# UAB

## Universitat Autònoma de Barcelona

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**Universitat Autònoma de Barcelona**

Escola d'Enginyeria

**Departament d'Enginyeria Química, Biològica i Ambiental**

# Study on the gaseous emissions during the biological treatment of sewage sludge. Characterization of VOCs and odour emissions

## PhD Thesis

Programa de Doctorat en Ciència i Tecnologia Ambientals

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CERTIFIQUEM:

Que l'enginyer químic DANIEL GONZÁLEZ ALÉ ha realitzat sota la nostra direcció el treball amb títol "Study on the gaseous emissions during the biological treatment of sewage sludge. Characterization of VOCs and odour emissions" que es presenta en aquesta memòria i que constitueix la seva Tesi per optar al Grau de Doctor per la Universitat Autònoma de Barcelona.

I per a què se'n prengui coneixement i consti als efectes oportuns, presentem a l'Escola d'Enginyeria de la Universitat Autònoma de Barcelona la Tesi esmentada, signant el present ceritficat.


Dr. Antoni Sánchez i
Ferrer

Dr. David Gabriel i
Buguña

Dr. Joan Colón i
Jordà


Bellaterra, 3 de desembre de 2019

## Agraïments

Arriba el moment d'escriure les últimes línies d'aquest document, i ho faig molt feliç per tot el que m'emporto d'aquests quasi 4 anys com a doctorand, immers a la vida del Departament d'Enginyeria Química, Biològica i Ambiental de la Universitat Autònoma de Barcelona. Molts moments viscuts, molt coneixement adquirit i algunes persones que sé que quedaran per sempre.

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*Keep the time, set the pace for music, make minds trip and bodies react.*

## Resum de la tesi

La gestió dels fangs generats durant el tractament de les aigües residuals a les estacions depuradores d'aigües residuals (EDARs) és un dels grans reptes als quals s'enfronten les autoritats Europees, estatals i locals, alhora que els gestors de plantes industrials de tractament d'aquests residus. La producció anual d'aquest residu als països Europeus supera els 7.5 milions de tones en matèria seca, essent necessari el seu tractament per tal de minimitzar o evitar els impactes mediambientals negatius associats. En aquest sentit, existeixen diverses alternatives de tractament biològic per tal de gestionar les grans quantitats de llots d'EDAR produïts, com ara la digestió anaeròbia o el compostatge, a més de tecnologies emergents com el bioassecatge. Els objectius d'aquestes tecnologies de tractament biològic, les quals són considerades tecnologies de baix impacte mediambiental, són els de reduir el volum, la quantitat i l'activitat biològica d'aquests llots, a més de l'obtenció de productes finals amb un valor afegit. No obstant això, aquests processos de tractament biològic tenen associats uns impactes mediambientals i socials, com poden ser les emissions gasoses i odoríferes generades al llarg de les diferents etapes del cicle de tractament, les quals tendeixen a augmentar degut a la proliferació de plantes de tractament de fangs d'EDAR.

El compostatge i el bioassectage de fangs d'EDAR són dos processos de tractament similars amb objectius diferents. Per una banda, amb el compostatge es busca reduir tant el volum com l'activitat biològica del material per obtenir un producte que pugui ser emprat com a fertilitzant o esmena per al sòl. Per altra banda, el bioassectatge de fangs promou la disminució de la humitat present per mitjà del calor metabòlic generat durant la degradació biològica de la matèria orgànica juntament amb l'aplicació d'alts cabals d'aeració per obtenir un producte final que pugui ser emprat com a biocombustible. Com s'ha comentat prèviament, ambdues tecnologies tenen associats impactes mediambientals i socials ineludibles, dels quals destaquen les emissions gasoses i odoríferes que deriven de la degradació biològica de la matèria orgànica. Entre tots els compostos gasosos que poden estar presents en aquestes emissions gasoses, l'amoníac, el sulfur d'hidrogen i els compostos orgànics volàtils (COVs) mereixen una menció especial quant a la seva

contribució a l'olor generat, mentre que el metà i l'òxid nitrós són els principals compostos d'efecte hivernacle.

En aquesta tesi, l'estudi de les emissions gasoses i odoríferes generades durant el tractament biològic de fangs d'EDAR s'ha centrat en una planta industrial de compostatge de llots d'EDAR i en una planta pilot de bioassecatge de llots d'EDAR.

Primerament, es va avaluar l'influencia del temps de compostatge sobre les emissions gasoses i odoríferes i sobre l'estabilitat biològica assolida pel material a una planta real de compostatge de fangs d'EDAR. El procés de compostatge es divideix en dues fases principals, una primera de descomposició de la matèria orgànica duta a terme en canals de compostatge dinàmics amb un temps de residència de 4 dies, seguida d'una segona fase de maduració en piles trapezoïdals d'una duració de 30 dies. A l'augmentar el temps de residència del material als canals dinàmics de 4 a 14 dies, la degradació biològica de la matèria orgànica va millorar substancialment, mentre que les emissions gasoses i odoríferes generades durant la fase de maduració es van veure reduïdes. A més, es va realitzar una caracterització completa dels COVs, mostrant que els compostos organosulfurats, les cetones i els terpens són els grups de COVs predominants a les emissions gasoses generades durant aquest procés de compostatge. Per últim, amb aquesta caracterització es van poder identificar els COVs amb major contribució odorífera.

Finalment, es va operar un reactor de bioassecatge de llots d'EDAR a escala pilot per monitorar i caracteritzar completament les emissions gasoses i odoríferes d'aquest procés innovador, proporcionant el primer inventari d'emissions d'amoníac, sulfur d'hidrogen, compostos orgànics volàtils totals i específics, olors, metà i òxid nitrós. Els resultats obtinguts durant el procés de bioassecatge de fangs d'EDAR es van comparar amb la bibliografia existent referent a emissions gasoses i odoríferes en processos de compostatge de fangs d'EDAR, mostrant que, de forma general, les emissions gasoses i odoríferes generades al llarg del procés de bioassecatge són menors que les associades als processos de compostatge de llots d'EDAR.

A més de l'interès científic d'aquesta tesi, el qual queda reflectit pels tres articles científics de recerca publicats en revistes d'alt impacte al camp de l'enginyeria mediambiental, aquesta ajuda a incrementar l'expertesa dels grups d'investigació GICOM, GENOCOV i BETA en relació a les metodologies de mostreig i anàlisi d'emissions gasoses i odoríferes generades en processos a escala pilot i industrial.

## Resumen de la tesis

La gestión de los lodos generados durante el tratamiento de las aguas residuales en las estaciones depuradoras de aguas residuales (EDARs) es uno de los grandes retos a los cuales se enfrentan las autoridades europeas, estatales y locales, al igual que los gestores de plantas industriales de tratamiento de estos residuos. La producción anual de este residuo en los países europeos supera los 7.5 millones de toneladas expresado en materia seca, siendo necesario su tratamiento con tal de minimizar o evitar los impactos medioambientales negativos asociados. En este sentido, existen diversas alternativas de tratamiento biológico con el objetivo de gestionar las grandes cantidades de lodos de EDAR producidos como la digestión anaerobia o el compostaje, además de tecnologías emergentes como el biosecado. Los objetivos de estas tecnologías de tratamiento biológico, consideradas tecnologías de bajo impacto medioambiental, son los de reducir el volumen, la cantidad i la actividad biológica de estos lodos, además de la obtención de productos con valor añadido. Sin embargo, estos procesos de tratamiento biológico traen asociados unos impactos medioambientales y sociales como son las emisiones gaseosas y odoríferas generadas a lo largo de las diferentes etapas del ciclo de tratamiento, las cuales tienden a aumentar debido a la proliferación de plantas de tratamiento de lodos de EDAR.

El compostaje y el biosecado de lodos de EDAR son dos procesos de tratamiento similares con objetivos diferentes. Por un lado, con el compostaje se busca reducir tanto el volumen como la actividad biológica del material para obtener un producto que pueda ser utilizado como fertilizante o enmienda para el suelo. Por otro lado, el biosecado de lodos promueve la disminución de la humedad presente en el material por medio del calor metabólico generado durante la degradación biológica de la materia orgánica junto con la aplicación de altos caudales de aireación para obtener un producto que pueda ser utilizado como biocombustible. Como se ha mencionado previamente, ambas tecnologías presentan impactos medioambientales y sociales ineludibles, de los cuales destacan las emisiones gaseosas y odoríferas asociadas a la degradación biológica de la materia orgánica. Entre todos los compuestos gaseosos que pueden estar presentes en dichas emisiones, el amoníaco, el sulfuro de hidrógeno y los compuestos orgánicos volátiles (COVs) merecen una mención

especial en cuanto a su contribución al olor generado, mientras que el metano y el óxido nitroso son los principales compuestos con efecto invernadero.

En esta tesis, el estudio de las emisiones gaseosas y odoríferas generadas durante el tratamiento biológico de lodos de EDAR se ha centrado en una planta industrial de compostaje de lodos de EDAR y en una planta piloto de biosecado de lodos de EDAR.

En primer lugar, se evaluó la influencia del tiempo de compostaje sobre las emisiones gaseosas y odoríferas y sobre la estabilidad biológica alcanzada por el material en una planta industrial de compostaje de lodos de EDAR. El proceso de compostaje se divide en dos fases principales, una primera de descomposición de la materia orgánica llevada a cabo en canales de compostaje dinámicos con un tiempo de residencia de cuatro días, seguida de una segunda fase de maduración en pilas trapezoidales con una duración de 30 días. Al aumentar el tiempo de residencia del material en los canales dinámicos de 4 a 14 días, la degradación biológica de la materia orgánica mejoró sustancialmente, mientras que las emisiones gaseosas y odoríferas generadas durante la fase de maduración se vieron reducidas. Además, se realizó una caracterización completa de los COVs, mostrando que los compuestos organosulfurados, las cetonas y los terpenos son los grupos de COVs predominantes en las emisiones generadas durante este proceso de compostaje. Por último, con esta caracterización se pudieron identificar los COVs con mayor contribución odorífera.

Finalmente, se operó un reactor de biosecado de lodos de EDAR a escala piloto para monitorizar y caracterizar completamente las emisiones gaseosas y odoríferas de este proceso, proporcionando el primer inventario de emisiones de amoníaco, sulfuro de hidrógeno, compuestos orgánicos volátiles totales y específicos, olores, metano y óxido nitroso. Los resultados obtenidos durante el proceso de biosecado de lodos de EDAR se compararon con la bibliografía existente referente a emisiones gaseosas y odoríferas en procesos de compostaje de lodos de EDAR, mostrando que, de forma general, las emisiones gaseosas y odoríferas generadas durante el proceso de biosecado de lodos de EDAR son menores que las asociadas a los procesos de compostaje de lodos de EDAR.

Además del interés científico de esta tesis, el cual queda reflejado por los tres artículos de investigación publicados en revistas de alto impacto en el campo de la ingeniería ambiental, esta ayuda a incrementar el conocimiento de los grupos de investigación GICOM, GENOCOV y BETA en relación a las metodologías de muestreo y análisis de emisiones gaseosas y odoríferas generadas en procesos a escala piloto e industrial.

## Thesis abstract

Sewage sludge management is one of the main challenges pointed out by the European and local authorities, together with plant managers, in the past years. Its annual production in the European countries is over the 7.5 million Mg in dry basis, which must be treated to minimize or avoid its negative environmental impacts. In this sense, different biological alternatives exist to handle and manage the huge quantities of sewage sludge produced, such as anaerobic digestion or composting, or more novel technologies such as sewage sludge biodrying. The aim of these treatment technologies, which are regarded as environmental friendly technologies, is to reduce the volume, the quantity and the biological activity of the sewage sludge, as well as obtaining end products with an added value. However, unavoidable environmental and social impacts arise from these biological treatment processes, such as gaseous and odorous emissions generated during the different stages of the integrated treatment cycle, which tend to increase due to the proliferation of the sewage sludge treatment facilities.

Sewage sludge composting and biodrying processes are two similar treatment processes seeking different objectives. On one hand, sewage sludge composting aims at reducing both the volume and the biological activity of the material to obtain a product that can be used as fertilizer or soil amendment. On the other hand, sewage sludge biodrying seeks to remove moisture by using both the metabolic heat generated during the biodegradation of organic matter and high aeration rates to obtain a final product that can be used as biofuel. As mentioned, both technologies present unavoidable environmental and social impacts among which gaseous and odorous emissions derived from the biological degradation of organic matter stand out. Among all the gaseous compounds that can be present in these emissions, special mention is deserved for ammonia, hydrogen sulphide and volatile organic compounds (VOCs) as the main odour contributors and for methane and nitrous oxide as the main greenhouse gases.

In this thesis, the study of the gaseous and odorous emissions generated during the treatment of sewage sludge has been focused on a full-scale sewage sludge composting process and on a bench-scale sewage sludge biodrying process.

Firstly, the influence of the composting time on the gaseous and odorous emissions and on the biological stability achieved was assessed in a full-scale sewage sludge composting plant. The composting process was divided into two main phases, a first organic matter biodegradation phase performed in dynamic windrows with a retention time of 4 days, followed by a curing step performed in trapezoidal piles lasting about 30 days. By increasing the dynamic windrow retention time to 14 days, the organic matter biodegradation was enhanced, while the gaseous and odorous emissions generated during the curing phase were reduced. In addition, a full VOCs characterization was done, showing that organosulphur compounds, ketones and terpenes were the main VOC groups present in the gaseous emissions generated during the composting process. Moreover, from this VOC characterization it was possible to identify the main VOC odour contributors.

Finally, a bench-scale bioreactor for the sewage sludge biodrying was operated to monitor and fully characterize the gaseous and odorous emissions derived from this process, providing the first inventory of ammonia, hydrogen sulphide, total and specific VOCs, odour, methane and nitrous oxide emissions for this sewage sludge treatment technology. To put the obtained results into context, the gaseous and odorous emissions generated during the sewage sludge biodrying process performed were compared with gaseous and odorous emissions from sewage sludge composting literature, showing that, in general, lower gaseous and odorous emissions were generated during the biodrying process.

In addition to the scientific interest of this thesis, which is reflected by the three scientific research articles published in high impact journals in the field of environmental engineering, it helps to increase the GICOM, GENOCOV and BETA research groups expertise on the sampling and analytical methodologies for gaseous and odorous emissions generated in bench and full-scale sewage sludge treatment facilities.

