phase separated in the laboratory.

3.2.1 Self-heating test

Four different mixtures of bulking agent and SPS_f and two different mixtures of bulking agent and SPS_i were elaborated. The mixtures were prepared in such proportion to use the maximum amount of solid fraction admitted by the bulking agent, taking into account the C/N ratio and the moisture content of the final mixture, trying to keep the C/N ratio around 20-25 and the moisture content between 55-80% (optimum conditions for composting). The proportions of the mixtures, on a fresh weight basis, were the following:

SPS_f + Cotton gin: 83% of SPS_f + 17% of cotton gin;

SPS_f + Maize stalk: 92% of SPS_f + 8% of maize stalk;

SPS_f + Barley straw: 94% of SPS_f + 6% of barley straw;

SPS_f + Garden pruning: 87% of SPS_f + 13% of garden pruning;

SPS_i + Cotton gin: 88% of SPS_i + 12% of cotton gin;

SPS_i + Garden pruning: 86% SPS_i + 14% of garden pruning;

Once the mixtures were prepared, a sample was taken for to analysis and for the respiration test and the rest was placed inside the reactors. Self-heating tests (Figure 7, 8a and 8b) were carried out in batch reactors of 5L (in duplicate for each mixture). The batch reactors consist on thermal insulated

cylinders with 14 cm of inner-diameter and 40 cm height. Weight, height, and density of the different mixtures inside the batch reactors are shown in Table 6.

During 10-15 days (depending on the intensity of the reaction) the temperature inside and outside of the reactor was recorded using temperature probes placed inside, in the centre of the reactors and a portable meteorological station for the room temperature.

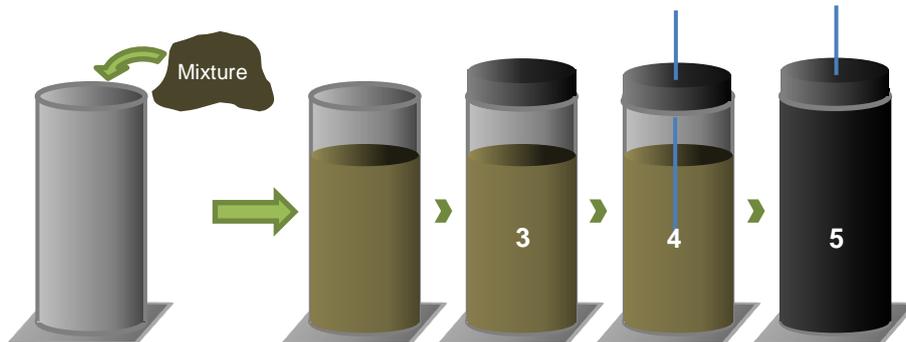


Figure 7 - Schematic of the different filling phases of the self-heating reactors.

The filling process of the reactors included several steps: 1 – weighting of the mixture that will be putted inside the reactor; 2 – simulate a natural compaction of the materials inside the reactor by letting drop softly the reactor from an height of $\approx 10\text{cm}$, 10 times and read the headspace left; 3 – closing the reactor with an isolating lid; 4 – insertion of the temperature probe from the lid to the centre of the reactor and until half of the height of the mixture; 5 – covering of the reactor with an isolating material to avoid heat losses.



Figure 8 – a: Mixture inside the reactor; b: Final disposition of the reactors.

Table 6 - Physical characteristics of the mixtures inside the batch reactors.

	Cotton gin + SPS_f	Maize stalks + SPS_f	Barley straw + SPS_f	Garden Pruning + SPS_f	Cotton gin + SPS_i	Garden Pruning + SPS_i
Weight (Kg f.w.)	2.3	3.0	2.3	3.0	2.66	2.4
Height (m)	0.31	0.30	0.31	0.31	0.33	0.29
Density (Kg/m ³)	479	652	479	625	524	538

f.w.: fresh weight

The temperature probes were connected to a datalogger, allowing an automatic register of the temperatures. This system also made it possible to check the temperatures inside the batches daily and at the instant, permitting the monitoring of the process.

The mixtures with garden pruning and maize stalks were turned at day seven in order to improve aeration, since the temperature was dropping to values near to room temperature, and to check if re-heating occurred.

When internal temperature was close to the external values (11-15d) the test was ended. Then the reactor was emptied and a homogeneous sample was taken for analysis and respiration test.

The samples were taken at the beginning and at the end of the batch experiment, were homogenised with a Robot Coupé mill and divided into fractions in the laboratory: one fraction was oven-dried at 105°C for 24 h to determine the moisture content, the second was immediately frozen (-18°C) and kept for the determination of NH₄⁺-N, and the third was freeze-dried and grounded to less than 0.5 mm for the rest of the analytical determinations; other fraction was stored at -4°C to perform the respiration tests

3.2.1 Respiration test

The degradability of the samples taken at the beginning and at the end of the self-heating test was measured by a respiration test, determining the CO₂ emission from the microbial activity during 10 days at aerobic incubation. The 5g of each fresh sample was placed in a hermetic jar containing CO₂ trap (10mL of 0.5M NaOH in vials) (Figure 9) and incubated under the dark for 10 days at 26°C. The temperature used allowed a good microbial development. The NaOH vials were changed every 2-3 days of interval, to avoid saturation,

and the amount of CO₂ emitted was quantified by titrating the unreacted NaOH with 0.5M HCl, in an excess of BaCl₂. The incubation was run in triplicate for each sample.



Figure 9 - a: Aspect of the mixture after being taken from the reactor; **b:** hermetic jars with sample and CO₂ traps.

3.2.3 Thermodynamic evaluation

The energy produced by microorganisms (q), responsible for the temperature increase in the self-heating test, was calculated considering the specific heat capacity of the samples (C_{p_s}) according to Sundberg (2005). For that, the increase in temperature of the water after immersing a pre-heated bag of sample (Figure 10) was determined considering that:

$$q_s = m_s \cdot C_{p_s} \cdot (100 - T_f) \quad (1)$$

$$q_{\text{water}} = m_w \cdot C_{p_w} \cdot (T_f - T_i) \quad (2)$$

Where m_s and m_w , are the mass of sample and water, respectively, and C_{p_s} and C_{p_w} are the specific heat capacity of the sample and water ($4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$), respectively; T_i is the temperature of water at room temperature and T_f , the final temperature after immersing the heated bag of sample, being $T_f > T_i$.

The bag was initially at 100°C, considering the basic thermodynamic concept that when you immerse a material on water and increase the water temperature up to 100°C, the temperature of material immersed is also at 100°C.

The energy gained from the water will be equal to the energy lost from the sample:

$$q_s = q_{\text{water}} \quad (3)$$

Then, C_p of sample (C_{p_s}) can be calculated, using equations (1-2).

The energy produced by the microbial activity during the self-heating test was calculated as:

$$q(J) = m_s \cdot C_{p_s} \cdot \Sigma\Delta T \quad (4)$$

Being $\Sigma\Delta T$ the accumulated increase of temperature of the mass of pig slurry mixture in the 15-d self-heating test; C_{p_s} was previously calculated (eq. 1-3) and m_s was the mass of sample in the batch reactor (Table 6).

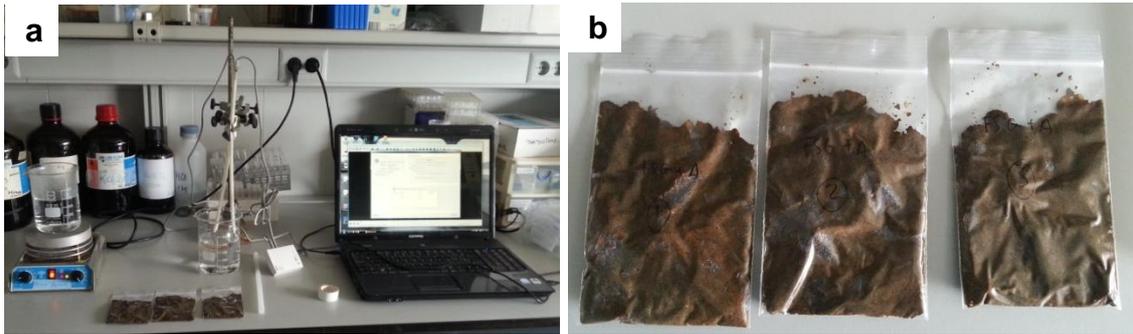


Figure 10 - a: Experimental setup to determine C_{p_s} ; **b:** Compost bags.