## List of abbreviations

| Abbreviation | Definition |
| --- | --- |
| $A_{FC}$ | Surface of the flux chamber |
| $A_S$ | Area of the emitting surface |
| $AT_4$ | Cumulative oxygen consumption in 4 days |
| BOC | Biodegradable organic carbon |
| C/N | Carbon to Nitrogen |
| DE | Diatomaceous earth |
| DL | Detection limit |
| DM | Dry matter |
| DMDS | Dimethyl disulphide |
| DMS | Dimethyl sulphide |
| DM-SS | Dry matter from sewage sludge |
| DMTS | Dimethyl trisulphide |
| DRI | Dynamic respiration index |
| $DRI_{24h}$ | Dynamic respiration index during the 24 hours of maximum biological activity |
| ECD | Electron capture detector |
| EDGAR | Emission Database for Global Atmospheric Research |
| EF | Emission factor |
| FC | Flux chamber |
| FID | Flame ionization detector |
| GC | Gas chromatography |
| GHG | Greenhouse gas |
| GWP | Global warming potential |
| HCV | Higher calorific value |
| IPCC | Intergovernmental Panel on Climate Change |
| LCV | Lower calorific value |
| MC | Moisture content |
| MPN | Most probable number |
| MS | Mass spectrometry |

| Abbreviation | Definition |
| --- | --- |
| MSW | Municipal solid waste |
| NIOSH | National Institute for Occupational Safety and Health |
| OAV | Individual odour activity value |
| OAV$_{SUM}$ | Sum of individual odour activity values |
| OC | Odour concentration |
| ODT | Odour detection threshold |
| OEF | Odour emission factor |
| OER | Odour emission rate |
| OFMSW | Organic fraction of municipal solid waste |
| OM | Organic matter |
| OSHA | Occupational Security and Health Administration |
| PEL | Permissible exposure limit |
| PID | Photoionization detector |
| PLC | Programmable logic controller |
| PTFE | Polytetrafluoroethylene |
| PW | Pruning waste |
| RS | Raw sludge |
| SOER | Specific odour emission rate |
| SS | Sewage sludge |
| STEL | Short term exposure limit |
| TD-GC/MS | Thermal desorption and gas chromatography coupled to mass spectrometry |
| TOC | Total organic carbon |
| tVOCs | Total volatile organic compounds |
| TWA | Time weighted average |
| USEPA | United States Environmental Protection Agency |
| VF | Vegetal fraction |
| VOC | Volatile organic compound |
| VS | Volatile solids |
| WRT | Windrow residence time |
| WWTP | Wastewater treatment plant |

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# RESEARCH MOTIVATION AND THESIS OVERVIEW

## Research motivation

The thesis work has been conducted in the Department of Chemical, Biological and Environmental Engineering of the Universitat Autònoma de Barcelona (UAB), between the Composting Research Group (GICOM) and the Biological Treatment and Valorisation of Liquid and Gas Effluents Research Group (GENOCOV), and in collaboration with the BETA Technology Centre of the Universitat de Vic – Universitat Central de Catalunya. This thesis has been developed in the framework of the projects "URBASER: Optimización de compostaje, biosecado y olores (COMPOBIOL)", "TIRME S.A.: Estudio de mejoras en la planta de compostaje de lodos de depuradora de Ariany, Mallorca (Proyecto COPCO)" and "SMART Plant Innovation Action founded from the EU's Horizon 2020 research and innovation programme under grant agreement No. 690323".

The main motivation to develop this thesis was to increase the knowledge related to the gaseous and odorous emissions generated by different sewage sludge biological treatment strategies. Gaseous emissions from sewage sludge composting have been studied in the past years in lab, bench and pilot scale reactors, but few information is available from real full-scale composting plants. These gaseous emissions are marked by its malodorous characteristic and its high variability, which depends on different operational or process parameters such as feedstock characteristics or process scale. For this reason, an extended knowledge about the kind and quantity of the different compounds that may be found in these emissions can be helpful in order to mitigate odour nuisance from full-scale sewage sludge composting facilities over nearby population. On the other hand, sewage sludge biodrying technology, which is a novel technology that aims to recover energy from this kind of organic waste, has been a hot topic for researchers during the last years. However, an assessment of the gaseous emissions and the environmental impact related to this biological process has never been accounted. For this reason, and to help improving this novel technology, a bench-scale bioreactor was operated to assess the gaseous and odour emissions generated during the biodrying of conventional sewage sludge.

## Thesis overview

The thesis document is divided into 7 chapters.

**Chapter 1** presents a general introduction to the topic, with a review of the available literature.

**Chapter 2** shows the main objectives of the thesis.

**Chapter 3** describes the general materials and methods used to fulfil the objectives of the thesis.

**Chapter 4** comprises the results obtained during the thesis work. Three different scientific articles have been published in international indexed journals corresponding to the first quartile, conforming the results section. Each contribution presents its individual introduction section, materials and methods, results, conclusions and references. The first contribution (*The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant, Science of the Total Environment, 2018*) shows the influence of the composting time over the biological stability reached by the sewage sludge at the end of the process and the related gaseous emissions in a full-scale facility. The second scientific article (*A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant, Journal of Hazardous Materials, 2019*) comprises a thorough characterization of the odour and VOCs emitted during the sewage sludge composting in a full-scale plant, comparing two different composting times. The last scientific article (*Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions, Bioresource Technology, 2019*) presents a complete description of the gaseous emissions (GHG, VOCs and odours) generated during the sewage sludge biodrying process performed in a bench-scale bioreactor.

**Chapter 5** presents the general discussion of the results obtained.

**Chapter 6** shows the general conclusions obtained from the thesis work and the future work.

**Chapter 7** presents the references used along the thesis document.

# CHAPTER 1: INTRODUCTION

## 1.1. General perspective and legislation on sewage sludge management

The exponential growth suffered by the European Union (EU) and the United States of America, followed by Asian economic giants, in terms of industrial activity, population and urban planning, has led to a great increase in the total generation of wastes, both industrial or municipal ones. The generation and management of wastes have become one of the principal problems of the actual society due to the quick collapse of landfills and their related environmental impacts. In this sense, different requirements for the European Member States have been stablished by means of the Directive 1999/31/EC (European Commission, 1999a), which limits the landfills as the final disposal route for biodegradable wastes in order to enhance its valorisation, and subsequently by means of the Directive 2008/98/EC (European Commission, 2008), which aims to treat wastes in a proper way, protecting the environment and the human health. This management procedure is based on a waste hierarchy, with the aim of giving priority to environmental friendly actions that help to decrease the final disposal of the wastes by:

1. Preventing the generation of wastes

2. Re-using

3. Recycling

4. Other recovery such as energy recovery

5. Final disposal

One of the main and common objectives of these two Directives (1999/31/EC & 2008/98/EC) is to shift the paradigm of the utility of wastes as resources. Therefore, in the last years, the priority for waste management routes that bet for recycling and for matter and/or energy valorisation processes has increased. In this sense, biological treatment processes such as composting or anaerobic digestion have been applied to enhance the organic matter and nutrients recirculation, avoiding the final disposal of organic wastes into landfills.

From a general point of view, it is estimated that over 250 million Mg of municipal wastes are generated by the European countries, which constitute only a 10% of the

total waste generation of the region (Eurostat, 2016). Focusing on sewage sludge (SS) generation and according to the published data by Eurostat, the EU estimates that more than 7.5 million Mg of sewage sludge, in dry basis, are produced yearly during the treatment of wastewater (Eurostat, 2015; MITECO, 2019), being Germany, the United Kingdom, Spain, Italy and France the countries with higher sewage sludge production (Figure 1.1).
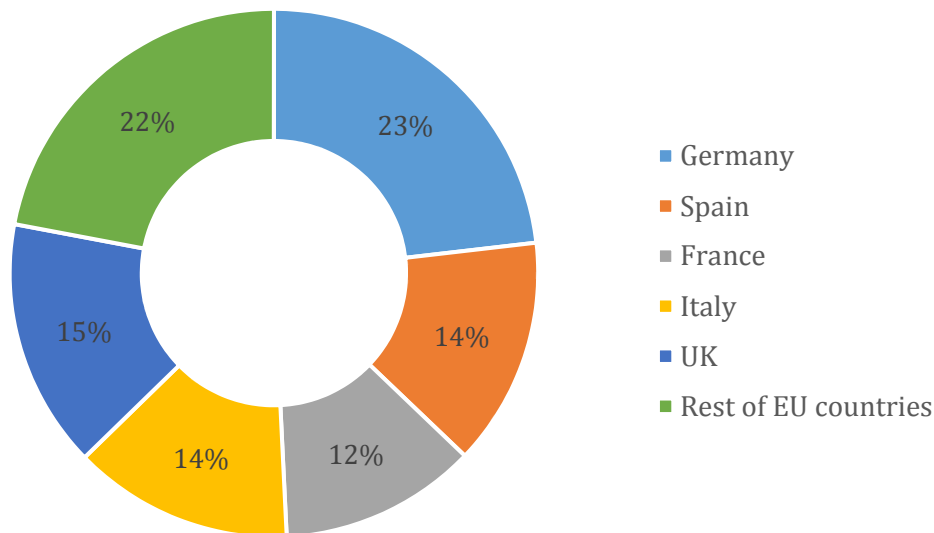


**Figure 1.1.** Distribution of the sewage sludge production in the European Union countries during 2015 (Eurostat, 2015).

Sewage sludge is an organic waste produced during the wastewater depuration cycle, and it is characterized by being a high moisture content waste (90-95% water) with a highly variable composition that depends on the pollutant load of the initial wastewater and the characteristics of the treatments applied to this wastewater. In fact, sewage sludge is composed by a wide diversity of suspended and dissolved matter, some of them with an agronomic interest (organic matter, nitrogen, phosphorous or potassium), and some others with a potential pollutant character such as heavy metals (cadmium, chrome or copper), pathogens or other emergent contaminants (Colón et al., 2014). Its management is regulated by the Directive 86/278/EEC (European Commission, 1986), which promotes the use of sewage sludge for agricultural purposes in a way to prevent harmful effects on soil, vegetation, animals and humans. In this Directive, it is highlighted the special need

of meeting different control parameters such as the amount of heavy metals and/or other contaminants present in sewage sludge or its biological stabilization, prior to its use as fertilizer or soil amendment. This fact, as well as the application of more restrictive standards by the European Member States makes necessary the research for new treatment technologies (or the improvement of the existing ones) aiming at reducing the volume of sludge, reaching its biological stabilization and improving its manageability without compromising the health of the population or the contamination of the natural resources. Figure 1.2 presents different disposal alternatives used by the European countries during 2015 (last data available, Eurostat, 2015), which shows that more than the 60% of the sewage sludge produced was thermally treated and used for agricultural purpose.
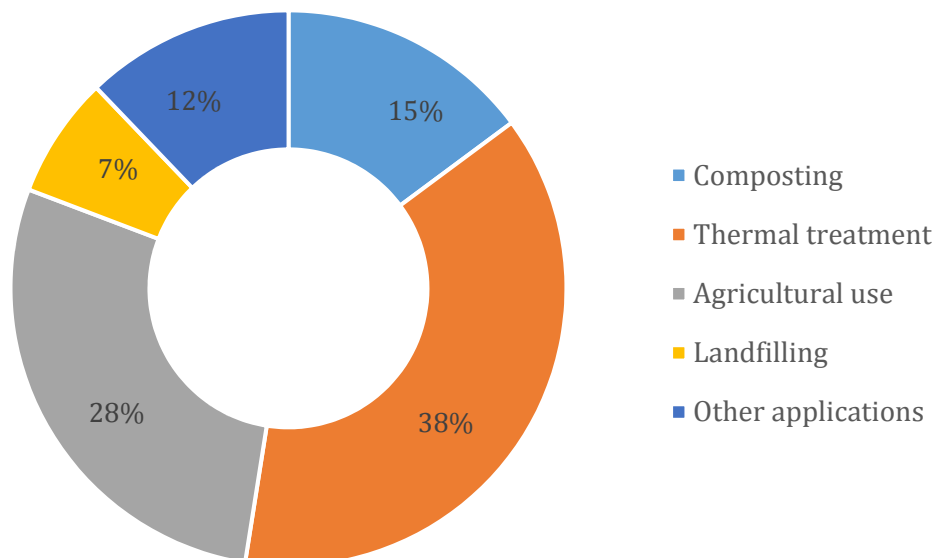
**Figure 1.2.** Distribution of the sewage sludge disposal alternatives in the European Union countries during 2015 (Eurostat, 2015).

In this sense, different stablished biological technologies such as anaerobic digestion or composting, or emerging ones such as biodrying, can face the challenge of reducing the volume of sewage sludge and its biological activity, aiming at valorising it and giving it a suitable reuse as soil amendment, fertilizer or biomass fuel.

## 1.2. Sewage sludge composting process

Haug (1993) defined the composting process as a biological decomposition and stabilization process of organic matter under specific conditions that allow the development of thermophilic temperatures due to the biological heat generated, from which a stable product is obtained, free of pathogens and seeds and that can be stored and applied to soil. Figure 1.3 represents the general equation of the composting process proposed by Tchobanoglous (1994).

$$\left.\begin{array}{l} \text{Proteins} \\ \text{Aminoacids} \\ \text{Lipids} \\ \text{Carbohydrates} \\ \text{Cellulose} \\ \text{Lignine} \\ \text{Ashes} \end{array}\right\} + O_2 + \text{Nutrients} + \text{Microorganisms} \longrightarrow \begin{array}{l} \text{Compost} + \text{New cells} + CO_2 \\ + NO_3^- + SO_4^{2-} + \text{Heat} \end{array}$$
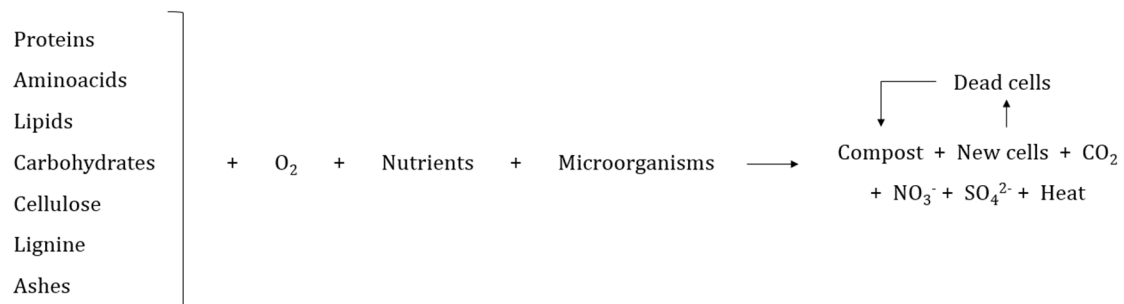
**Figure 1.3.** General equation of the composting process (Tchobanoglous, 1994).

Historically, the composting process has been used to treat organic wastes with different objectives (Adani et al., 2004):

- The production of high quality compost, which can help the proper maintenance and enhance the quality of soil, the agricultural crops and the environmental conservation.
- The production of low quality compost for the use in degraded soil and/or in soils in restoration stage.
- The reduction of the biodegradability, the moisture, the weight, the volume and the generation of odours of the materials prior to its disposal in landfills.
- The increase of the material's calorific power by decreasing its water and biodegradable matter content.

Generally, the sewage sludge full-scale composting process is divided into 3 main areas or phases:

- Decomposition phase
- Maturation phase
- Screening and refining phase

However, it should be accounted that prior to initiate the decomposition phase and due to the physical characteristics of the sewage sludge (high water content, low porosity), it is necessary to mix the sewage sludge with a bulking agent, which can be vegetal fraction, wood chips, etc. This is a key step, because the optimization of important parameters such as the moisture content, porosity or C/N ratio can affect largely on the proper development of the composting process.

During the decomposition phase, the complex organic compounds are biodegraded into simple organic molecules and inorganic molecules by the action of the microorganisms. Because of the high microbial activity, oxygen consumption increases as well as the matrix temperature. Temperature can easily rise over the 41 ºC during the first steps of the decomposition phase, which is known as thermophilic phase. At this point, a transition between mesophilic to thermophilic microbial communities happens, what allows the continuity of the organic matter biodegradation at high temperatures and contributes to increase the rate of biodegradation. Thanks to the high temperatures reached at the solid matrix, the sanitization of the mixture occurs (destruction of pathogens and seeds). This sanitization is considered to be achieved when temperatures over 55 ºC are maintained during 4 hours or more in a period of 5 days at a temperature of at least 40 ºC (United States Environmental Protection Agency (USEPA), 1999). However, there are other norms which also specifies a number of minimum turnings of the material to ensure temperature homogenization and better sanitization (CIC, 2019; Inserra et al., 2006).

Once the easily biodegradable carbon sources have been consumed, the activity of the thermophilic microorganisms falls and temperature decreases. At that point, there is a progressive shift from thermophilic to mesophilic community, and the composting process enters into the maturation phase. During the maturation phase, the most difficult biodegradable compounds are degraded and most important, the nitrogen coming from the dead biomass is mineralized and fixed into bigger and more stable molecules, creating a nitrogen reservoir (Haug, 1993; Tchobanoglous, 1994). At the end of this phase, the material is considered to be stabilized, obtaining a granular compost.

The main objective of the screening and refining phase is to obtain a quality compost by means of the separation of the inert material that can be present in the mixture as well as the bulking agent that has not been degraded, which can be recirculated again into the process. Then, the obtained compost must comply minimum quality requirements, which are set by the RD 506/2013 in Spain (Table 1.1, Gobierno de España, 2013), to enter the market.

**Table 1.1.** Limit values for quality and classification of compost (RD 506/2013).

| Parameter | Value | | |
|---|---|---|---|
| Total organic matter (% db.*) | > 35 | | |
| Moisture content (%) | < 40 | | |
| C/N | < 20 | | |
| **Grading** | | | |
| Gravel and stones > 5 mm (%) | < 2 | | |
| Inert material > 2 mm (%) | < 1.5 | | |
| Particulate matter < 25 mm (%) | 90 | | |
| **Microorganisms** | | | |
| *Salmonella* | Not present in 25 g of product | | |
| *Escherichia coli* | < 1000 MPN** per g of product | | |
| **Heavy metals** **(solids: mg·kg$^{-1}$ db.*; liquid: mg·kg$^{-1}$)** | | | |
| | Class A | Class B | Class C |
| Cadmium | 0.7 | 2 | 3 |
| Copper | 70 | 300 | 400 |
| Nickel | 25 | 90 | 100 |
| Lead | 45 | 150 | 200 |
| Zinc | 200 | 500 | 1000 |
| Mercury | 0.4 | 1.5 | 2.5 |
| Chrome (total) | 70 | 250 | 200 |
| Chrome (IV) | 0 | 0 | 0 |

*db.: dry basis

**MPN: Most probable number

Since microorganisms are the principal responsible for the biological degradation of organic matter, all the factors that could limit their development would limit the composting process too. The most critical parameters to perform a proper composting process are temperature, moisture content, porosity, C/N ratio and aeration.

The composting process temperature is a consequence of the increase of microbial activity. The typical temperature rise of the first phase of the composting indicates the presence of easily biodegradable matter. The chemical bounds of these organic molecules contain high-energy content that is released once these molecules are biodegraded into more simple molecules, increasing the temperature of the mixture. Reaching thermophilic conditions is important because it permits the quick biodegradation of the organic matter present and its sanitization, but it cannot last too long due to the possibility of inhibiting the microbial activity (Richard, 1992). Water is necessary for microorganisms to develop their activity, to absorb and metabolize nutrients and to grow because they can just assimilate dissolved organics. In case of low moisture content, the biological activity ceases. However, excess of moisture can limit the oxygen transfer to the microorganisms, which will stop the process too. Therefore, to keep biological activity working, moisture content has to be maintained over 35%, in optimum values between 40-60% (Haug, 1993). Another factor that plays an important role in the composting process is the porosity of the material. Sewage sludge does not present an appropriate porosity so it is improved by the mixing with a bulking agent. The adjustment of the mixture porosity helps ensuring the air movement through the composting material, maintaining an optimum oxygen level, removing the excess of $CO_2$ and water vapour and limiting excessive heat accumulation (Sánchez et al., 2015). Aeration of the composting material is also crucial because, as it was reported by Haug (1993), its application provides the oxygen necessary for the aerobic microorganisms responsible for the biodegradation of the organic wastes, apart from regulating the excess of moisture content and limiting heat accumulation. Generally, the oxygen concentration is set between 10-15% in air, high enough to ensure the proper diffusion of oxygen to the microorganisms and avoid the appearance of anaerobic conditions but low enough to avoid the cooling or drying of the material (Jiang et al., 2011). Finally, nutrient balance (which is normally defined by the C/N ratio), is

important to guarantee proper biodegradation, to improve quality of end products and to minimize ammonia emissions (de Guardia et al., 2010; Gao et al., 2010). Theoretically, the optimum C/N ratio has to be maintained between 20 and 30 (Sánchez et al., 2015).

## 1.2.1. Composting technologies for sewage sludge management

For the treatment of sewage sludge at full-scale, different composting technologies and strategies have been developed. Industrial composting technologies can be grouped into two categories: simple windrow systems and "in-vessel" processes. The most important ones are briefly described below, but a full description of these technologies can be found in Haug (1993).

- Static pile technology (aerated and non-aerated)

Static piles can be divided into two main groups: aerated and non-aerated. The main characteristic of the aerated static piles is the presence of a forced-aeration system, which if used in an intermittent way, ensuring aerobic conditions (5 – 15% of oxygen in air). However, due to fact that no turning of the material is done, the bulking agent plays an important role in ensuring enough structural strength and porosity to prevent compaction, preferential air-pathways and anaerobic conditions along the pile profile. The major problem of this technology is the poor homogenization of the mixture between the inner and outer part of the piles, what does not ensure the achievement of the high temperatures needed for a proper sanitization. It is considered an expensive technology due to the extensive use of aeration and it is used in both the decomposition and the maturation phases. On the other hand, non-aerated static pile processes are slow composting processes that are useful when the particle size is uniform. It is considered a very cheap technology, which is normally used during the maturation phase and can last between 1 and 3 months.

- Turned windrow technology

Material is placed in rows that are periodically turned. Oxygen is mainly supplied by natural convection produced by the "chimney effect" of hot gases in the windrow, although turning also helps to oxygenate the mixture. Turning of the material, which ideally should be performed every three to four days, also helps to increase

homogeneity of the mixture, to prevent compaction and to ensure that all the material is exposed to high temperatures to achieve sanitization and high biodegradation rates. This technology is considered a cheap composting alternative as no air supply is needed. It is normally used during the first decomposition phase, although it can be used during the maturation phase by decreasing the turning frequency.

- Composting tunnels

Composting in tunnels is the most widespread "in-vessel" composting technology. The composting process is performed in a closed space, under highly controlled conditions and usually in batch mode. Aeration is provided through a perforated floor and key parameters such as temperature, moisture or air supplied are monitored and adjusted as needed. In fact, some composting tunnels recirculate the processed air in order to reduce the loss of moisture and heat. Although being a costly technology, it is considered a highly efficient system normally used during the decomposition phase. Depending on the characteristics of the material, the process can last between 1 to 4 weeks.

- Composting channels

This composting technology consists of reactors operated continuously, where the material is loaded through one end and moved longitudinally to the end of the reactor. A turning machine travels over the material, doing the longitudinally movement as well as the mixing of it. Moreover, a forced-aeration system is normally used to provide air through the floor. As other "in-vessel" technologies, composting channels are an expensive alternative, but the normal retention times are reduced in comparison with the simple industrial systems. In this case, this technology can be used during both the degradation and the maturation phases.

## 1.3. Sewage sludge biodrying process

The biodrying of organic wastes has been a research topic mainly focused on the pre-treatment of municipal solid wastes (MSW). Due to the high water content of this kind of waste (up to 75%, He et al., 2005), a drying process is regarded as a good option to facilitate the mechanical separation of mixed materials with organic wastes, which can be unfavourable if moisture content of the mixture is high

(Dongqing et al., 2008). In addition, it is helpful to dry and partially stabilize MSW prior to landfill or combustion (Adani et al., 2002; Yuan et al., 2017). Moreover, the interest in reusing MSW and other organic wastes as a biomass fuel for energy production spread the interest in research for the application of this novel technology to other organic wastes such as sewage sludge.

Due to the high water content present in sewage sludge, a pre-treatment step to reduce its moisture content is normally necessary if a thermal processing of the sewage sludge is desired for energy recovery. In this sense, the biodrying process has caught the attention of the researchers during the last years as a novel strategy for sewage sludge biological treatment (Frei et al., 2004; Villegas and Huiliñir, 2014; Zhao et al., 2010). The main objective of the sewage sludge biodrying process, which is based on the principles of composting, is to remove water from biowastes with high moisture content and to partially reduce the biodegradability of the solid matrix in order to obtain a product with a considerable Lower Calorific Value (LCV) and low moisture content that can be used as a biomass fuel. To achieve that goal, both the metabolic heat generated during the biodegradation of organic matter as well as high-rate forced aeration are required (Frei et al., 2004).

The main mechanisms by which biodrying and moisture transport within the solid mixture are described are evaporation, convection and diffusion. Convection is related to temperature, humidity and air flowrate through the porous material, whereas diffusion from within particles is controlled by temperature and moisture concentration gradients. Air carries away moisture by convection from the surfaces of the solid matrix that is in contact with. After surface moisture is removed, moisture must transfer from individual particles to the surface for evaporation. Aerobic biological activity here is essential for the success of the biodrying process. The optimal conditions for a proper biological activity (temperature range, aeration and oxygen levels) have been widely described for composting processes (Haug, 1993; Sánchez et al., 2015) and they are applicable to biodrying. Thermophilic conditions will favour moisture removal by enhancing evaporation, whereas high-rate aeration will help to achieve a proper diffusion throughout the solid mixture and boost the moisture removal by convection, as well as supplying the oxygen needed for biological activity.

It is important to notice some differences between composting and biodrying. First, composting seeks to biodegrade the easily accessible carbon sources, resulting in a stabilized soil amendment, whereas biodrying goal is energy recovery from biowaste by a drying process. During composting, temperatures are high and oxygen is sufficiently supplied for microorganisms to respire. In contrast, during biodrying large excess of air is supplied to quickly remove moisture as well as to meet microorganisms respiration needs. This high aeration rate causes the cooling of the solid material, so lower temperatures are reached in relation to composting. Moreover, the higher supply of air during biodrying implies an extra energetic cost in comparison with composting, and the global efficiency of the process in terms of energy balance should be assessed, amongst other factors, for each individual case to validate if a biodrying process is economically feasible or not. Finally, during composting the carbon consumption will lead to a product with less solids, reducing its calorific value. In contrast, during biodrying low carbon consumption rates are desired to maintain the calorific content for dried sewage sludge combustion.

During the past years, some researchers have focused their studies on different operational parameters to improve the SS biodrying process, from lab-scale to full-scale systems (Huiliñir and Villegas, 2015; Winkler et al., 2013). Aeration rates, initial moisture and mixing ratios have been recognized as the key parameters to undergone a proper SS biodrying process. The optimization of aeration rate as well as initial moisture content have been studied by different authors (Cai et al., 2013; Huiliñir and Villegas, 2015; Zhao et al., 2010), concluding that higher aeration rates and lower initial moisture content enhance water removal from solid matrix. However, during the first steps of the process, aeration needs to be low to enable sufficient self-heating of the material due to microorganisms' activity. Moreover, Zhang et al. (2018) reported good performances during the co-biodrying of SS with organic fraction of municipal solid waste (OFMSW), concluding that the best biodrying efficiency was obtained by mixing the same percentage of SS and OFMSW (in w.b.).

## 1.4. Gaseous emissions from sewage sludge biological treatments

During the biological treatment of sewage sludge, unavoidable environmental and social concerns can arise. Especially, gaseous emissions are responsible for

odour nuisance and atmospheric pollution, where a large list of different compounds can be found, being ammonia, hydrogen sulphide, nitrous oxide, methane and many kinds of volatile organic compounds (VOCs) the most remarkable (Maulini-Duran et al., 2013). All these gaseous compounds are related to the biological decomposition of organic matter, nitrogen and sulphur-based compounds.

With the aim of improving environmental impact assessment and being able to compare the gaseous emissions of specific compounds between different treatment strategies or technologies, the USEPA defined the term emission factor. This tool relates the quantity of a specific pollutant emitted to atmosphere during a process with a representative activity or index related to the release of the pollutant, such as the mass of waste to be treated, the emitting surface or time units amongst others (United States Environmental Protection Agency (USEPA), 1995a). Later on, this tool has been referenced and used during odour impact assessment in the same way as emission factors for different treatment processes or facilities, namely odour emission factor (OEF) (Capelli et al., 2014; Sironi et al., 2006).

## 1.4.1. Odorous gaseous emissions

The term "odour" is defined as the organoleptic property perceived by the olfactory organ when an individual breeds certain volatile substances (European Committee for Standardization, 2006). From a public administration point of view, odour is the sensation generated by substances or industrial, commercial and/or service activities that produce a nuisance to the receptor, even though it does not harm human health. Odour emissions have been traditionally a second interest in environmental concern since they represent a lower risk for human health and natural ecosystems, in contrast with solid and/or liquid emissions. However, the emission of unpleasant odours produced at some facilities such as composting or wastewater treatment plants has become an important public concern in the last years due to their proximity to residential areas and the fact that, although not being a direct cause of disease, long-term exposure to these emissions can negatively affect on human well-being, causing nausea, headaches or respiratory problems among others. When these unpleasant odours are detected in residential areas, they

lead to a negative perception of quality of life and can even create a significant economic cost for housing surrounding odour sources (Lebrero et al., 2011).