3.3 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 the self-heating tests, while the Tukey test at $P < 0.05$ was used to test the statistically significant differences in the parameters studied among the mixtures at the beginning and at the end of the experiment. Normality and homogeneity of the variances were checked using the Kolmogorov-Smirnov and Levene test, respectively, before ANOVA. Univariate general linear model was also applied to assess any significant effect of bulking agent, time and/or type of SPS among the mixtures. These operations were performed including both SPS mixtures. The standard error of the mean values was also determined for the chemical and physico-chemical parameters of the mixtures and for the respiration test. Also, Pearson's correlation coefficient was obtained between C_w and the CO_2 -C emissions of the 4 mixtures with SPS_f and both samplings ($n=8$) and for CO_2 -C emissions and all the mixtures studied ($n=24$). Data analysis was carried out using the SPSS v.21.0 statistical software package.

4. RESULTS AND DISCUSSION

4.1 Properties of the input materials and of the mixtures before and after the self-heating test

4.1.1 Input materials

All the bulking materials used were characterised by high organic matter (OM) concentrations (Table 5), with values ranging between 87.9% and 93.1%, with high concentrations of TOC and thus, with high values of the C/N ratios (36.9 - 81.2). These values were similar to those found by other authors in similar bulking materials, agricultural wastes such as wine shoot pruning and cereal straw (Paredes et al., 1996; Bustamante et al., 2013). Garden pruning had the highest total N (TN) concentration, and therefore the lowest C/N ratio.

The solid fractions of pig slurry (SPS_f and SPS_i) were rich in OM and TOC, with 2.3% and 8.8% of TOC as water soluble, respectively. Both OM and TOC were lower than those of the bulking materials. The low C/N ratios in SPS_f and SPS_i were due to the high concentration of TN, mainly as NH_4^+ -N (11.9 g kg^{-1} and 15.45 g kg^{-1} ; 62.6% and 40.9% of TN), as well as a high concentration of water-soluble organic C ($C_w = 7.7$ g kg^{-1} and 33.9 g kg^{-1}). The higher TOC, C_w and TN of SPS_i than SPS_f were due to the different “age” (storage time) of both materials, SPS_i freshly separated and SPS_f stored during 3 months in the farm. During such storage time, degradation of OM (organic-C) as well N-losses could have occurred. Also, both SPS had a high moisture content (76.5 % and 83.6 %), which together with the high TN proportion as NH_4^+ -N could difficult its composting without a bulking agent.

The solid fractions presented similar concentrations of macro and micronutrients but higher, in general, than the bulking agent, in particular for Cu and Zn. These high values of Cu and Zn are frequently found in pig slurry (Moller et al., 2007a, 2007b) due to the use of pharmacological substances rich in those component, which are used as growth promoters and to prevent animal diseases, especially for piglets (Jondreville et al., 2003).

The values of lignin in the bulking agent materials were in a range of 47.54 - 52.66%, being higher for the maize stalk and barley straw materials. Considering the macro and micronutrients of the bulking agents, high

concentrations of Ca, K, Mg, Cr, Cu, Fe and Mn in the cotton gin material was found, suggesting that it can provide better fertiliser properties to the compost. The other bulking agent materials presented similar results of macro and micronutrients.

4.1.2 Mixtures with solid pig slurry from the farm (SPS_f)

Concerning the characteristics of the mixtures before and after the self-heating test, the EC values increased in all the mixtures, this can be a consequence of the partial mineralisation of the OM, increasing the salts concentration in the matrix (Raviv et al., 1987). The moisture content ranged between 65.1% and 69.7% (Table 7). The incorporation of the bulking agents adjusted favourably the high water content observed in the SPS material (76.5%), avoiding leaching during the process (Liao et al. 1993). The moisture content values were in an acceptable range for composting and along this experiment significant changes in the moisture content, between all of the samples were not observed (Table 5).

Nonetheless, statistically significant differences ($p < 0.001$) in the decrease of OM and C_w in the mixtures with cotton gin were found, during the self-heating test, indicating the degradation of the organic compounds by the microorganisms. Paredes et al. (1996) found that changing the bulking agent from cotton waste to maize straw decreased OM degradation, organic-N mineralisation and therefore, NH_3 -losses in sewage sludge composting. In fact, OM content of the cotton gin mixtures decreased 5.8%, without a significant change in the mixture with maize. The concentration of C_w decreased practically in all the mixtures, indicating the degradation of the most labile compounds. This behaviour is usually found during composting (Bustamante et al. 2008) and this parameter has been established as a maturity index for different source compost (Bernal et al. 1998; 2009).

Non-significant changes were found in the TN concentration during the self-heating test, indicating low or no N-losses. Besides, Zhu (2007) reported high N-losses when C/N ratio was lower than 20 in a study about the effect of low initial C/N ratio on aerobic composting of pig manure with rice straw. However, microbial immobilisation process can explain the NH_4^+ -N

concentration decreased in all mixtures during the experiment, where cotton gin mixture presented higher decrease (73 %) and maize stalk mixture the lower decrease (23 %). The NH_4^+ -N rich wastes, such as pig slurry, tend to present an initial NH_4^+ -N immobilisation by microorganisms during composting (Bernal et al. 1993, Bernal et al. 2009, Paillat et al. 2005 and Liang et al. 2006), being a key-factor for controlling NH_3 volatilization.

4.1.3 Mixtures with pig slurry separated in the laboratory (SPS_i)

The values of the pH in the mixtures prepared with SPS_i were greater than the mixtures with SPS_f, with lower EC (Table 7). EC values decreased slightly for both mixtures after the self-heating test, where statistically significant differences ($p < 0.01$) were found in the mixture with cotton gin, between the beginning and end of the self-heating test. The moisture content of these mixtures ranged between 74.7% and 77.1%, within an acceptable range for the good development of the composting process (Table 7). Again, the incorporation of the bulking agents was an efficient measure to adjust the values for composting (Liao et al. 1993). During the experiment, the moisture content of the mixtures did not significantly change in any of the mixtures (Table 7).

The OM of the mixtures slightly decreased during the 12-d self-heating test, and the same occurred for the TOC and C_w parameters, but the differences were not statistically significant, indicating that degradation of the organic compounds was scarce. However, the concentration of C_w , decrease in all the mixtures, indicating that these labile compounds are degraded first, since they are in a more available form. As mentioned before, this parameter tends to decrease during composting (Bustamante et al. 2008, Garcia et al., 1991) being C_w established as a maturity index for different source compost (Bernal et al. 1998; 2009).

Also for these mixtures, the concentration of TN did not statistically change during the 12-d self-heating test, indicating low or no N-losses. According to Zhu (2007), a low initial C/N ratio can lead to high N-losses. In the present experiment high NH_4^+ -N concentrations were found at the beginning of the test, showing a decrease of 22% for the mixture with cotton gin and 41% for

the mixture with garden pruning during the experiment, which can be due to the different microbial activity. Since TN did not decreased, the microbial immobilisation of $\text{NH}_4\text{-N}$ could have occurred.

Table 7 - Chemical and physico-chemical characteristics of the mixtures of SPS with different bulking agents at the beginning and at the end of the 15-d self-heating tests in 5L batch reactors.

Mixtures		<i>pH</i>	<i>EC</i> ($dS\ m^{-1}$)	<i>Moisture</i> (%)	<i>OM</i> (%)	<i>TOC</i> ($g\ kg^{-1}$)	<i>C_w</i> ($g\ kg^{-1}$)	<i>TN</i> ($g\ kg^{-1}$)	<i>NH₄⁺-N</i> ($mg\ kg^{-1}$)	<i>C/N</i>
Cotton gin + SPS _f	Initial	7.7±0.02 ab	4.9±0.06 c	65.1±0.25	77.7±0.27 a	324±4 b	21.5±0.51 a	20.1±1.18	271±22 ab	16.1±0.74
	End	7.7±0.03 a	6.2±0.22 a	69.8±0.24	73.2±0.56 bc	371±5 a	11.9±1.10 ab	20.1±6.12	73±12 b	19.8±6.09
Maize stalks + SPS _f	Initial	7.2±0.01 d	4.2±0.06 d	69.4±0.24	72.5±0.34 c	327±5 b	8.8±0.35 bc	15.3±0.59	353±63 a	21.4±0.50
	End	7.4±0.02 cd	4.7±0.20 c	60.0±4.13	72.8±0.97 bc	331±20 b	6.4±1.90 c	17.8±9.05	144±99 ab	23.6±13.1
Barley straw + SPS _f	Initial	7.5±0.01bc	4.1±0.01 d	69.7±0.52	73.7±0.14 bc	350±2 ab	8.6±1.78 bc	14.5±2.49	368±17 a	24.4±4.29
	End	7.3±0.20 cd	5.5±0.13 b	74.2±0.41	71.7±1.91 c	343±15 ab	10.9±1.10 bc	14.4±3.56	275±316 ab	25.1±7.00
Garden pruning + SPS _f	Initial	7.2±0.00 d	4.4±0.08 cd	68.7±0.41	76.2±0.26 ab	370±9 a	22.0±0.27 a	16.8±0.74	334±85 a	22.1±1.52
	End	7.7±0.02 ab	4.5±0.09 cd	57.9±4.35	73.0±0.99 bc	343±2 ab	7.2±2.32 bc	12.5±1.78	139±109 ab	28.0±4.08
ANOVA		***	***	n.s.	***	**	***	n.s.	*	n.s.
Cotton gin + SPS _i	Initial	8.01±0.10	2.67±0.09 a	76.2±0.69	80.6±1.09	417±9	27.7±0.08	27.8±0.06	1043±13 a	14.5±0.28
	End	8.03±0.06	2.11±0.13 b	76.2±0.37	78.6±0.75	403±3	23.8±0.20	27.4±2.5	234±36 d	14.7±01.79
Garden pruning + SPS _i	Initial	8.25±0.06	2.22±0.01 bc	74.7±0.04	84.0±0.43	353±24	27.5±0.08	20.7±0.66	977±67 b	16.3±0.68
	End	7.98±0.06	1.79±0.07 c	77.1±0.31	81.9±0.22	412±12	22.9±0.16	23.8±4.26	402±31 c	17.5±3.07
ANOVA		n.s.	**	n.s.	n.s.	n.s.	n.s.	n.s.	***	n.s.