The odorous emissions generated during the biological treatment of sewage sludge are composed of a mixture of different compounds such as hydrogen sulphide, ammonia and a wide range of VOCs (e.g. organosulphur compounds, nitrogenated compounds, ketones and terpenes among others) (Lebrero et al., 2013; Maulini-Duran et al., 2013). Even though these odorant compounds are normally emitted in low concentration, the problematic arises due to their low odour detection threshold (ODT), which is defined as the minimum concentration of a specific compound perceived by the human nose. Table 1.2 reports typical odorant chemical compounds found in the gaseous emissions generated during SS biological treatment processes such as composting or biodrying, with its related odour descriptor and ODT.

**Table 1.2.** Odour character and odour detection threshold of selected individual odorant compounds typically found in SS biological treatment gaseous emissions.

| Chemical compound | Odour character | Odour detection threshold (ODT, $ppb_v$) |
|---|---|---|
| *Organosulphur compounds* | | |
| Hydrogen sulphide | Rotten eggs | 0.41[a] |
| Methanethiol | Rotten cabbage | 0.07[a] |
| Dimethyl sulphide | Rotten cabbage | 3.0[a] |
| Dimethyl disulphide | Garlic and decaying fish | 2.2[a] |
| Dimethyl trisulphide | Rotten cabbage | 0.005 – 0.01[b] |
| *Nitrogen derived compounds* | | |
| Ammonia | Pungent, irritating | 1500[a] |
| Indole | Faecal, nauseating | 0.30[a] |
| Skatole | Faecal, nauseating | 0.0056[a] |
| Pyridine | Fishy | 63[a] |
| Trimethylamine | Fishy, amoniacal | 0.032[a] |

(Continuation)

| Carboxylic acids | | |
|---|---|---|
| Acetic acid | Vinegar, pungent | 6.0[a] |
| Butanoic acid | Rancid | 0.19[a] |
| Propanoic acid | Rancid, sweat | 5.7[a] |
| **Alcohols** | | |
| 2-butanol | Fruity | 220 |
| 3-pentanol | Herbal | 1.7 – 290[a] |
| **Aldehydes** | | |
| Isovaleraldehyde | Pungent | 0.10[a] |
| Benzaldehyde | Almond | 350[b] |
| Acetaldehyde | Pungent, fruity | 0.0015[a] |
| **Aromatic hydrocarbons** | | |
| Benzene | Sweet, petrol | 2700[a] |
| Ethylbenzene | Gasoline | 170[a] |
| Toluene | Pungent, solvent | 330[a] |
| Xylene (m-, p-) | Sweet | 41 – 58[a] |
| **Ketones** | | |
| 2-butanone | Sharp, sweet | 440[a] |
| 2-nonanone | Fruity | 5 – 200[b] |
| **Terpenes** | | |
| α-pinene | Woody, herbal | 18[a] |
| β-pinene | Woody, pine | 33[a] |
| Limonene | Citric fruit | 38[a] |
| γ-terpinene | Lemon | 330[b] |
| Eucalyptol | Pungent, camphor | 12[b] |

[a] Nagata (2003)

[b] Leffingwell (2018)

Due to the subjectivity of human odour perception and the chemical complexity of odorous emissions generated during SS biological treatments, odour characterization and odour management become a complex task. For this reason, during the last years, complementary odour characterization by means of both

sensorial and chemical techniques has been recommended to improve the assessment of odour impact from different SS treatment technologies and/or facilities (Capelli et al., 2013a).

Sensorial methodologies can characterize odours by employing human noses as odour detectors. Then, four different attributes are used to describe odours: odour concentration, odour intensity, odour character and hedonic tone (Odotech, 2019).

- **Odour concentration** describes the pervasiveness of an odour. It is based on the ODT, and it corresponds to the lowest concentration at which a 50% of the human population would detect an odour. This concentration is defined as 1 odour unit per cubic meter (1 ou·m$^{-3}$) for that specific odour, which is equivalent to 123 µg of N-butanol in 1 m$^3$ of clean air (40 ppb$_v$) (European Committee for Standardization, 2006).

- **Odour intensity** is the perceived strength of an odour sensation above its ODT. It is used to locate the source of odours and it is mostly related to odour nuisance. It is expressed using an odour intensity scale, which is a verbal description of the odour sensation which progress from *"Not perceptible"*, *"Very Weak"*, *"Distinct"*, *"Strong"*, *"Very Strong"*, *"Extremely Strong".* These categories are benchmarked using n-butanol as a reference odorant.

- **Odour character** is what the odour smells like. It is normally described by using descriptive adjectives such as herbal, pungent, irritating, etc. An odour character may change with dilution.

- **Hedonic tone** is the degree in which an odour is perceived as pleasant or unpleasant. Such perceptions widely differ from individuals and are strongly influenced by previous experiences and emotions at the time hedonic tone is evaluated. A nine levels scale is used to describe the hedonic tone of an odour from *"Very Pleasant"* to *"Offensive".*

From the four described attributes, odour concentration is the most interesting one from a technical point of view, because its application in atmospheric dispersion allows estimating odour immission and the final effect of a considered emission source. To determine odour concentration, the dynamic olfactometry methodology is used, which has been developed in the European Standard EN 13725 (European Committee for Standardization, 2006). Dynamic olfactometry is defined as the

technique that uses a dynamic olfactometer to mix a flow of odorous sample with a flow of clean, non-odorous air into well-known dilution factors as shown in Figure 1.4.
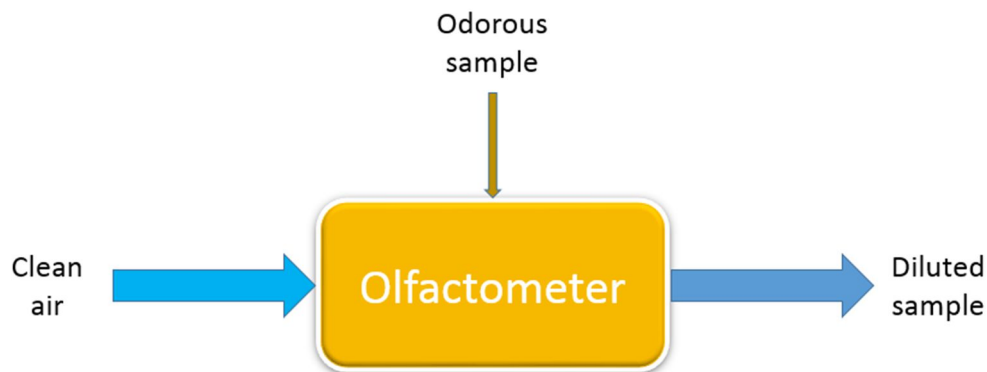


**Figure 1.4.** General functioning of a dynamic olfactometer.

The outgoing mixed flow is presented to a set of panellists, who are the people previously calibrated responsible of smelling the diluted sample to determine its odour concentration.

On the other hand, chemical analysis techniques such as gas chromatography coupled to mass spectrometry (GC/MS), on-line methods based on MS, or the use of electrochemical or photoionization sensors/detectors have been historically and extensively used to characterize and quantify the individual compounds present in an odorous sample. However, these techniques can turn out to be highly complex and not always effective when characterizing complex odour emissions such as the ones originated during SS biodegradation processes (Capelli et al., 2013a). As it has been reported, a complex odour mixture can present synergistic (enhancing) and/or antagonistic (masking) effects between the individual compounds that conform it (Hanajima et al., 2010; Ruth, 1986), what makes difficult to relate the sensation provoked by this odour mixture to a human nose with its chemical composition. Nevertheless, knowing the composition, the abundance and the quantity of each odorant in a complex odorant mixture can help to understand better the odour emission, the major odour contributors, and the effect that an odour emission can cause to the surrounding area, aiming at developing mitigation strategies in order to reduce its environmental and social impact.

Differently to MSW treatment facilities or wastewater treatment plants (WWTP) (Capelli et al., 2009; Sironi et al., 2006; Zarra et al., 2016), few studies reporting odorous emissions from sewage sludge composting plants can be found (Rincón et al., 2019). Table 1.3 shows the odour emission factors (OEF) reported by different authors for different SS and MSW biological treatment technologies.

**Table 1.3.** Odour emission factors (OEF) reported for different SS and MSW biological treatment technologies.

| Reference | Organic waste | Treatment technology | OEF ([1] ou·Mg$^{-1}$ DM-SS[*] [2] ou·Mg$^{-1}$ MSW) |
|---|---|---|---|
| Rincón et al. (2019) | SS | 300-L aerated bench-scale composting reactor | 9.35E+08 [1] |
| Sironi et al. (2006) | MSW | Full-scale treatment facilities | 1.01E+08 [2] |
| Zarra et al. (2016) | MSW | Full-scale treatment facility | 4.15E+06 [2] |
| González et al. (2019) | SS | Full-scale composting plant | 9.45E+07 [1] |
| González et al. (2019b) | SS | 100-L bench-scale biodrying reactor | 3.10E+07 [1] |

[*]DM-SS: dry matter from sewage sludge

### *1.4.1.1. Ammonia*

Ammonia is the main nitrogenous compound emitted during the aerobic and anaerobic sewage sludge biodegradation processes, being the most nitrogenous gas compound studied. The *National Institute for Occupational Safety and Health* (NIOSH, 1989) stablishes an $NH_3$ exposition limit of 25 ppm$_v$ during a maximum of 8 hours-TWA (Time Weighted Averaged), being throat, eyes and skin irritation or even severe pulmonary damage the main health risks faced if increased exposure. As mentioned before, $NH_3$ is one of the main contributors to odour generated during the SS biological treatment, even though its ODT is quite high in comparison with

other typical odour contributors such as hydrogen sulphide (1500 ppb$_v$ and 0.41 ppb$_v$, respectively) (Nagata, 2003). Moreover, $NH_3$ plays an important role in atmospheric processes. It is the main alkaline component in atmosphere and highly reactive, so it can easily form aerosols and can be deposited over any surface (Seinfeld and Pandis, 1997). Therefore, $NH_3$ also contributes to the acidification and eutrophication of natural ecosystems, compromising its resources and diversity (Sutton et al., 2007).

During aerobic sewage sludge treatment, proteins and amino acids are biodegraded, microorganisms assimilate part of the available nitrogen and the rest is maintained basically in $NH_3$ form, which is found in equilibrium with dissolved $NH_4^+$. During the first steps of the SS biodegradation process, the presence of fatty acids can provoke the acidification of the substrate and the $NH_3/NH_4^+$ equilibrium is displaced to $NH_4^+$, what limits the emission of $NH_3$. However, when the biodegradation process moves forward to a thermophilic phase and the fatty acids are degraded, mixture's pH increases, displacing $NH_3/NH_4^+$ equilibrium to $NH_3$, increasing its volatilization and emission (He et al., 2017).

As it has been reported by different authors, temperature is a key parameter affecting $NH_3$ emissions during aerobic biodegradation of organic wastes such as SS (Hellebrand and Kalk, 2001; Maulini-Duran et al., 2013; Pagans et al., 2006a). During aerobic treatments, the higher $NH_3$ emissions coincide with thermophilic temperatures of the material. Pagans et al. (2006) found an exponential relationship between solid matrix temperature and $NH_3$ emissions during the thermophilic phase when composting different organic wastes, while during the mesophilic phase a linear relationship was observed. Lately, these temperature-$NH_3$ emission relationships were confirmed by Maulini-Duran et al. (2013) when composting different types of sludge. Moreover, as determined by Grunditz and Dalhammar (2001), the inhibition of the nitrifying microorganisms when temperatures are above 45 ºC favours the volatilization of $NH_3$, increasing its emission when solid matrix temperature is high.

Initial composition of the organic waste to be treated is another determining parameter for $NH_3$ emissions. For example, low initial C/N ratios (high nitrogen content) can promote considerable $NH_3$ formation and emission. On the other hand,

if a high content of easily biodegradable carbon molecules is present in the solid matrix at the beginning of the process, the ammonia-nitrogen will be retained easily thanks to proteins' microbial synthesis and lower $NH_3$ emissions during the active composting and maturation phases will be generated. However, it has to be taken into account that the $NH_3$ emissions are not directly dependant on the total carbon and nitrogen content, but on their bioavailability degree for microorganisms (Komilis and Ham, 2006). In this sense, Puyuelo et al. (2011) demonstrated that the chemical analysis of total organic carbon (TOC) overestimates the real content of biologically available carbon, what leads to a wrong estimation of the initial C/N ratios. If biodegradable organic carbon (BOC) is not taken into account when formulating initial mixtures for SS biological treatments, it is possible that high levels of difficult-to-biodegrade-carbon are added to the mixture (cellulose and lignin content), which would enhance the emission of $NH_3$. For different types of organic wastes, Puyuelo et al. (2011) stablished that the C/N ratio obtained from TOC analysis is always higher than the one obtained by using BOC methods and, as an example, sewage sludge presents a TOC/N ratio of 6.3 whereas its BOC/N is between 2.4 and 2.7.

In order to minimise $NH_3$ emissions during SS composting or biodrying processes, the optimization of the previous mentioned parameters is the key. However, at full-scale, the control of some of these parameters is not trivial. For example, pH control is not an option due to its inherent difficulty and its related high investment and operational costs. Temperature control has the restriction of sanitization of the material during SS composting or the necessity of a high water removal during SS biodrying. On the other hand, the previous conditioning of the initial mixture it can be easily accomplished at full-scale, and some composting studies have reported the benefits in terms of decreased $NH_3$ emissions when increasing the initial C/N ratio (Hansen et al., 1989; Jiang et al., 2011).

Table 1.4 shows the $NH_3$ emission factors reported by different authors for different SS biological treatment technologies. It can be observed a high variability in the emission factors reported due to the differences in scale, operation and feedstocks characteristics, with values from 0.31 to 25.32 kg $NH_3 \cdot Mg^{-1}$ of DM of SS.

**Table 1.4.** $NH_3$ emission factors reported for different SS biological treatment technologies.

| Reference | SS treatment technology | $NH_3$ emission factor (kg $NH_3 \cdot Mg^{-1}$ DM-SS[*]) |
|---|---|---|
| Maulini-Duran et al. (2013) | 50-L aerated bench-scale composting reactor | 1.33 – 4.12 |
| He et al. (2017) | 150-L aerated bench-scale composting reactor | 0.31 – 1.26 |
| Rincón et al. (2019) | 300-L aerated bench-scale composting reactor | 2.16 |
| Han et al. (2019) | Full-scale composting plant | 9.70 |
| González et al. (2019a) | Full-scale composting plant | 25.32 |
| González et al. (2019c) | 100-L bench-scale biodrying reactor | 1.23 |

[*]DM-SS: dry matter from sewage sludge

### 1.4.1.2. Volatile organic compounds

The term volatile organic compound (VOC) comprises a huge group of organic compounds different to methane, of biogenic and/or anthropogenic origin, with a relatively high vapour pressure (over 0.01 kPa at 20 ºC) and a boiling point below 80ºC. Even its definition, the term VOC is also used to include semi-volatile organic compounds with a boiling point between 80 and 180 ºC (Komilis et al., 2004). Its emission in the plastic, fuel and solvents industrial sectors is regulated by the Directive 1999/13/EC (European Commission, 1999b), which limits its emission due to the use of organic solvents in determined activities or facilities.