Mean ± Standard deviation (n=2); 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 for the same column are not statistically different according to the Tukey test.

4.2 Thermal profile and respiration test

4.2.1 Mixtures with SPS_f

The thermal profile obtained for the mixtures elaborated with SPS_f during the self-heating test (Figure 11) indicates that the mixture with cotton gin quickly developed higher temperatures, when compared with the other bulking agents tested. In the first day of experiment, cotton gin mixture presented an increase of 12 °C with respect to the external temperature, while garden pruning, barley straw and maize stalks mixtures only presented an increase of 8, 7 and 3 °C, respectively. The increase in temperature in cotton gin mixture indicates a high microbial activity.

All mixtures were able to maintain the temperature raised for at least 3-4 days, before starting to decrease. However, at day 7, the mixtures elaborated with garden pruning and maize stalks were turned, in order to improve the homogeneity and the aeration of the mixtures, since the temperature was dropping to values close to the external values. Re-heating occurred, temperature slightly increased in both mixtures, showing a small second peak of temperature, which indicated that the material was still biologically active. A constant temperature profile was observed in the mixture with barley straw, maintaining ≈4 °C above the external values at the end of the 15-d self-heating test, while in the garden pruning mixture the temperature decreased quickly after 6 days. Georgacakis et al. (1996) found that higher temperatures were achieved during composting (45-55°C) for the mixtures elaborated with the solid fraction of pig slurry and cotton gin, when comparing with mixtures prepared with cereal straws (40-45°C) or with peat (30-35°C). These results are well related to the degradation of the OM and TOC that occurred in the mixture with cotton gin (Table 5).

The different behaviour of the mixtures can be due to their physical and chemical characteristics. However, it does not seem to be related to the bulk density (Table 6), however, it can be related to the degradability of the chemical compounds present in the bulking agents.

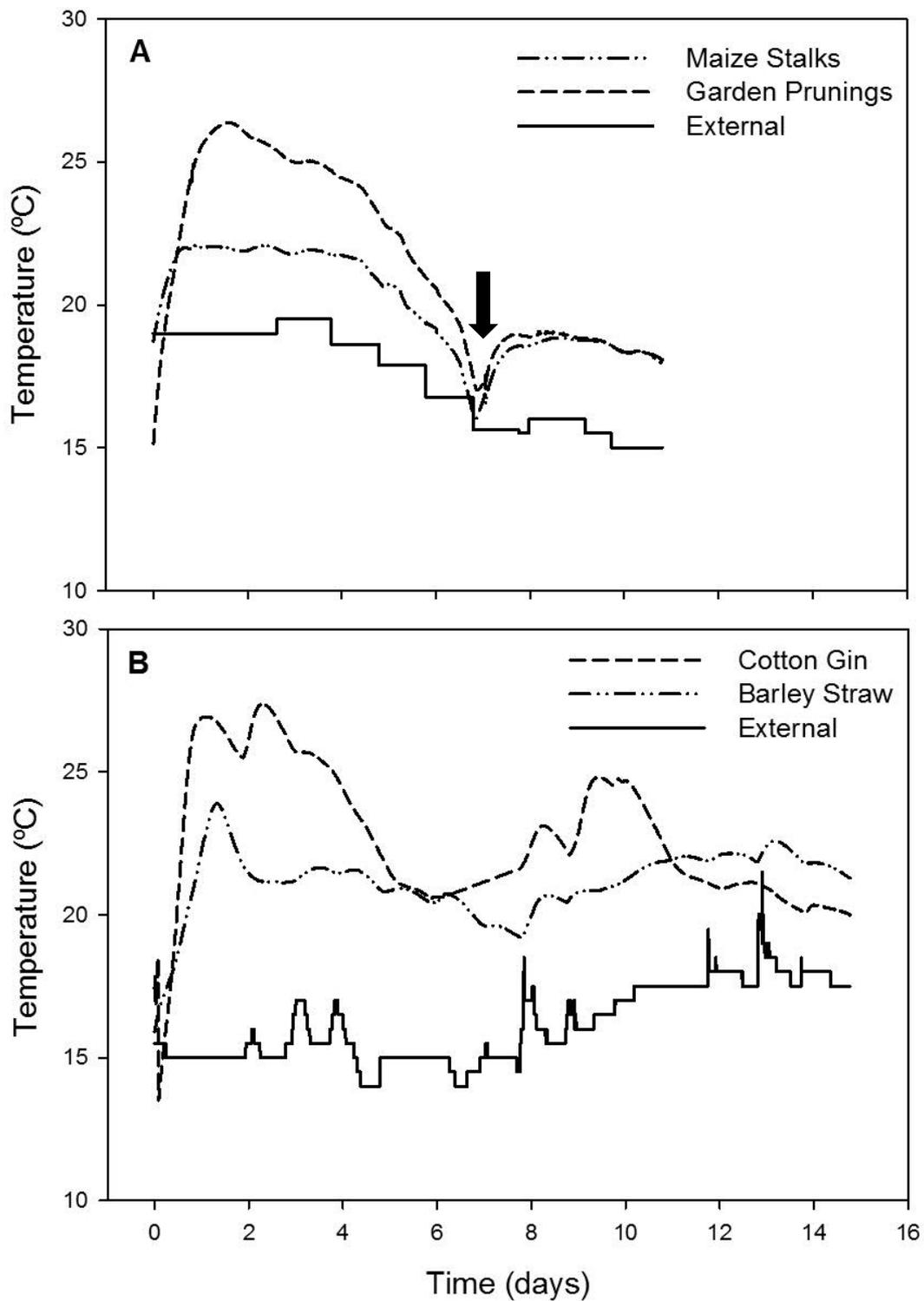


Figure 11 - Thermal profiles of the mixtures with SPS_f and corresponding external temperature. The arrow indicates the turning. **A:** mixtures with maize stalks and garden pruning; **B:** mixtures with cotton gin and barley straw.

Puyuelo et al. (2010), Brinton et al. (1995) and Chrometza et al. (1968) showed that O₂ consumption and CO₂ emission quickly increases in the first days, decreasing slowly until the end of the composting process, relating then, the stability of the compost with the respiration index. A more stable product should produce less CO₂, due to it lower microbial activity. This type of test can also indicate the degree of degradability of a determined material. Microorganisms respire at higher rates in the presence of large amounts of bioavailable organic matter while respiration rate is slower if this type of material is scarce, indicating that CO₂ production is directly correlated with the aerobic respiration. (Barrena-Gomez et al 2006). A more biodegradable material should have a higher CO₂ emission/O₂ consumption, since it have more available or easily degradable components to be used by the microorganisms.

The degradability of the materials before and after the self-heating test was measured by CO₂-C released from the samples during 10 days of aerobic incubation (Barrena-Gomez et al 2006) (Table 8).

Table 8 - CO₂-C emission values (accumulated during 10 days) from microbial activity of the mixtures with SPS_f at the beginning and at the end of self-heating tests (mg CO₂-C/g DM in 10-d). Mean ± Standard deviation (n=3).

	<i>Cotton gin + SPS_f</i>	<i>Maize stalk + SPS_f</i>	<i>Barley straw + SPS_f</i>	<i>Garden pruning + SPS_f</i>	<i>ANOVA (bulking)</i>
Initial	26.73±6.98 a	12.05±3.56 b	17.80±1.34 ab	24.16±2.21 a	*
End	15.55±3.59 a	12.60±1.35 ab	15.57±3.79 a	10.83±0.16 b	*
ANOVA (time)	*	n.s.	n.s.	**	

n.s.: not significant $P>0.05$; *, **, ***: significant at $P<0.05$, 0.01, 0.001, respectively. Values followed by the same letter in a row are not statistically significant according to the Tukey test for the different mixtures.

The initial mixtures with cotton gin waste and garden pruning had the highest values of CO₂-C emissions when comparing with the other materials, the maize straw 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. In this study, the authors observed that the mixture with cotton

waste showed a quick temperature development and consumed more O₂ when comparing to maize stalks, therefore producing more CO₂.

The results indicated a reduction in the CO₂-C production on the samples with cotton gin and pruning waste at the end of the experiment in comparison with the samples at the beginning of the self-heating test. The reduction of the CO₂ emission was more significant in the pruning mixture, with a reduction of 57%, indicating a high degradability and microbial activity of the mixture. Since CO₂ emission is a sign of microbial activity and OM degradation, its slowdown may indicate that easily accessible compounds were already degraded.

At the end of the self-heating test, the samples with cotton gin and barley straw evolved similar values CO₂-C to their initial values; all these mixtures had not statistically different C_w values (Table 5). Also the temperature profile showed the highest values at the end of the self-heating test (Figure 11). However, the mixture with maize stalk did not reduce the CO₂-C production during the experiment, showing low temperature values during the process, low initial C_w values and slow degradability. The C_w contains the simple water-soluble organic compounds such as sugars, amino acids, and peptides which are easily metabolized by microorganisms during composting (Bernal et al., 1996). Several authors referred 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 mixtures with maize stalks, which may be due to the liberation of simple, soluble organic compounds exceeding their degradation (Castaldi et al., 2005). A positive highly significant correlation ($r=0.935$; $p<0.001$; $n=8$) between the CO₂ released and the C_w concentration for the 4 mixtures at both sampling times was found, indicating that an increase in C_w is associated with an increase in CO₂ production and vice-versa, referring to degradability.

The absence of significant changes in the CO₂-C production (degradability) for the mixtures with maize and barley straw after the self-heating test can be related with the fact that these mixtures have more recalcitrant compounds, being more resistant to degradation. Both bulking agents are lignocellulosic materials and so, these materials are mainly composed by cellulose, hemicellulose and lignin (50.25 - 52.66% of lignin, respectively). Cellulose and hemicellulose are the main C sources for microbial

activity, responsible for most of CO₂ and heat produced. Cellulose chains are packed by hydrogen bonds in so-called “elementary and microfibrils”. These fibrils are attached to each other by hemicelluloses, amorphous polymers of different sugars as well as other polymers such as pectin, and covered by lignin. Lignin is an integral cell wall constituent, which provides plant strength and resistance to microbial degradation (Argyropoulos and Menachem, 1997) and 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 et al., 2008). Also, the internal part of the big particles could not be physical accessible for the microbial attack and thus, the period of 11-15 days can be considered as a pre-treatment for breaking down the surface of the straw and stalks particles. Similar results were reported by Paredes et al. (1996), who observed in an experiment of co-composting of olive-mill wastewater sludge with different bulking agents a greater degradation in the mixture elaborated using cotton gin as bulking agent due to its smaller particle size. Also, Nolan et al. (2011) conclude that woodchips, due to the presence of recalcitrant lignin and its large surface area, were not a suitable bulking agent when used on its own, but when mixed with sawdust, provided good quality compost.

4.2.2 Mixtures with SPS_i

The thermal profile of the mixtures of cotton gin and garden pruning with SPS_i developed during the 12-d self-heating test is shown in Figure 12.

The mixture made with cotton gin reached higher temperatures than the mixture made with garden pruning, but in general, both mixtures presented a similar trend line along the 12-d self-heating test. It can be observed that cotton gin and pruning wastes developed high temperatures but a quicker temperature development in the mixtures with garden pruning, increasing 12 and 9 °C with respect to the external values, indicating a high microbial activity. All mixtures were able to maintain the temperature raised for at least 3-4 days, before starting to decrease.

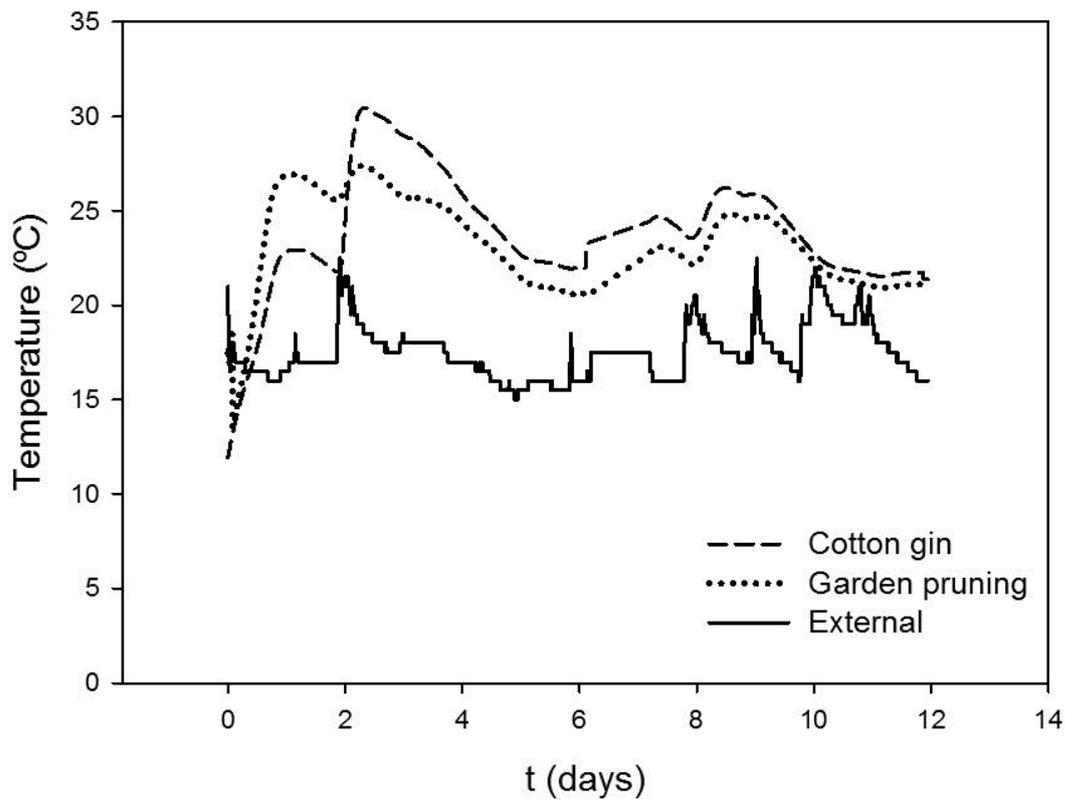


Figure 12 - Thermal profiles of the mixtures with SPS₁ and corresponding external temperature.

A constant temperature profile was observed in the both mixtures, maintaining ≈ 5 °C above the external values at the end of the 12-d self-heating test.

The degradability of the materials before and after the self-heating test was measured by CO₂-C released from the samples during 10 days of aerobic incubation (Barrena-Gomez et al 2006) (Table 9). The results indicated a scarce non-significant reduction in the CO₂-C production on the samples with cotton gin and garden pruning waste at the end of the experiment in comparison with the samples at the beginning of the self-heating test. Since CO₂ emission is a sign of microbial activity and OM degradation, its high value at the end of the test indicated that the mixtures were still very active microbiologically.

Table 9 - CO₂-C emission values (accumulated during 10 days) from microbial activity of the mixtures with SPS_I at the beginning and at the end of self-heating tests (mg CO₂-C/g DM in 10-d). Mean ± Standard deviation (n=3).

<i>Mixtures</i>		CO₂-C
<i>Cotton gin + SPS_I</i>	Initial	31.42±1.76
	End	27.95±0.40
<i>Garden pruning + SPS_I</i>	Initial	33.60±1.87
	End	32.14±1.56
Anova		n.s.

n.s.: not significant $P>0.05$;

The absence of significant changes in the CO₂-C production after the self-heating test may indicate that perhaps, this period of time was not enough to degrade all the available biodegradable materials present in the reactor, indicating also that the mixtures were still very active microbiologically.

4.3 Energetic evaluation

The energy produced by the microorganisms was calculated using the differences in temperature between the internal reactor and the external values (equation 4). Analysing the accumulative energy production graphic showed in Figure 13 for the mixtures with SPS_f, a smooth initial curve for the mixture with maize stalk was observed, indicating a slower degradation of the material when comparing with the other materials studied. The mixture with cotton gin (also with garden pruning) showed a quick energy production for the first day of experiment, indicating a fast microbial activity. Also, the mixtures with cotton gin and garden pruning presented the highest energy production in the first 24h of experiment, reaching a production of 125 KJ and 110 KJ, while those with barley straw and maize stalk produced 53 KJ and 36 KJ, respectively.