Its environmental impact is associated to different aspects. Firstly, as aforementioned many VOC species such as organosulphur or nitrogen based

compounds present low ODT, what can lead to odour nuisance. Moreover, the toxicity of some VOCs together with long time exposure can derive in health problems such as hypersensitivity, nausea, or even renal or neurologic alterations (Domingo et al., 2015). On the other hand, VOCs are one of the key precursors of the tropospheric ozone and other photochemical oxidants formation due to its reactivity (Horowitz, 2010).

During aerobic SS biological treatment such as composting or biodrying, the higher VOC concentration observed correspond to the first steps of the process, during the thermophilic phase, being easily volatilized as the biological activity present in the solid matrix and its temperature increase. VOCs can be formed and emitted due to aerobic or anaerobic biodegradation processes that occur during SS composting or biodrying (D'Imporzano et al., 2008). For example, malodorous organosulphur compounds such as dimethyl sulphur (DMS) or dimethyl disulphur (DMDS) are produced by anaerobic biodegradation, when oxygen is limited and microorganisms use sulphur as electron acceptor (Brown et al., 2008). On the other hand, incomplete aerobic degradation can lead to the formation of some alcohols, ketones and esters, amongst others. Moreover, as aforementioned, different kinds of VOC species can be formed and emitted along the aerobic SS biological treatment, such as terpenes (α-pinene or limonene), organosulphur compounds (DMS or DMDS), ketones (2-butanone or 3-pentanone), carboxylic acids (acetic or butyric acid), aromatic hydrocarbons (xylenes, toluene or ethylbenzene), etc. Many of them are formed and emitted at the first stages of the biological treatment during the thermophilic phase, but there is not enough scientific information to stablish a clear trend of emission of the different families along the SS biological treatment process due to its strong relation with the characteristics of the feedstock. For example, ketones have been reported to present a different pattern, increasing its emission along the biological process undergone by MSW as they are emitted as by-products of microbial metabolism during the biodegradation of complex molecules (Eitzer, 1995). Finally, the influence of the kind and quantity of bulking agent used to conform the initial mixtures on the type and quantity of VOC species present in the gaseous emissions have been studied (Pagans et al., 2006b). In this sense, part of the VOCs emitted come from the vegetal fraction, wood chips or other "vegetal" bulking

agents, which generally increases the emission of terpenes ($\alpha$-pinene and limonene) as the quantity of bulking agent used is increased.

Table 1.5 shows the VOC emission factors reported by different authors for different SS biological treatment technologies. A high variability can be observed in the emission factors reported due to the differences in scale, operation and feedstocks characteristics, with values from 0.14 to 6.17 kg C-VOC$\cdot$Mg$^{-1}$ of DM of SS.

**Table 1.5.** VOCs emission factors reported for different SS biological treatment technologies.

| Reference | SS treatment technology | VOCs emission factor (kg C-VOC$\cdot$Mg$^{-1}$ DM-SS[*]) |
|---|---|---|
| Pagans et al. (2006b) | 30-L aerated lab-scale composting reactor | 3.31 |
| Maulini-Duran et al. (2013) | 50-L aerated bench-scale composting reactor | 0.66 – 1.00 |
| Rincón et al. (2019) | 300-L aerated bench-scale composting reactor | 1.21 |
| Shen et al. (2012) | Full-scale composting plant | 1.45 |
| González et al. (2019a) | Full-scale composting plant | 6.17 |
| González et al. (2019c) | 100-L bench-scale biodrying reactor | 0.14 |

[*]DM-SS: dry matter from sewage sludge

## 1.4.2. Greenhouse gases emissions

Apart from the previously cited odorant compounds, other gaseous pollutants such as greenhouse gases (GHG, mainly $CO_2$, $CH_4$ and $N_2O$) are emitted during the SS biodegradation processes. From those, even though $CO_2$ is the principal product of the biological respiration emitted during the biological degradation processes

undergone by SS, $CO_2$ is not accounted into the total amount of GHG due to its biogenic source (Colón et al., 2012). Moreover, $CH_4$ and $N_2O$ present a higher Global Warming Potential, 28 and 265 times than that of $CO_2$, respectively (IPCC, 2014).

### *1.4.2.1. Methane*

Methane is an important GHG with a 100-year Global Warming Potential (GWP) 28 times larger than $CO_2$, which is emitted in huge quantities by different activities such as waste management or agricultural operations. As observed in Figure 1.5, a decreasing trend in the $CH_4$ emissions from the 28 EU Member States has been observed in the last decades, representing just a 6% of the global $CH_4$ emitted worldwide (EDGAR, 2017; Van Dingenen et al., 2018). This decrease in the annual total emitted $CH_4$ is a consequence of the strict regulations stablished by the EU, which by the introduction of the Climate & Energy package (406/2009/EC, European Commission, (2009)) aims at reducing GHG emissions a 20% by 2020 compared to 1990. In contrast, worldwide $CH_4$ emissions increased by a 17% between 1990 – 2012, showing the strong necessity of cooperation and implication of the different countries to shift this tendency during the next years.
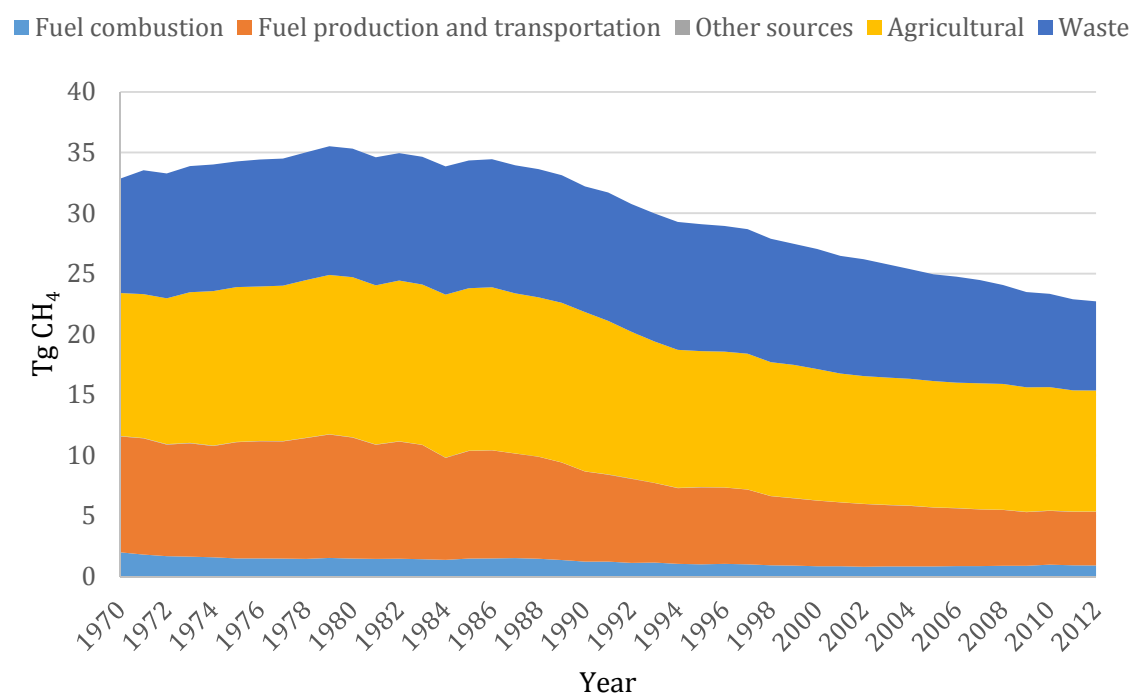


**Figure 1.5.** Evolution of the $CH_4$ emissions from different sources generated by the 28 EU Member States (EDGAR, 2017).

Biologically, methane is produced from the degradation of soluble lipids, carbohydrates, organic acids and proteins. It is formed as a by-product of methanogens respiration in severe anaerobic conditions, when carbon is the only available electron acceptor. In this sense, during SS biodegradation processes such as composting or biodrying, the fact that a heterogeneous ambient is present in the solid matrix makes clear that oxygen availability plays an important role on the generation of $CH_4$. Thus, the optimization of process parameters affecting the oxygen availability in the different points of the solid matrix is a key factor in order to minimize $CH_4$ emissions (Yuan et al., 2016).

Different authors have studied the emission of methane during composting and its relationship with operational parameters. There is a clear relationship between $CH_4$ emissions and temperature, being these higher during the thermophilic phase (Jiang et al., 2011; Manios et al., 2007). In this sense, Ahn et al. (2011) stated that higher emissions of $CH_4$ are found during the period of maximum biological activity of the composting material, corresponding to thermophilic temperatures. However, other key factors such as the material's porosity, moisture content, the aeration or oxygen level present in the solid matrix or the mixing frequency can also affect greatly to the emission of $CH_4$. Due to the presence of easily biodegradable organic matter, oxygen can be rapidly consumed, which can promote the formation of anaerobic zones in the solid matrix, enhancing $CH_4$ emissions (Hellmann, 1995). Moreover, the progressive degradation of organic matter can cause the compaction of the material and a decrease of its porosity, hampering the proper circulation of air through the material and its oxygenation, promoting the emission of $CH_4$. Even though the emission of methane cannot be avoided during a SS biodegradation process, the optimization of different key parameters affecting $CH_4$ emission should be the pathway in order to minimize them.

Table 1.6 shows the $CH_4$ emission factors reported by different authors for different SS biological treatment technologies. A high variability on the emission factors reported can be observed, with values ranging from 0.07 to 4.70 kg $CH_4 \cdot Mg^{-1}$ of DM of SS.

**Table 1.6.** $CH_4$ emission factors reported for different SS biological treatment technologies.

| Reference | SS treatment technology | $CH_4$ emission factor (kg $CH_4 \cdot Mg^{-1}$ DM-SS*) |
|---|---|---|
| Yuan et al. (2016) | 60-L aerated bench-scale composting reactor | 2.49 – 4.70 |
| Maulini-Duran et al. (2013) | 50-L aerated bench-scale composting reactor | 0.06 – 0.07 |
| Pan et al. (2018) | 150-L bench-scale composting reactor | 0.10 – 0.35 |
| Åkerman et al. (2010) | Full-scale composting plant | 0.18 – 3.40 |
| González et al. (2019c) | 100-L bench-scale biodrying reactor | 0.05 |

*DM-SS: dry matter from sewage sludge

### 1.4.2.2. Nitrous oxide

From a biological origin point of view, nitrous oxide is the GHG with the highest 100-year GWP, being 265 times that of $CO_2$. As shown in Figure 1.5, different activities or operations contribute to $N_2O$ emission, being fuel combustion and agricultural activity the most important sources of emission registered by the EU 28 Member States (EDGAR, 2017). Similarly to $CH_4$, $N_2O$ emission in the EU 28 Member States were progressively reduced during the last decades (Figure 1.5) due to the application of the Climate & Energy package (406/2009/EC, European Commission (2009).
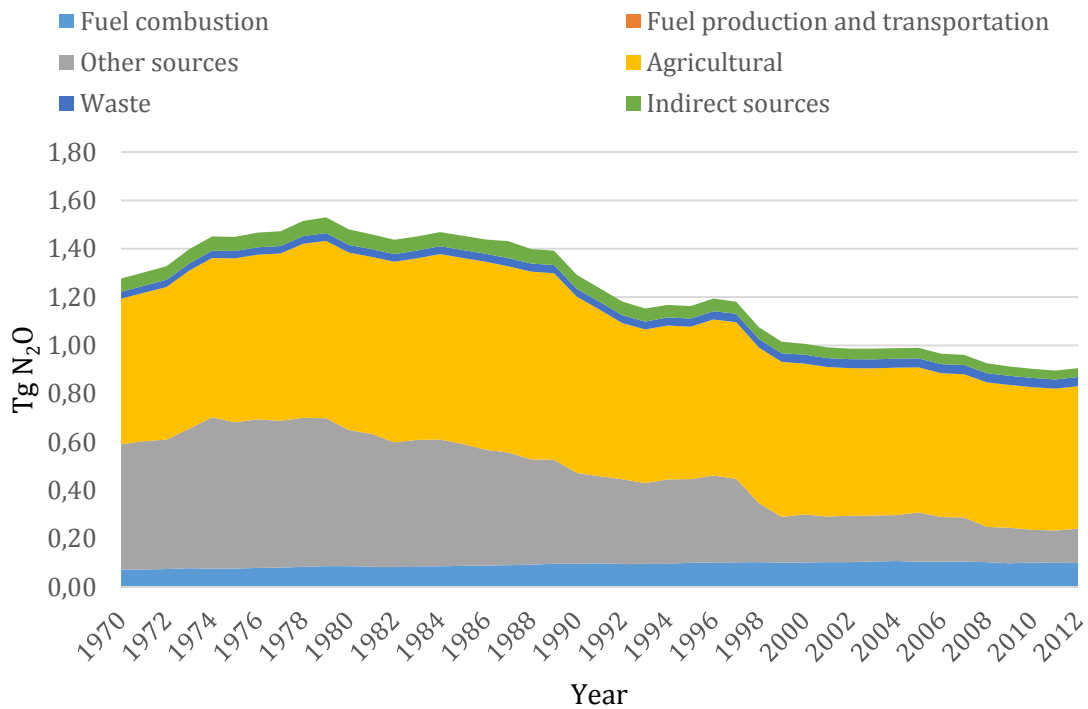
**Figure 1.5.** Evolution of the N₂O emissions from different sources generated by the 28 EU Member States (EDGAR, 2017)

N₂O can be generated by the incomplete oxidation of ammonia or by incomplete denitrification processes. On one hand, denitrifying bacteria use nitrate as final electron acceptor under anaerobic conditions, when carbon and nitrate are available but oxygen is limited, generating N₂O as product of the incomplete denitrification. On the other hand, ammonia-oxidizing bacteria are strictly aerobic bacteria. However, during nitrification processes, incomplete reaction can lead to the formation of N₂O. Therefore, two N₂O formation pathways can arise during the SS biodegradation process, one requiring oxygen (nitrification) and the other requiring anaerobic conditions (denitrification) (Beck-Friis et al., 2000). Moreover, an oxygen gradient can exist between aerobic and anaerobic spots present in the solid matrix, which would permit the formation of N₂O due to incomplete nitrification or incomplete denitrification.