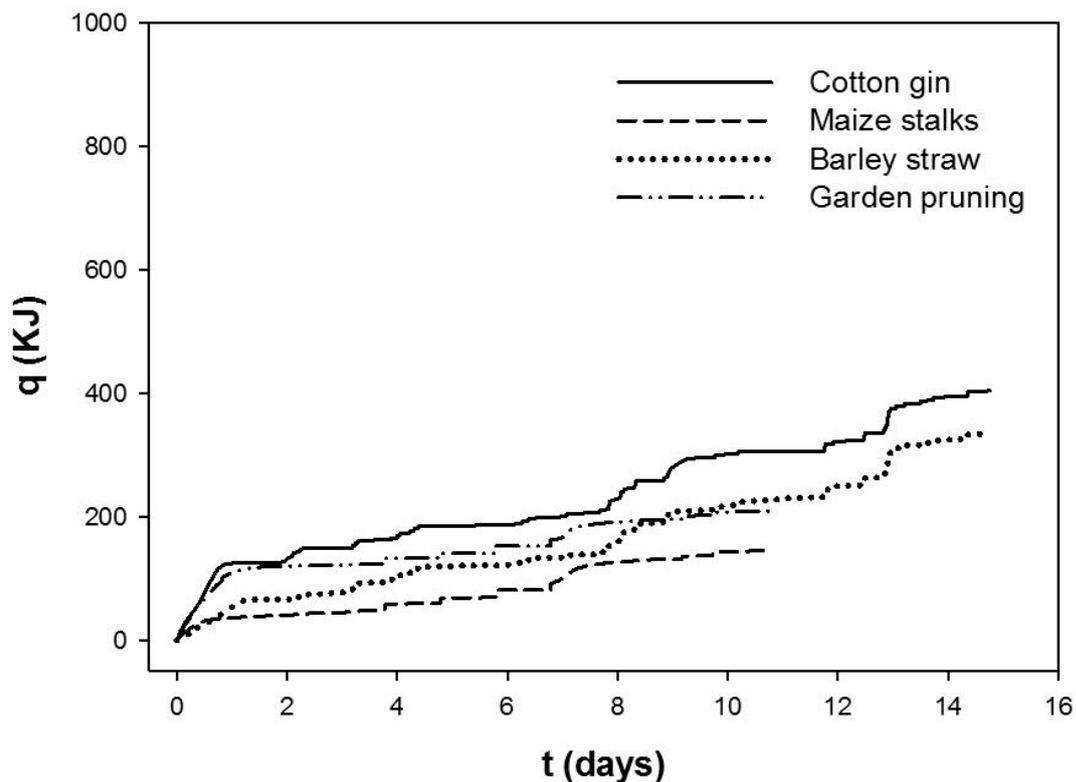


Figure 13 - Accumulative values of energy production from the mixtures with SPS_f during the self-heating test.

A reduction in the size of the maize particles could increase the breakdown surface and therefore, can speed the degradation, as observed in

the experiment in the mixtures with cotton gin and garden pruning with small particles size.

The accumulative values of energy production for the mixtures with SPS_i are shown in Figure 14. As observed previously, both mixtures with SPS_i present a quick energy production at the beginning of the experiment, suggesting a high microbial activity. SPS_i seems to work better in terms of energy production than SPS_f , reaching higher values of production for the same time. In the first 24h, cotton gin and garden pruning mixtures with SPS_i produced 169KJ and 160KJ, respectively, but 125KJ and 110KJ were produced with the same bulking agent but with a different SPS. These can be due to the storage time of SPS_f , which was collected from the storage system in the far. Such storage could have caused the partial degradation of the most labile organic matter (as observed, SPS_f had lower C_w than SPS_i), also having lower microbial activity in the SPS_f than the SPS_i (freshly separated). In fact, after 12 days, the energy generated by the microbial activity (Figure 14) was almost the double than in the previous experiment, using the same bulking agents.

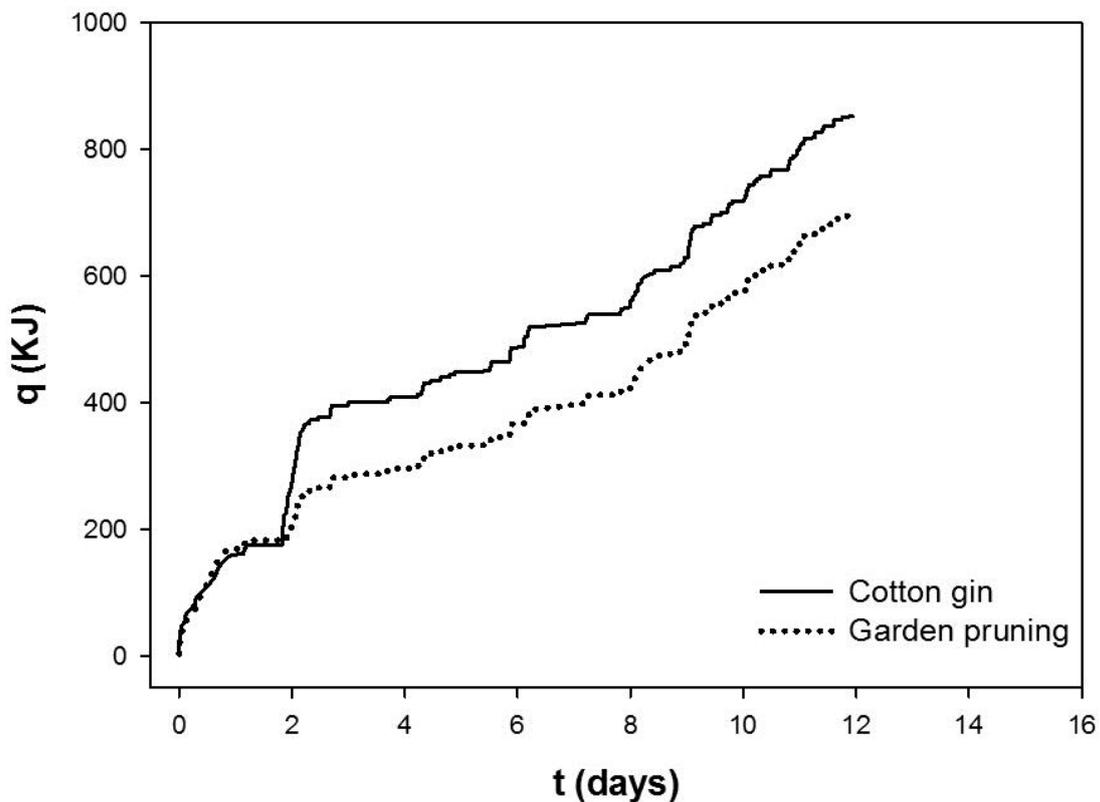


Figure 14 - Accumulative values of energy production from the mixtures with SPS_i during the self-heating test.

4.4 Comparison of the behaviour of the different solid fraction of pig slurry (SPS_f vs. SPS_i)

Comparing the chemical and physico-chemical characteristics of the SPS_f and SPS_i mixtures with cotton gin and garden pruning, those with SPS_f presented lower pH than the mixtures with SPS_i, which can be beneficial to reduce ammonia losses to the atmosphere, the moisture content tend to be lower as well as the NH₄⁺-N concentration. Univariate general linear model and one-way ANOVA analysis verified that SPS presented statistically significant differences for all the parameters studied (Table 10 and 12). This effect is observed in Table 12, where most of the parameters show higher values in the mixtures with SPS_i. Statistically significant differences were also found in the effect of bulking, time, SPS and all the possible combinations between these factors in the pH and EC parameters. The pH values are higher in SPS_i mixtures, while EC presents lower values for the same mixtures. The statistically significant differences found between time and SPS for OM and C_w in both mixtures, are related with the degradation of these parameters by the microorganisms during the self-heating test.

Table 10 - Univariate general linear model comparison between the chemical and physico-chemical parameters from the mixtures of cotton gin and garden pruning with different SPS.

Factors	pH	EC	Moisture	OM	TOC	C_w	TN	NH₄⁺-N	C/N
Bulking (B)	**	***	n.s	n.s	n.s	*	*	**	**
Time (T)	**	*	n.s	n.s	n.s	**	n.s	*	n.s
SPS	***	***	***	***	***	***	***	*	**
B x T	*	***	**	n.s	n.s	*	n.s	n.s	n.s
B x SPS	**	***	*	n.s	n.s	n.s	n.s	*	n.s
T x SPS	*	***	n.s	***	*	***	n.s	n.s	n.s
B x T x SPS	**	***	***	n.s	***	**	n.s	n.s	n.s

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

In general, concentrations of TOC, C_w, OM, TN and NH₄⁺-N in the mixtures with SPS_f were lower than the mixtures with SPS_i, which may indicate that the fact of this SPS have been stored for a certain amount of time, it already suffered a natural process of biodegradation, limiting the microbial activity during composting. This hypothesis is corroborated by the EC values

that were higher for the mixtures with SPS_f, suggesting that partial mineralisation had occurred during storage, increasing the salts concentration in the matrix.