The emission of N₂O related to SS biological treatment processes are highly influenced by temperature, aeration, nitrogen content and C/N ratio (Hellebrand and Kalk, 2001). If the waste is stored for some time before its processing by composting or biodrying, it is possible that N₂O is formed during this time and emitted at the very beginning of the treatment process (Yang et al., 2013). Then,

different authors reported high $N_2O$ emissions during the first steps of the composting process, when temperature is increasing. However, when temperature reaches thermophilic conditions, $N_2O$ emissions decrease to very low levels due to the inhibition of the biological activity of denitrifying bacteria by high temperatures, contrasting with what has been observed with $CH_4$ emissions (Ahn et al., 2011; Amlinger et al., 2008; Fukumoto et al., 2003). Other authors observed significant $N_2O$ emissions after the mixing of composting piles, which can be explained by the displacement of the nitrate formed in the aerobic zones to oxygen-limited zones, where they can be used in denitrification processes, producing $N_2O$ (Fukumoto et al., 2003; Sommer and Moller, 2000). Nevertheless, further evaluation of $N_2O$ emissions are warranted due to the lack and/or controversial information found in literature.

Table 1.7 shows the $N_2O$ emission factors reported by different authors for different SS biological treatment technologies. Even though treating the same kind of waste, high variability in the emission of $N_2O$ can be observed due to differences in chemical composition of the SS, difference in operation parameters, etc.

**Table 1.7.** $N_2O$ emission factors reported for different SS biological treatment technologies.

| Reference | SS composting technology | $N_2O$ emission factor (kg $N_2O \cdot Mg^{-1}$ DM-SS[*]) |
|---|---|---|
| Yuan et al. (2016) | 60-L aerated bench-scale composting reactor | 0.38 – 0.53 |
| Maulini-Duran et al. (2013) | 50-L aerated bench-scale composting reactor | 0.01 – 0.03 |
| Pan et al. (2018) | 150-L bench-scale composting reactor | 0.10 – 0.50 |
| Wang et al. (2018) | 40-L bench-scale composting reactor | 0.05 – 1.89 |
| Åkerman et al. (2010) | Full-scale composting plant | 0.48 – 0.74 |
| González et al. (2019c) | 100-L bench-scale biodrying reactor | 0.10 |

[*]DM-SS: dry matter from sewage sludge

# CHAPTER 2: OBJECTIVES

The general objective of this thesis is to extend the knowledge in relation to the gaseous and odour emissions generated during the composting of sewage sludge in full-scale facilities and its variability depending on different operational conditions to finally define operational strategies that help to mitigate these gaseous emissions. Moreover, a novel sewage sludge biological treatment such as biodrying has been studied in order to assess and present the first description on greenhouse gases, odours and VOCs derived from this technology.

To fulfil the general objectives, different specific objectives were defined:

- To set-up and develop sampling and analytical techniques for odour samples by means of a flux chamber and a portable dynamic olfactometer.
- To set-up and develop sampling and analytical procedures for VOCs characterization by means adsorption tubes and thermal desorption and gas chromatography coupled to mass spectrometry (TD-GC/MS).
- To set-up and develop sampling and analytical techniques for $N_2O$ and $CH_4$ quantification by means of gas chromatography.
- To plan and execute two different treatment strategies for the composting of sewage sludge mixed with vegetal fraction (used as bulking agent) in a full-scale facility in order to follow the performance of both processes and to compare them in terms of material's temperature profile, biological stability achieved and total VOCs (tVOCs) and $NH_3$ emitted.
- To plan and execute two different treatment strategies for the composting of sewage sludge mixed with vegetal fraction (used as bulking agent) in a full-scale facility in order to characterize and compare the odour emissions generated by both processes in terms of odour concentration, odour emission rates, odour emission factors and VOC speciation.
- To perform bench-scale biodrying experiments with conventional sewage sludge to study and characterize the related gaseous and odour emissions, monitoring tVOCs, $NH_3$, $H_2S$, $CH_4$, $N_2O$, odour concentration and the specific VOC emission.

# CHAPTER 3: MATERIALS AND METHODS

## 3.1. Full-scale sewage sludge composting plant

### 3.1.1. Overview of the full-scale composting plant

The full-scale sewage sludge composting plant studied during this thesis is located in Ariany, Mallorca (Spain). It is an opened facility where a mix of non-digested sewage sludge from primary and secondary settlers from different urban WWTPs is processed. About 8000 Mg per year of SS are treated altogether with 5000 Mg per year of vegetal fraction (VF) provided by the pruning of parks and gardens, which is used as bulking agent, to produce approximately 4000 Mg of compost per year.

The SS is normally mixed with the VF the day of reception in a 1:3 volumetric mixing ratio (1:1.2 w/w ratio), where two parts of the VF is fresh bulking agent and the other part is reused VF from previous processes. Then, the typical operation of the composting process in the plant is divided into two different stages after the mixing of the feedstocks. Firstly, an initial high-rate decomposition stage of controlled degradation of the organic matter is carried out in four dynamic windrows of 30 m long, 3 m wide and 1.5 m height, as shown in Figure 3.1, with a windrow residence time (WRT) of 4 days (4-d WRT). The dynamic windrows work in a semi continuous way, where the mixed material is loaded and unloaded daily and mixed 3 times per day with an automatic mixer. Thanks to that mixing, the material is moved forward and aerated at the same time. Afterwards, the material treated by the first stage is directed to a curing or maturation stage, which is performed in static trapezoidal piles, as shown in Figure 3.2. This second stage lasts 31 days and the entire piles are mixed once every two weeks by means of a front loader tractor. Finally, once the material has undergone both stages of the composting process, it is sieved and refined with an industrial screening machine to remove the bulking agent, which is recycled, and to obtain the final compost. This operational strategy is referred in the text as the 4-d WRT strategy.

**Figure 3.1.** Dynamic windrows and automatic mixer.



**Figure 3.2.** Curing or maturation piles and front loader tractor used for mixing.

To evaluate the effect of the composting time on the organic matter degradation, the biological stability achieved during the composting process and on the gaseous and odorous emissions generated in both scenarios, the WRT was increased from 4 to 14 days in two out of four dynamic windrows (14-d WRT) by decreasing the automatic mixing from three times per day to one time every three days. These operational changes are explained in more detail in the *"Materials and methods"* sections found in the first and second scientific articles that conform *"Chapter 4: Results"* of this thesis. This new operational strategy is referred in the text as the 14-d WRT strategy.

**3.1.2. Solid sampling**

Different solid samples were obtained during the studies performed in the full-scale sewage sludge composting plant to determine different physical-chemical parameters and biological stability along the composting process. Because of the heterogeneity of the material to be treated, the representative samples from different points and stages of the whole process were obtained by means of the quartering method (Cosenza et al., 2018). Integrated solid samples were obtained from the raw SS, the SS – VF mixture before entering the process, from the material at the end of each dynamic windrow, from the material at the middle of the curing stage, from the material at the end of the curing stage and from the final compost. The protocol followed to obtain each sample from the different sampling points is explained below.

- Raw SS and SS – VF mixture solid sampling:

A sub-sample of 3.5 to 4 kg was obtained from eight different points of the material's pile to conform an integrated sample of 28 to 32 kg. This integrated sample was well mixed and reduced into different sub-samples of 1 to 1.5 kg using the quartering method. Finally, a final integrated sample of 3 to 4 kg was obtained to be frozen and stored at -20 ºC until analysis.

- Dynamic windrow solid sampling:

A sub-sample of about 2 kg was obtained from four different points distributed along the last 2 meters of the dynamic windrow, to conform an integrated sample of about 8 kg, which was representative of the end of the first high-rate decomposition stage undergone in the dynamic windrows. This integrated sample was well mixed and reduced into different sub-samples of 1 to 1.5 kg using the quartering method. Finally, a final integrated sample of 3 to 4 kg was obtained to be frozen and stored at -20 ºC until analysis.

- Curing pile solid sampling:

The surface of the curing pile was divided into eight equal parts and a sub-sample of 3.5 to 4 kg was obtained from each point to obtain an integrated and representative sample of 28 to 32 kg, as shown in Figure 3.3.
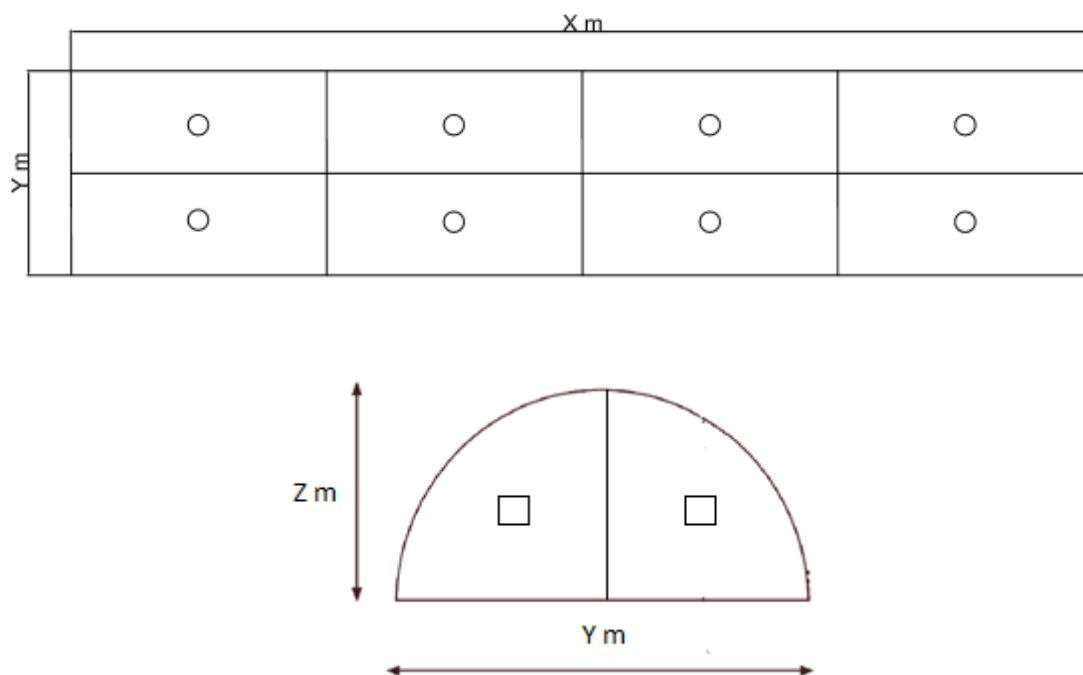
**Figure 3.3.** Top and profile scheme of a curing pile and the distribution of the sampling points.

This integrated sample was well mixed and reduced into different sub-samples of 1 to 1.5 kg using the quartering method. Finally, a final integrated sample of 3 to 4 kg was obtained to be frozen and stored at -20 ºC until analysis.

### 3.1.3. Gaseous and odour emissions sampling and determination

Two different sampling points' distributions and methodologies for gas sampling and/or analysis were used during the studies done in the full-scale sewage sludge composting plant.

Following the methodology proposed by Cadena et al. (2009), during the first study, which is described and discussed in detail in section *"4.1. The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant"*, a matrix of sampling points covering the emitting surface of each dynamic windrow and curing pile was defined, as shown in Figure 3.4. Once the dynamic windrows of both operational strategies reached stable conditions (at least one WRT was completed) and the curing piles were prepared, the exhaust gas velocity $(m·s^{-1})$ and the pollutant concentration $(mg·m^{-3})$ present in

the gas emission of each sampling point were determined three times a week during one WRT in the dynamic windrow and two times a week during the curing stage.
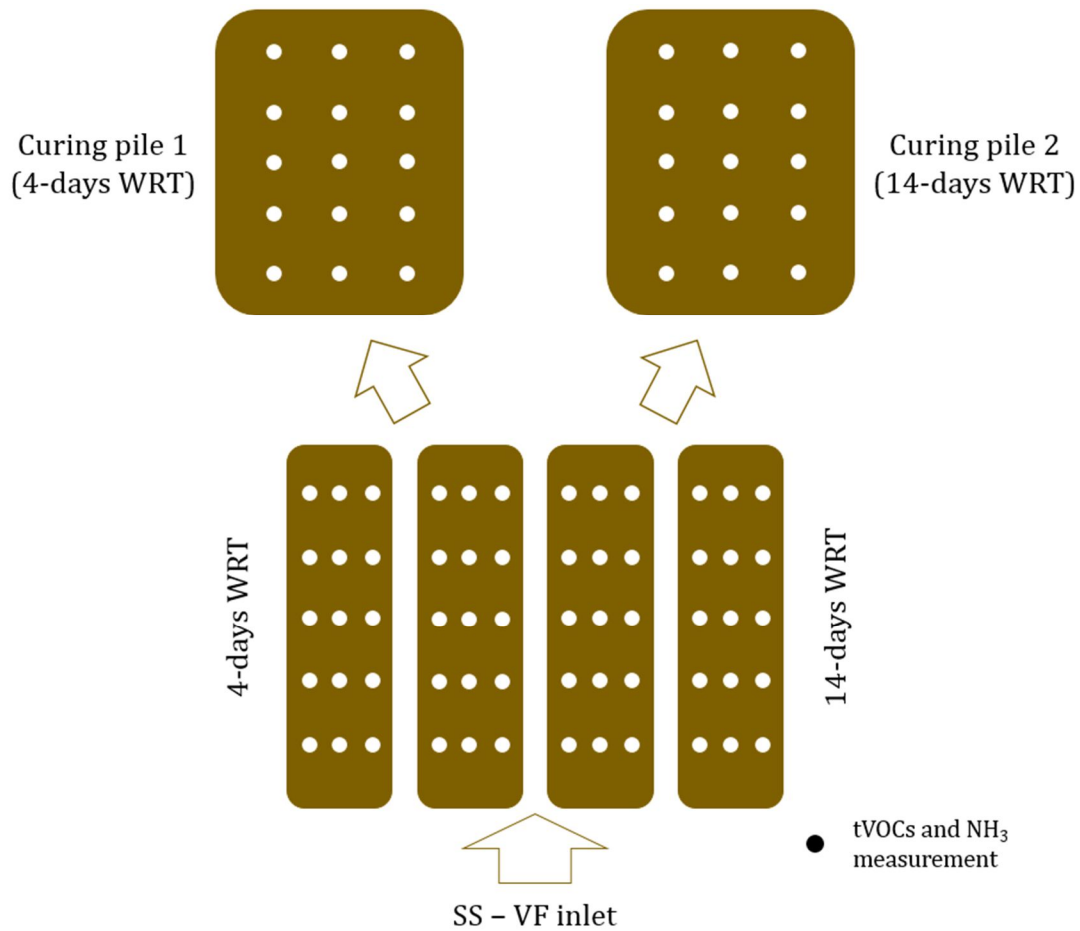


**Figure 3.4.** Scheme of the composting process for both treatment strategies (4 and 14 days WRT) and the distribution of the measurement points (dots).