The values of the different chemical and physico-chemical parameters suggests that SPS_i mixtures were a best candidate to be used during composting, because there is a higher amounts of OM, TOC, C_w and TN which promotes a higher microbial activity and temperature development due to the high energy released by microbial activity. However, the pH values obtained for the SPS_i mixtures could promote ammonia volatilisation, decreasing NH₄⁺-N concentration between the initial and the final sample of the self-heating test, which is not recommended from the environmental point of view.

From the analysis of the thermal profiles of the mixtures of cotton gin and garden pruning with SPS_f and SPS_i, SPS_i mixtures developed higher temperatures with a maximum of 30.4°C and 27.4°C, respectively, during the first 2 days, while the mixtures with SPS_f had as maximum 27.3°C and 26,4°C, respectively. Also it was noticed in terms of energy produced by the microbial activity, where cotton gin and garden pruning with SPS_f mixtures showed lower values for this parameter (125KJ and 110KJ, respectively), when compared to the 169KJ and 160KJ produced by the same bulking but using SPS_i.

After correlating the CO₂-C emissions with all the chemical and physico-chemical parameters of all the mixtures studied (Table 11), it was found that all these parameters are significantly correlated. The OM content of the samples showed a high positive significant correlation (r=0.925; p<0.001) the CO₂-C emissions indicating that the mixtures with higher OM content were more easily degradable, producing more CO₂-C, due to the higher C source for microbial activity, which is the case of the mixtures with SPS_i.

Table 11 - Pearson's correlation coefficient (r) and significance (P) between CO₂-C emissions and all the chemical and physico-chemical parameters from all the mixtures at the beginning and the end of the self-heating test (n=24).

	<i>pH</i>	<i>EC</i>	<i>Moisture</i>	<i>OM</i>	<i>TOC</i>	<i>C_w</i>	<i>TN</i>	<i>NH₄⁺-N</i>	<i>C/N</i>
<i>r</i>	0.738	-0.713	0.614	0.925	0.660	0.679	0.485	0.560	-0.587
<i>P</i>	0.000	0.000	0,001	0.000	0.000	0.000	0.016	0.004	0.003

Table 12 - Chemical and physico-chemical characteristics of the mixtures of cotton gin and garden pruning with different SPS at the beginning and at the end of the 15-d self-heating tests in 5L batch reactors.

Mixtures		<i>pH</i>	<i>EC</i> (<i>dS m⁻¹</i>)	<i>Moisture</i> (%)	<i>OM</i> (%)	<i>TOC</i> (<i>g kg⁻¹</i>)	<i>C_w</i> (<i>g kg⁻¹</i>)	<i>TN</i> (<i>g kg⁻¹</i>)	<i>NH₄⁺-N</i> (<i>mg kg⁻¹</i>)	<i>C/N</i>
Cotton gin + SPS _f	Initial	7.7±0.02 b	4.9±0.06 b	65.1±0.25 c	77.7±0.27 bc	324±4 d	21.5±0.51 a	20.1±1.18 ab	271±22 ab	16.1±0.74 b
	End	7.7±0.03 b	6.2±0.22 a	69.8±0.24 bc	73.2±0.56 d	371±5 bc	11.9±1.10 b	20.1±6.12 ab	73±12 b	19.8±6.09 ab
Garden pruning + SPS _f	Initial	7.2±0.00 c	4.4±0.08 c	68.7±0.41 c	76.2±0.26 cd	370±9 bc	22.0±0.27 a	16.8±0.74 ab	334±85 ab	22.1±1.52 ab
	End	7.7±0.02 b	4.5±0.09 bc	57.9±4.35 d	73.0±0.99 d	343±2 cd	7.2±2.32 c	12.5±1.78 b	139±109 b	28.0±4.08 a
Cotton gin + SPS _i	Initial	8.01±0.10 a	2.67±0.09 d	76.2±0.69 a	80.6±1.09 ab	417±9 a	27.7±0.08 d	27.8±0.06 a	1043±13 a	14.5±0.28 b
	End	8.03±0.06 a	2.11±0.13 e	76.2±0.37 ab	78.6±0.75 ab	403±3 bc	23.8±0.20 d	27.4±2.5 a	234±36 ab	14.7±0.179 b
Garden pruning + SPS _i	Initial	8.25±0.06 a	2.22±0.01 e	74.7±0.04 a	84.0±0.43 abc	353±24 ab	27.5±0.08 d	20.7±0.66 a	977±67 b	16.3±0.68 b
	End	7.98±0.06 a	1.79±0.07 e	77.1±0.31 a	81.9±0.22 a	412±12 ab	22.9±0.16 d	23.8±4.26 ab	402±31 b	17.5±3.07 ab
ANOVA		***	***	***	***	***	***	**	*	**

Mean ± Standard deviation (n=2); 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 in a column are not statistically different according to the Tukey test.

4.5 Implication of the bulking agent on soil conservation C

Cotton gin and garden pruning mixtures are easily degradable materials, which will offer a quicker availability of C for the microbial growth, but this source will also be consumed promptly. For composting the materials should provide a quick process, high temperature development for a high degree of hygenisation. However, maize stalks and barley straw as bulking agents, showed low degradation ratio, indicating that if a compost was made from this materials, the process would take longer time to achieve the maturation than with the other bulking agents and would possibly need more time to achieve hygenisation, as lower temperatures may be reached.

Even if the major observations obtained from this experiment indicates that cotton gin and garden pruning materials are the best suited to be used as bulking agents on a fast composting, in a soil C conservation and environmental point of view, the maize stalk and barley straw may led to a greater amount of C present in the final compost, returning higher proportion of C to the soil system, favouring C conservation strategies.

Also, the maturation phase is a key step for soil C-conservation. As demonstrated by Bernal et al. (1998) and Bernal (2008) the addition of mature compost to the soil is the best strategy for C-conservation over poorly-matured compost, as during the maturation, the humification of the OM occurs, being such humic substances of low degradability.

However, in order to eliminate pathogens and weed seeds, reaching high temperatures is required. The mixture should present higher degradability than maize and barley mixtures but at the same time, the characteristics that preserve part of its slow release type of C in the final product.

Compost made with any of the mixtures described before, should be a better option, when comparing to the direct application of the SPS (fresh and untreated) in soils.

5. CONCLUSIONS

From the results obtained from the present experiments, it can be concluded that the age of the SPS proved to be an important but not limiting factor of the composting process. The use of a recently separated SPS (SPS_i) showed a better temperature development with higher energy produced than stored SPS, indicating higher microbial activity, which will reduce the composting time.

The degradation of OM detected by CO₂-C was affected by the physico-chemical parameters of the composting mixture: pH, moisture, OM, TOC, C_w, TN and NH₄⁺-N.

The analyses of the thermal profile of composting materials at laboratory scale during a self-heating test, together with the microbial degradation measured by CO₂-C emissions are adequate parameters to define the degradability of the material and to predict their behaviour during composting.

Although pruning waste and cotton gin showed a quick temperature developed and degradability, their fast OM degradation quickly released high CO₂ into the atmosphere, and will produce compost with low OM and TOC. However, the use of maize stalks during composting of the solid fraction of pig slurry, although led to low temperature development, its slow degradability could have lower impact on the environment due to CO₂ emissions, helping to improve C-conservation by producing compost rich in OM. Also the low thermal energy could imply less turning requirements for composting, and the humification of the OM can be enhanced during composting producing a material rich in humified OM. However, these must be tested on a field composting experiment.

6. BIBLIOGRAPHY

- 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.
- Amon B, Amon T, Boxberger J, Alt C. (2001) Emissions of NH₃, N₂O and CH₄ from dairy cows housed in a farmyard manure tying stall (housing, manure storage, manure spreading), *Nutr Cycl Agroecosyst.* 60: 103–113.
- Amon B, Kryvoruchko V, Amon T, Zechmeister-Boltenstern S (2006) methane, nitous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. *Agr Ecosyst Environ.* 112: 153-162.
- 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 n°. 631, International Fertiliser Society, York, UK (ISBN: 987-0-85310-268-7).
- Bernal MP, Albuquerque JA, Moral R (2009) Composting of animal manures and chemical criteria for compost maturity assessment. A review. *Bioresour Technol.* 100: 5444-5453.
- Bernal MP, Lopez-Real JM, Scott KM (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 MP, Navarro AF, Roig A, Cegarra J, García D (1996) Carbon and nitrogen transformation during composting of sweet sorghum bagasse. *Biol Fert Soils.* 22: 141–148.
- Bernal MP, Paredes C, Sánchez-Monedero MA, Cegarra J, (1998) Maturity and stability parameters of composts prepared with a wide range of organic wastes. *Bioresour Technol.* 63: 91–99.
- Bishop PL, Godfrey C (1983) Nitrogen transformation during sewage composting. *Biocycle.* 24: 34-39.

- BOE, 2013. Real Decreto 506/2013, de 28 de junio, sobre productos fertilizantes. Boletín Oficial del Estado 164: 51119-51207.
- BORM. 2011. Orden de 27 de junio de 2011, de la Consejería de Agricultura y Agua, por la que se establece el programa de actuación sobre la zona vulnerable a la contaminación por nitratos del Valle del Guadalentín, en el término municipal de Lorca. BORM 166: 34715-34741.
- Brinton WF, Evans E, Droffner ML, Brinton RB. (1995) A standardized Dewar test for evaluation of compost self-heating. *BioCycle*. 36:1-16.
- Brown S, Kruger C, Subler S (2008) Greenhouse gas balance for composting operations. *J Environ Qual*. 37:1396–1410.
- 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.
- Bustamante MA, Paredes C, Marhuenda-Egea FC, Pérez-Espinosa A, Bernal MP, Moral R, (2008a) Co-composting distillery wastes with animal manure: carbon and nitrogen transformations and evaluation of compost stability. *Chemosphere*. 72: 551-557.
- Bustamante MA, Restrepo AP, Albuquerque 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.
- California Compost Quality Council (CCQC) (2001) *Compost Maturity Index, Technical Report*. California Compost Quality Council.
- CARM (2009) *Censo Agrario* (Centro Regional de Estadística de Murcia).
- 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.
- Chefetz B, Hatcher PG, Hadar Y, Chen Y (1996) Chemical and biological characterization of organic matter during composting of municipal solid waste. *J Environ Qual*. 25: 776–785.
- Christensen ML and Sommer SG (2013) Manure characterization and inorganic chemistry in *Animal manure recycling: treatment and*

- management* (eds Sommer SG, Christensen ML, Schmidt T and Jensen LS) Wiley publishing, West Sussex, 41-63.
- Chrometza P (1968) Determination de la consommation d'oxygène des composts en voie de maturation. Bull Inf GIROM. 33: 253-256.
- Cunalt C, Burton C, Pourcher AM (2010) Effectiveness of thermal sanitization of piggery slurry using heat exchanger. Ramiran 2010, Lisbon, Portugal.
- Das K, Keener HM (1997) Moisture effect on compaction and permeability in composts. J Environ Eng. 123: 275-281.
- Davidson EA (2009) The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860. Nat Geosci. 2:659–662.
- de Bertoldi M, Vallini G, Pera A (1983) The biology of composting: a review. Waste Manag Res. 1: 157-176.
- 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) Environment and energy. Theme 8–1/2003.
- EC (2001). Working document: Biological treatment of biowaste, 2nd draft. European Commission, Directorate General Environment.
- Estévez-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: 43-52.
- Finstein MS, Miller FC (1985) Principles of composting leading to maximization of decomposition rate, odor control, and cost effectiveness. In: Gasser JKR (Ed.), Composting of Agricultural and Other Wastes. Elsevier Applied Science Publ, Barking, Essex, 13-26.
- Finstein MS, Miller FC, MacGregor ST, Psarianos KM (1985) The Rutgers strategy for composting: process design and control. EPA Project Summary, EPA 600/S2-85/059, Cincinnati, Ohio.
- 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.

- Gajalakshmi S, Abbasi SA (2008) Solid waste management by composting: State of the art. *Critical Reviews in Environ Sci Technol.* 38: 311-400.
- Garcia C, Hernandez T, Costa F (1991) Changes in carbon fractions during composting and maturation of organic wastes. *Environ Manag.* 15: 433-439.
- 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.
- Gibbs PA, Parkinson RJ, Misselbrook TH, Burchett S (2002) Environmental impacts of cattle manure composting, in: *Microbiology of Composting*, Springer-Verlag Berlin, Berlin, 445–456.
- Hansen MN, Henriksen K, Sommer, SG (2006) Observations of production and emission of greenhouse gases and ammonia during storage of solids separated from pig slurry: Effects of covering. *Atmos Environ* 40: 4172–4181.
- Haug RT (1993) *The Practical Handbook of Compost Engineering*. Lewis Publishers, Boca Raton, FL.
- Hue NV, Liu J, (1995) Predicting compost stability. *Compost Sci Util.* 3: 8-15.
- Huang GF, Wong JWC, Wu QT, Nagar BB (2004) Effect of C/N on composting of pig manure with sawdust. *Waste Manag.* 24: 805–813.
- Hsu J, Lo S (2001) Effect of composting on characterization and leaching of copper and manganese, and zinc from swine manure. *Environ Pollut* 114: 119-127.
- Iannotti DA, Grebus ME, Toth BL, Madden LV, Hoitink HAJ (1994) Oxygen respirometry to assess stability and maturity of composted municipal solid-waste. *J Environ Qua.* 23: 1177 -1183.
- Imbeah M (1998) Composting piggery waste: a review. *Bioresour Technol.* 63: 197-203.
- IPTS-JRC (2012). Technical report for End- of-waste criteria on Biodegradable waste subject to biological treatment. Third Working Document. JRC European Commission, IPTS.Sevilla.
- Jensen LS (2013) Animal manure residue upgrading and nutrient recovery in biofertilisers in *Animal manure recycling: treatment and management*

- (eds Sommer SG, Christensen ML, Schmidt T and Jensen LS) Wiley publishing, West Sussex, 237-267.
- 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.
- Keener HM, Dick WA, Hoitink HAJ (2000) Composting and beneficial utilization of composted by-product materials. In: Dick, W.A. (Ed.). *Land Application of Agricultural, Industrial, and Municipal By-products.* Soil Science Society of America, Inc., Madison, 315-341.
- Kulcu R, Yaldiz O (2004) Determination of aeration rate and kinetics of composting some agricultural wastes. *Bioresour Technol.* 93: 49-57.
- Leip A, Weiss F, Wassenaar T, Perez I, Fellmann T, Loudjani P, Tubiello F, Grandgirard D, Monni S, Biala K (2010) Evaluation of the livestock sector's contribution to the EU greenhouse gas emissions (GGELS) – final report. European Commission, Joint Research Centre.
- Lesschen JP, van den Berg M, Westhoek HJ, Witzke HP, Oenema O (2011) Greenhouse gas emission profiles of European livestock sectors. *Anim Feed Sci Tech.* 166-167:16-28.
- Liang Y, Leonard, J.J., Feddes, J.J.R., McGill, W.B., (2006) Influence of carbon and buffer amendment on ammonia volatilization in composting. *Bioresour Technol.* 97: 748-761.
- Lo KV, Lau AK, Liao PH (1993) Composting of separated solid swine wastes. *J Agric Engng Res* 54: 307-317.
- MANEV (2012a) 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
- MANEV (2012b) Evaluation of manure management and treatment technology for environmental protection and sustainable livestock farming in Europe. Deliverable: A fertilisation plan using pig slurry for most frequent crops in Murcia. CEBAS-CSIC
- MANEV (2012c) Evaluation of manure management and treatment technology for environmental protection and sustainable livestock

- farming in Europe. Report on Definitions of the composting conditions for pig slurry. 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 Sci Util.* 13: 281-287.
- McCarthy 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.
- Miller FC (1992) Composting as a process based on the control of ecologically selective factors. In: Metting FB Jr (Ed.). *Soil Microbial Ecology. Applications in Agricultural and Environmental Management.* Marcel Dekker, Inc., New York, 515-544.
- Moller HB, Nielson AM, Nakakubo R, Olsen HJ (2007a) Process performance of biogas digesters incorporating pre-separated manure. *Livest sci.* 112: 217-223.
- Moller HB, Jensen HS, Tobiasen L, Hansen MN (2007b) Heavy metal and phosphorous content of fractions from manure treatment and incineration, *Environ Technol.* 28: 1403-1418.
- Montes F, Meinen R, Dell C, Rotz, Hristov AN, Oh J, Waghorn G, Gerber PJ, Henderson B, Makkar HPS, Dijkstra J (2011) Mitigation of methane and nitrous oxide emissions from animal operations: II. A review of manure management mitigation options-Special Topics. *J Anim Sci.* 91:5070-5094.
- Moral R, Pérez-Murcia MD, Pérez-Espinosa A, Moreno-Caselles J, Paredes C (2005) Estimation of nutrient values of pig slurries in Southeast Spain easily determined properties. *Waste Manag.* 25: 719-725.
- Navarro AF, Cegarra J, Roig A and Bernal MP (1991) An automatic microanalysts 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.