With this information, three-dimension contour emission maps were prepared for each sampling day and each dynamic windrow or curing pile by means of Sigmaplot 12.0 software (Systat Software Inc., CA, USA), with surface length and width (m) as $x$ and $y$-axis, and pollutant mass flow per surface area unit (mg·s$^{-1}$·m$^{-2}$) as $z$-axis. Multiplying the pollutant mass flow per area unit by the corresponding area of the contour map (m$^2$), the pollutant mass flow related to a specific area was obtained, and the sum of the different quantities obtained for each area resulted in the total pollutant mass flow (mg·s$^{-1}$). Finally, all the pollutant mass flow obtained for each sampling day were represented versus process time so the area below the curve represented the total pollutant mass emitted throughout the process evaluated.

On the other hand, during the second study, which is described and discussed in detail in section *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"*, a different distribution of sampling points was defined (Figure 3.5) due to time and logistic constrains, even though being representative enough for odour and specific VOCs emission's determination. Once the dynamic windrows of both operational strategies reached stable conditions (at least one WRT was completed) and the curing piles were prepared, five consecutive sampling points were set along the monitored dynamic windrows corresponding to specific material's age inside the dynamic windrows. Additionally, six different sampling points were set over the emitting surface of each curing pile, which were sampled during three consecutive days coinciding with the day before, the moment of and the day after the turning of the curing pile's material.
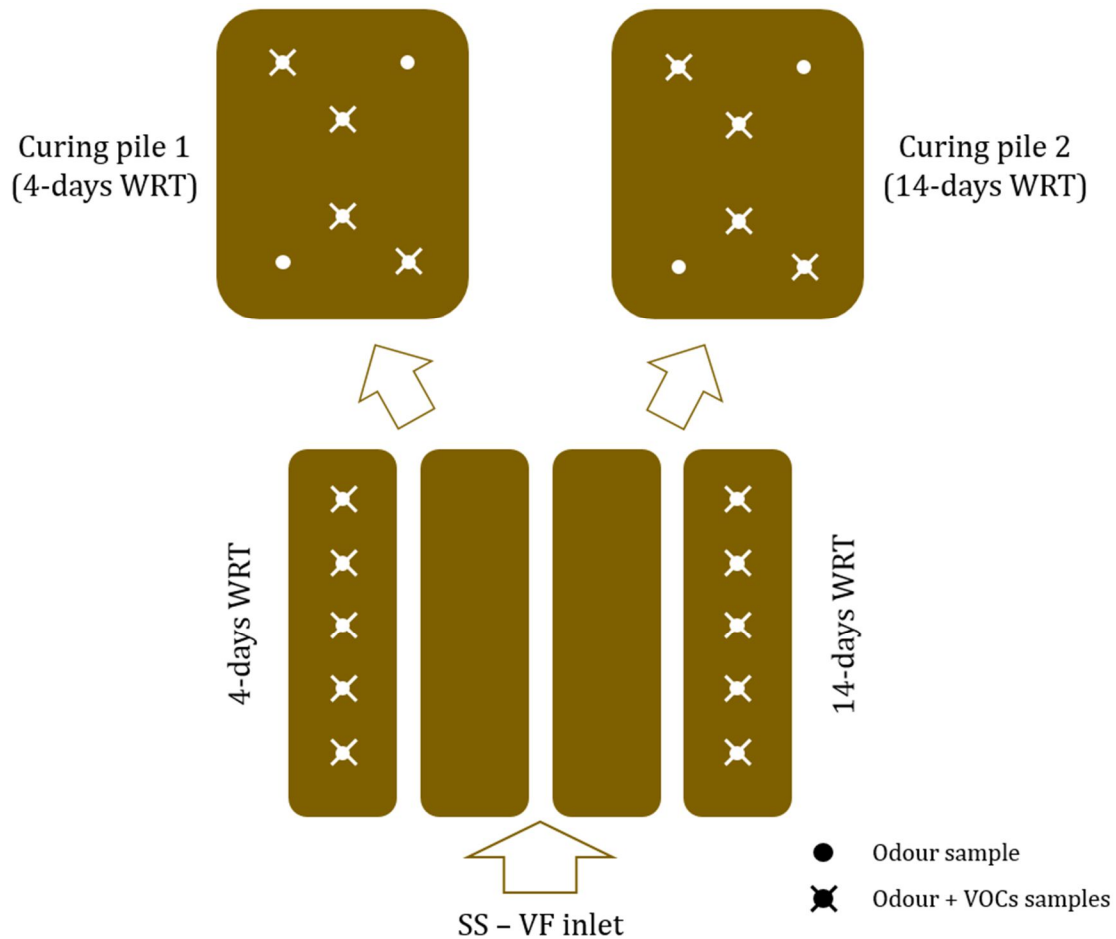


**Figure 3.5.** Scheme of the composting process for both treatment strategies (4 and 14 days WRT) and the distribution of the odour sampling (crossed dots + dots) points and VOCs sampling points (crossed dots).

The different odour samples were obtained using a flux chamber (FC) provided by Scentroid (IDES Canada Inc., ON, Canada), as shown in Figure 3.6. It is a semi-spherical stainless steel FC of 0.443 m of base diameter, 0.154 $m^2$ of base area and 0.045 $m^3$ of volume, equipped with stainless steel fittings and Teflon™ sampling lines. Pure $N_2$ gas was introduced into the FC at a flow rate of 4.0 L·$min^{-1}$ during 30 minutes, which is equivalent to 3 FC residence times, to reach constant concentrations inside the FC before sampling. Then, a Nalophan® bag was introduced inside a hermetic sampling drum where, by means of vacuum pump, the gaseous sample was directed from the FC into the Nalophan® bag, avoiding cross-contamination due to gas circulation through pumping circuits. This methodology is a USEPA recommended methodology (USEPA, 1986), which has been widely reported and discussed, and it is preferred as it provides more consistent, less variable results (Hudson and Ayoko, 2008; Navaratnasamy et al., 2009).



**Figure 3.6.** Flux chamber used for odour sampling.

Gaseous samples for VOCs characterization were obtained using adsorption tubes (Markes International Inc., CA, USA) coupled to a PCXR4 automatic gas sampling pump provided by SKC (SKC Inc., CA, USA), as shown in Figure 3.7. The adsorption tubes were packed with two different hydrophobic adsorbents (Tenax® TA and Carbograph™ 1TD) to maximise the retention of target VOCs. 1.8 L samples were obtained in each of the sampling points, using a sampling flow rate of

$60\ mL \cdot min^{-1}$. Immediately after sampling, the sorbent tubes were sealed with Swagelock end caps fitted with PTFE ferrules and stored at 4 ºC until the moment of sampling.



**Figure 3.7.** Adsorption tubes and automatic gas sampling pump used to obtain gaseous samples for VOCs characterization.

It is important to mention that the differences present in the sampling points' distribution and sampling and/or analysis methods were due to material, time and logistic limitations. For example, the flux chamber was not available when the first study was conducted, leading to surface gas concentration and gas velocity measurements for $NH_3$ and tVOCs emission determination. On the other hand, $N_2$ gas and clean breathable air was highly consumed for odour sampling and analysis during the second study conducted in the plant, limiting the number of total samples that could be obtained and analysed.

## 3.2. Bench-scale sewage sludge biodrying reactor

### 3.2.1. Overview of the bench-scale biodrying reactor

The bench-scale sewage sludge biodrying plant was located in the laboratories of the BETA Technology Centre of the "Universitat de Vic – Universitat Central de Catalunya". Figure 3.8 shows a scheme of the bench-scale biodrying plant.
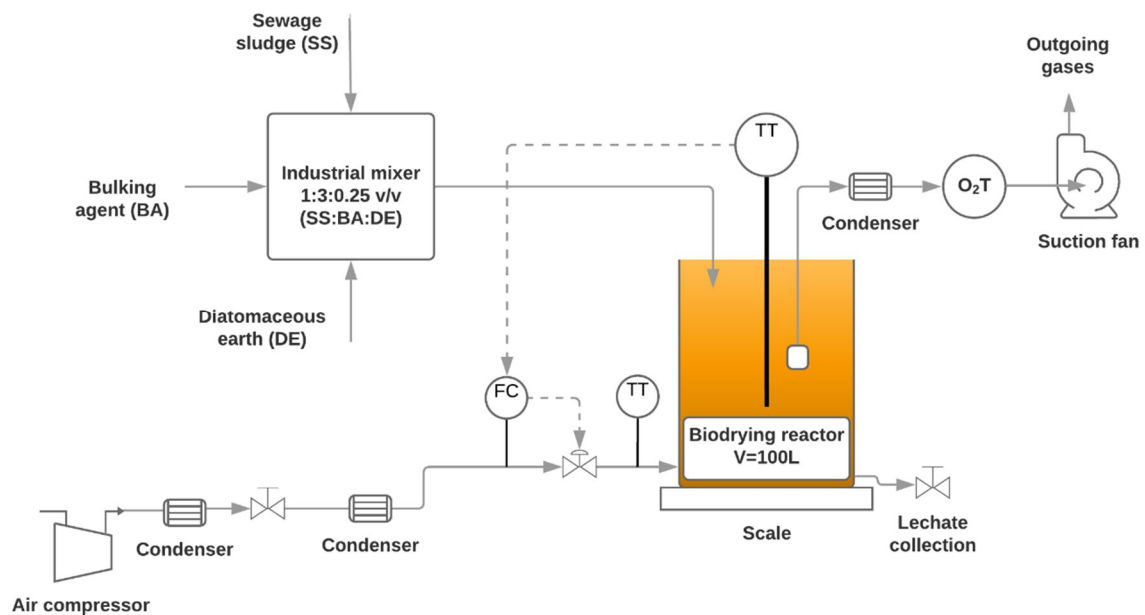


**Figure 3.8.** Scheme of the bench-scale biodrying plant used.

The reactor used to assess the biodrying of a mixture of conventional sewage sludge, diatomaceous earth (DE) and pruning waste (PW), and its related gaseous emissions was a stainless steel cylindrical reactor with an operative volume of 100 L, 0.85 m high and 0.50 m diameter. To maintain near-to-adiabatic conditions, a 2 cm thermal isolation layer of polyurethane foam was used. The reactor was opened at the top to avoid vapour condensation on the mixture. However, it was covered with a straw cover to prevent heat losses and to trap the moisture removed during the biodrying process. Temperature of the material was measured with a PT-100 temperature probe (Iserntech S.A., Spain). Continuous aeration was provided by a Dixair DNX 2050 air compressor (Worthington Creyssensac, Spain) and controlled by D-6311-DR digital mass flow controllers (Bronkhorst High-Tech B. V., Netherlands). The reactor was bottom aerated, and a perforated plate was fixed there to support the material and help distributing the inlet air working as a diffusor.

During the biodrying process, the aeration flowrate was regulated based on the temperature of the material using a feedback control loop. The control software adapted the aeration depending on different temperature ranges referred to the temperature in the middle of the reactor, as shown in Figure 3.9.
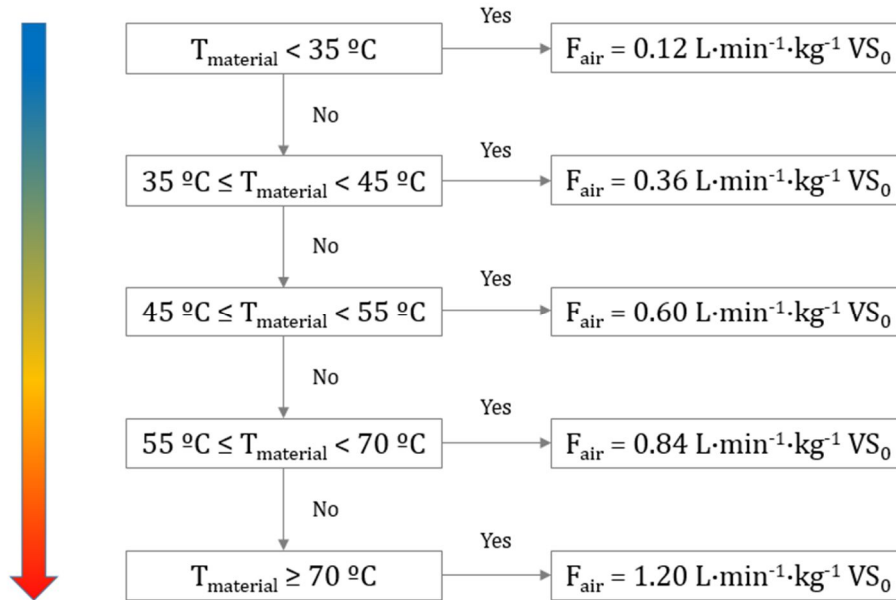


**Figure 3.9.** Specifications of the control system used for aeration control during the biodrying process.

To follow the biological performance of the process, part of the exhaust gases were continuously pumped and analysed using an oxygen sensor (O2 A1, Alphasense, UK) installed after a condensation trap to prevent sensor damage. Finally, water and volatile solid (VS) losses during the biodrying process were monitored by weight loss using a scale (Gram Group, Spain).

### 3.2.2. Solid sampling

During the SS biodrying process, just initial and final solid samples were obtained from the mixture for the analysis of different physical-chemical parameters, as well as biological stability and calorific content of the material. The samples were obtained in a representative manner, by mixing well all the material and grabbing different sub-samples from different points of the reactor to conform an integrated and representative sample.

### 3.2.3. Gaseous and odour emissions sampling and determination

Two different strategies were used during the SS biodrying process to sample and determine the concentration of the different gaseous compounds present in the corresponding gaseous emissions, which were always done before the mixing of the material inside the reactor.

First, tVOCs, $NH_3$ and $H_2S$ concentration were measured daily during the SS biodrying process by means of a MultiRAE Lite portable analyser (RAE Systems, CA, USA), equipped with a PID lamp for tVOCs measurement and two electrochemical sensors for $NH_3$ and $H_2S$ measurement. Part of the exhaust gases were directed by means of a suction pump, which was set at a lower suction flowrate than the bioreactor's aeration rate, to a hermetic box where the portable analyser was installed (Figure 3.10). After leaving the gas flowing through the hermetic box for at least one residence time, the concentration value was registered once it was stable.



**Figure 3.10.** MultiRAE Lite portable analyser installed in the hermetic box for tVOCs, $NH_3$ and $H_2S$ measurement.

On the other hand, for odour, $CH_4$, $N_2O$ analysis and VOCs characterization, gaseous samples were need to be grabbed into 8 L Nalophan® bags for its further processing and analysis by dynamic olfactometry, GC and TD-GC/MS, respectively. A stainless steel FC provided by Scentroid (IDES Canada Inc., ON, Canada) was used to perform the daily gaseous sampling following the same methodology as the one exposed in section *"3.1.3. Gaseous and odour emissions sampling and determination"* of this thesis, by inserting the FC on top of the biodrying reactor. Especially for VOCs characterization purposes, two individual samples were obtained, coinciding with the thermophilic and the mesophilic phases of the biodrying process. 1 L gaseous samples were pumped from the Nalophan® bags through adsorbent tubes (Markes International Inc., CA, USA) packed with two different hydrophobic sorbents (Tenax® TA and Carbograph™ 1TD from Markes International Inc., CA, USA) by means of a manual aspiration pump (Markes International Inc., CA, USA).