- Oenema O, Wrage N, Velthof GL, van Groenigen JW, Dolging J, Kuikman PJ (2005) Trends in global nitrous oxide emissions from animal production systems. *Nutr Cycling Agroecosyst.* 72:51–65.
- 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. Biodeter Biodegr.* 38: 205-210.
- Qiu S, McComb AJ, Bell RW, Davis JA (2003) Response of soil microbial activity to temperature, moisture, and litter leaching on a wetland transect during seasonal refilling. *Wetl Ecol Manag.* 13: 43–54.
- Raven, RPJM and Gregersen KH (2007) Biogas plants in Denmark: successes and setbacks. *Renw Sust Ener Rev.* 11: 116-132.
- Raviv M, Tarre S, Geler Z, Shelef G (1987). Changes in some physical and chemical properties of fibrous solids from cow manure and digested cow manure during composting. *Biol Wastes.* 19: 309-318.
- 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-Monedero MA, Roig A, Paredes C, Bernal MP (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.* 7: 301–308.
- 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. B, Soil Plant Sci.* 42: 146-151.
- Sommer SG, Hutchings NJ. (2001) Ammonia emission from field applied manure and its reduction - invited paper, *Eur J Agron.* 15: 1–15.
- Sommer SG and Christensen ML (2013) Animal production and animal manure management in *Animal manure recycling: treatment and management* (eds Sommer SG, Christensen ML, Schmidt T and Jensen LS) Wiley publishing, West Sussex, 5-23.

- Sorensen CAG, Sommer SG, Bochtis D, Rotz A (2013) Technologies and logistics for handling, transport and distribution of animal manures in *Animal manure recycling: treatment and management* (eds Sommer SG, Christensen ML, Schmidt T and Jensen LS) Wiley publishing, West Sussex, 211-234.
- 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 (2006) NH₃, N₂O and CH₄ 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.
- Tiquia SM, Tam NFY (1998) Elimination of phytotoxicity during co-composting of spent pig-manure sawdust litter and pig sludge. *Bioresour Technol* 65: 43-49.
- 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.
- 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 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.
- Yagüe MR, Bosch-Serra AD, Boixadera J (2012) Measurement and estimation of the fertiliser value of pig slurry by physicochemical models: Usefulness and constraints. *Biosystems Eng.* 3: 206-216.
- Zhu N (2007) Effect of low initial C/N ratio on aerobic composting of swine manure with rice straw. *Bioresour Technol.* 98: 9–13.

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.

Web links:

EUROSTAT (2013). [Online]

epp.eurostat.ec.europa.eu/statistics_explained/index.php/Statistical_themes.

FAOSTAT (2010). [Online]

<http://faostat3.fao.org/faostat-gateway/go/to/download/G1/GT/E>

FAOSTAT (2013). [Online]

[Faostat.fao.org](http://faostat.fao.org) – Agro-environmental indicators and emissions-agriculture statistics. Consulted in January, 2014.

www.carm.es – Estadísticas ganaderas.

MAGRAMA – Estadísticas ganaderas y de calidad y evaluación ambiental del Ministerio de Agricultura, Alimentación y Medio Ambiente. (www.magrama.gob.es) Consulted in February, 2014.

7. ANNEXES

7 – Analytical methods in organic materials

Sample preparation

Samples are homogenised and divided in 3 parts. One of them is dried in a drying-oven at 105°C for 24 h to determine the moisture content, the second is immediately frozen (-18°C) and kept for the determination of NH₄⁺-N, and the third is freeze-dried and ground to less than 0.5 mm for the rest of the analytical determinations.

7.1.1 Moisture content

Determination of the percentage of water in the wet sample, by weight difference after drying at 105 °C. Approximately 10 g of wet sample is weighted to a previously weighted (0.0001 precision) ceramic capsule and dried at 105°C in a drying-oven for 12h. The lost in weight is the moisture content of the sample, expressed in percentage referred to wet weight. All the data obtained by the different analytical methods was correct with this value, to refer them as dry weight.

7.1.2 Organic matter content

Ashes are the product of calcination of the sample. It is considered as organic matter, the lost in weight from the sample dried at 105°C after calcination at 550°C for 24h (Navarro et al., 1993). Weight lost is expressed as percentage of the dried sample.

7.1.3 pH

The pH is determined from a water extract of the sample obtained after mechanical stirring for 2h in a 1:10 ratio (w/v) using a glass electrode pH-meter (US Salinity Laboratory Staff, 1954).

7.1.4 Electrical conductivity

The electrical conductivity is determined from a water extract of the sample obtained after mechanical stirring for 2h in a 1:10 ratio (w/v), previously centrifuged and filtrated, through a conductivity bridge (US Salinity Laboratory Staff, 1954).

7.1.5 Total organic carbon (TOC) and Total nitrogen (TN)

C and N are determined in an elemental analyser by combusting the sample at 1020°C. Previous destruction of the carbonates with hydrochloric acid is required (Navarro et al., 1991).

The sample is finely grounded and is weighted between 1-2 mg to a tin capsule (0.001mg precision). The analysis begins after closing the tin capsules into a ball-like shape and after analysing the results from the calibration curve made with a standard substance (atropine). In this study an “EuroA elemental analyzer” was used.

7.1.6 Water-soluble carbon (C_w)

The sample is extracted with distilled water at a 1:20 ratio (w/v) for 2h, after centrifugation and filtration with a synthetic mesh, the extract is filtered again through a 0.45 μm filter. The determination is made by using a TOC-TN liquid analyser for liquid samples. In this study, a Shimadzu analyser, model “TOC-V CSN” with a model for nitrogen “TNM-1” was used.

7.1.7 Nitrogen in ammonium form ($\text{NH}_4^+\text{-N}$)

The sample is extracted with KCl 2N at a 1:20 ratio (w/v) for 2h, after centrifugation and filtration with acid wash paper filter (Sommer et al., 1992). Spectrophotometric measure of the intensive green complex coloration produced when reacting sodium salicylate with sodium dichloroisocyanurate, as source of Cl_2 , sodium nitroprusiate as catalyser and sodium citrate as

calcium complex and magnesium to avoid its precipitation as hydroxide to pH values higher than 12 (Kempers and Zweers, 1996).

An aliquot of 0.4 mL of extract was added to a reaction tube then add 1.6 mL of reactive A (sodium salicylate 78.1 g L^{-1} and sodium nitroprusiate 0.25 g L^{-1}), 6.4 mL of distilled H_2O , 0.8 mL of reactive C (sodium citrate 93.3 g L^{-1}) and 0.8 mL of reactive B as a source of chlorine (sodium hydroxide 40 g L^{-1} and sodium dichloroisocyanurate 5 g L^{-1}). The mixture was stirred and stored for 45 minutes in the darkness. NH_4^+ -N determination was made using a spectrophotometer ($\lambda = 660 \text{ nm}$) taking into account the standard curve (from 5 to 25 ppm of NH_4^+ -N) obtained from an ammonium sulphate dissolution equivalent to 400 ppm of NH_4^+ -N.

7.1.8 Nitrogen in nitrate form (N-NO_3^-)

Potentiometric determination of the soluble N-NO_3^- in a water extract through a selective electrode.

The sample was extracted with distilled water (miliQ quality) (1:5 ratio w/v) and after mechanical stirring for 2h, the extract is centrifuged and supernatant is filtered with an acid-wash paper filter. An aliquot of 25 mL of extract was added to a beaker, adding 0.25 mL of H_3BO_3 1M and 0.5 mL of $(\text{NH}_4)_2\text{SO}_4$ 2M (electrolyte). If the sample contains chlorines, Ag_2SO_4 0.05 M is added to avoid interferences. A calibration curve is made from 0 to 100 ppm of NO_3^- -N from a solution of KNO_3 with a concentration equivalent to 1000 ppm of NO_3^- -N. Finally, the determination is done using a selective electrode, previously stabilised (30-40 minutes) with a KNO_3 0.01M solution.

7.1.9 Lignin

The insoluble residue left after the acid attack of the sample is considered as lignin and it is determined following the ANSI/ASTM D 1106-56 (American National Standards Institute, 1977a) protocol.

Weight 1g of sample (W_1) in a 100mL vase and stir it well with 15mL of H_2SO_4 72%, leaving it making contact for all the night. Transfer it for a

volumetric flask of 1000mL and add 560mL of distilled water to dilute the 72% H₂SO₄ to 3% H₂SO₄.

The volumetric flask is connected to a refrigerating system and it is kept in ebullition for about 4h. In the end of this 4h, let sediment the solids and filter it in vacuum with a filtrating plate, previously dried at 105°C and weighted (W₂). The solids are washed with hot distilled water until that the water pH is not acid. After this step, the sample is dried on the plate at 105°C for 12h and weighted (W₃). The dried solids are putted in the oven at 430°C for 24h to determine their organic matter (OM_L). The lignin content is calculated using the follow equation:

$$\% \text{ Lignin} = \frac{(W_3 - W_2) \cdot (\% \text{MO}_L) \cdot 100}{W_1 \cdot (100 - \%H)}$$

Where %H is the moisture content of the sample.