## 3.3. Analytical techniques

### 3.3.1. Physical-chemical parameters

Physical-chemical characteristics play an important role in the evolution of biological processes such as sewage sludge composting or biodrying, as well as in the related gaseous and odour emissions. The typical physical-chemical parameters analysed during this thesis are listed below:

- Moisture content (% wet basis)
- Organic matter content (% dry basis)
- pH
- Electrical conductivity
- Density
- Total Kjeldahl Nitrogen (% dry basis)

These physical-chemical parameters were measured following the protocols of the *Test Methods for the Examination of Composting and Compost* (TMECC) (US Dept. of Agriculture and US Composting Council, 2001).

### 3.3.2. Biological stability assessment

Lasaridi and Stentiford (1998) focused on the necessity of obtaining reliable measurements of the biodegradable organic matter content in organic waste in order to assess the overall treatment efficiency of a biodegradation process such as composting. Different methodologies based on chemical and biological assays have been suggested (Ponsá et al., 2010). Nevertheless, the most used methodology in the past years is the Dynamic Respiration Index (DRI), which is a respirometric technique suitable for the biodegradability and/or biological stability assessment and has been proposed by the European Commission in its 2nd Draft of the Working Document on Biological Treatment of Biowaste (CIC, 2019). This respirometric technique has been proved to be very useful for monitoring the performance of full-scale waste treatment facilities, for the prediction of the stability of the final products such as compost or for monitoring the biostabilization of organic wastes when assessing environmental impacts of different waste treatment facilities (Barrena et al., 2014; Colón et al., 2012; Ponsá et al., 2008). The DRI is used to determine the biological stability of an organic solid sample. The term biological stability is defined as the measure of the decomposition grade of the easily biodegradable organic matter contained in the organic solid matrix. In other words, if an organic solid sample is highly stable, it will present a low biodegradation grade so its oxygen consumption will be also low. In this sense, the European Commission defined that a waste is biologically stable if its DRI is 1 g $O_2 \cdot kg^{-1}$ $VS \cdot h^{-1}$ or less (CIC, 2019).

Following the proposed methodology by Adani et al. (2006) and Ponsá et al. (2010), the DRI was measured using a dynamic respirometer as the shown in Figure 3.11. The determination consists on placing 120 to 150 g of the organic solid sample in a 500 mL Erlenmeyer flask, which is closed hermetically, and incubating the sample in a water bath at 37 ºC. Pre-humidified air is constantly supplied through the sample using digital mass flow meters (Bronkhorst Hi-Tech B.V., Netherlands) to ensure aerobic conditions inside the Erlenmeyer flask. The constant airflow supplied should vary depending on the biodegradability of the organic solid sample, using higher airflows for easily biodegradable samples and vice versa. The oxygen

content in the outgoing gases is measured by means of oxygen sensors (Alphasense, UK) and all the data is stored by a Programmable Logic Controller (PLC).
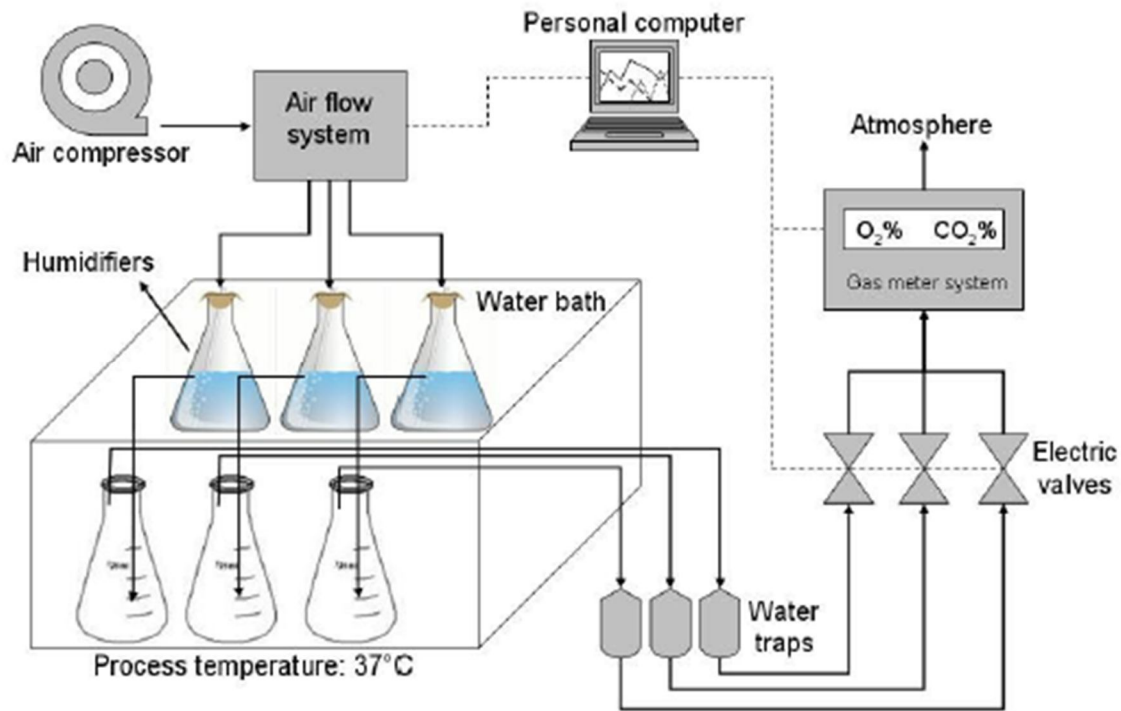


**Figure 3.11.** Scheme of the dynamic respirometer used for the biological stability assessment of organic solid samples (Pognani, 2011).

The measurement finishes once the oxygen content present in the off gases of the Erlenmeyer are equal to atmospheric conditions. The final DRI results are expressed as triplicates average in g $O_2 \cdot kg^{-1}$ VS·$h^{-1}$, and it is calculated by means of equation 3.1.

$$DRI_{24h} = \frac{(O_{2,24h} - O_{2,0}) \cdot F \cdot 31.98}{22.4 \cdot 10^3 \cdot VS} \qquad (Eq. 3.1)$$

where: $DRI_{24h}$ is the dynamic respirometric index during the 24 h of maximum biological activity (g $O_2 \cdot kg^{-1}$ VS·$h^{-1}$); ($O_{2,24h} - O_{2,0}$) is the difference in the $O_2$ content between inlet and outlet reactor's airflow during the 24 h of maximum biological activity (molar fraction); F is the volumetric airflow measured under normal conditions (mL·$h^{-1}$); 31.98 is the $O_2$ molecular weight (g·$mol^{-1}$); $22.4 \cdot 10^3$ is the volume occupied by a mole of ideal gas under normal conditions (mL); VS is the volatile solid mass of the organic solid sample (kg).

### 3.3.3. Determination of calorific values

The determination of the Higher and Lower Calorific Values (HCV and LCV, respectively) was done during the SS biodrying experiments to assess the final calorific content of the product obtained.

The HCV was determined using a bomb calorimeter (1341 Plain Jacket Calorimeter – 1108 Oxygen Combustion Vessel, Parr Instrument Company, IL, USA), according to manufacturer's instructions and following the DIN 51900-3:2005 methodology (German Institute for Standarisation, 2003). Then, the LCV was calculated from the HCV, taking into account the moisture content of the final product and its estimated hydrogen content, according to equation 3.2.

$$LCV = HCV \cdot \left(1 - \frac{MC}{100}\right) - \left(2.444 \cdot \frac{MC}{100}\right) - 2.444 \cdot \frac{H}{100} \cdot 8.936 \cdot \left(1 - \frac{MC}{100}\right) \, (Eq. \, 3.2)$$

where: LCV is the Lower Calorific Value of the biomass fuel (MJ·kg$^{-1}$ of product); HCV is the Higher Calorific Value of the biomass fuel (MJ·kg$^{-1}$ DM); MC is the moisture content of the biomass fuel (%); H is the estimated hydrogen content of the biomass fuel (%), which was considered a 5% (Choi et al., 2014); 2.444 is the enthalpy difference between liquid water at 25 ºC and gaseous phase; 8.936 is the molecular weight ratio between both molecules (m$H_2$O·m$^{-1}H_2$).

### 3.3.4. Total VOCs, NH$_3$ and H$_2$S analysis

Total VOCs were measured with two different instruments depending on the availability and feasibility of its use. During the sampling and measurements presented in section *"4.1. The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant"* of this thesis, the tVOCs concentration was measured by means of a MiniRAE 3000 PID equipped with a 9.8 eV lamp (RAE Systems, CA, USA). The detection ranged from 0.1 to 15000 ppm$_{veq}$ isobutylene with 0.1 ppm$_{veq}$ increments. On the other hand, for the tVOCs measurements presented in section *"4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions"* of this thesis, a MultiRAE Lite portable analyser equipped with a 10.6 eV PID lamp was used, which presented a detection range from 0 to 1000 ppm$_{veq}$ isobutylene with 1 ppm$_{veq}$ increments.

For $NH_3$ measurements, two different methodologies were used depending on the availability of the material at the moment of the sampling and measurement campaigns. During the sampling and measurements presented in section *"4.1. The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant"* of this thesis, $NH_3$ concentration was measured using a GV-100S manual aspiration pump (Gastec Corporation, Japan) to pass the gas through colorimetric tubes (Gastec Corporation, Japan) with a detection range from 2.5 to 2500 ppm$_v$. On the other hand, during the sampling and measurements presented in section *"4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions"* of this thesis, $NH_3$ concentration measurement was performed by means of a MultiRAE Lite portable analyser (RAE Systems, CA, USA), which had installed an electrochemical sensor for NH3 measurement with a detection range from 0 to 100 ppm$_v$ with 1ppm$_v$ increments.

$H_2S$ concentration analysis were conducted using a MultiRAE Lite portable analyser (RAE Systems, CA, USA) equipped with an electrochemical sensor for $H_2S$ measurement, which detection ranged from 0 to 100 ppm$_v$ with 1ppm$_v$ increments.

Each specific measurement methodology is detailed in the *"Materials and methods"* section of each specific section in *"Chapter 4: Results"* of this thesis document.

### 3.3.5. Odour concentration analysis

The odour concentration analysis of the gaseous samples were performed using the Scentroid SM-100 portable field dynamic olfactometer (IDES Canada, Inc., Whitchurch-Stouffville, ON, Canada) shown in Figures 3.12, 3.13 and 3.14.

Figure 3.12 shows the clean air supply-tank used to store clean and breathable air used to dilute the odorous sample to be analysed, the pressure reducer installed to regulate the pressure of the supplied air and the activated carbon filter. The tank can hold a maximum pressure of 4500 psi (300 bar), and the working pressure of the supplied clean air must be 80 psi, which corresponds to a 20 L·min$^{-1}$ airflow.

**Figure 3.12.** Clean air supply-tank, pressure reducer and activated carbon filter of the Scentroid SM-100 portable field dynamic olfactometer.

Figure 3.13 shows the manual olfactometer and the mask of the equipment. The manual olfactometer is the part of the instrument where the mixing of the clean breathable airflow and the odorous gas is done by manual dilution. It consists of three different valves: the main valve, which opens the clean airflow from the tank to the olfactometer, the dilution-regulating valve, which permits the manual regulation of the quantity of odorous gas that is sucked by the venturi, and finally the venturi valve, where the necessary void is created to suck the odorous gas and mix it with the clean breathable air to be presented to the panellist. The quantity of odorous gas entering the olfactometer is regulated by means of the manual screw, which has a numerical scale that ranges from 0 (closed) to 15 (fully opened). Moreover, the dilution of clean air with odorous gas is dependent on different interchangeable measurement plates, which are installed under the venturi valve and fix the measurement range of the equipment. Finally, the mask is the element that receives the mixture to be analysed by the panellist, and it is designed to present a 20 l·min$^{-1}$ flow at 2.5 m·s$^{-1}$ according to international standards as the European Standard EN 13725 (European Committee for Standardization, 2006).
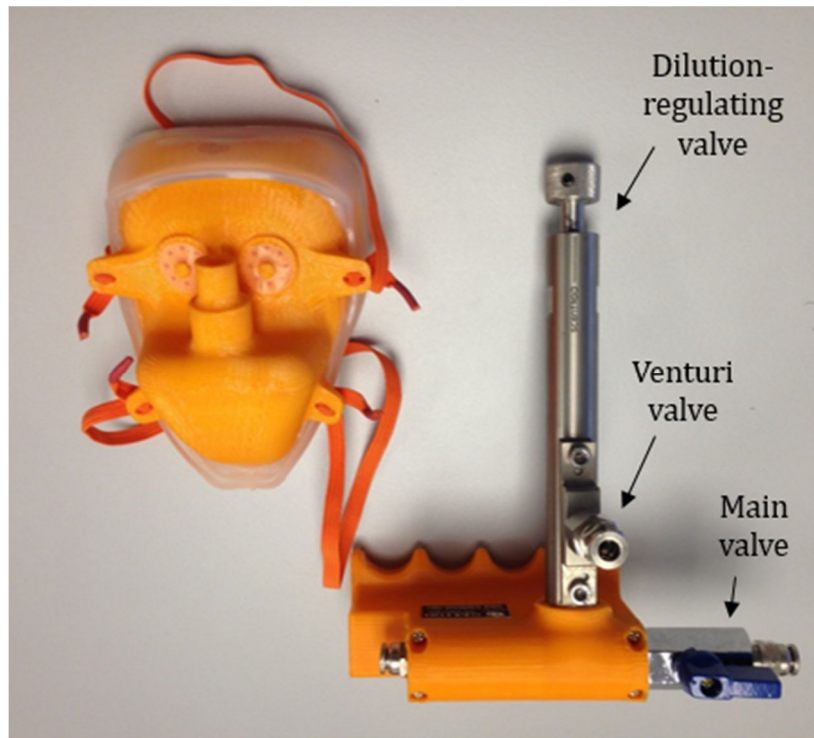
**Figure 3.13.** Mask and manual olfactometer of the Scentroid SM-100 portable field dynamic olfactometer.

Figure 3.14 shows the Scentroid SM-100 portable field olfactometer during a gaseous sample analysis in the laboratory. Due to its characteristics, this equipment can be used to perform odour concentration measurements both in-situ and in the laboratory. To avoid the possible odour interferences that can be faced during the in-situ analysis of some odour emission sources, the methodology used along this thesis was to grab gaseous sample and perform the odour measurement connecting the sampling bag to the olfactometer back in the laboratory.

**Figure 3.14.** Scentroid SM-100 portable field dynamic olfactometer.

The Scentroid SM-100 olfactometer is factory-calibrated. As aforementioned, five different interchangeable measurement plates are provided to fit the expected odour concentration range of a sample with the measurement range of the equipment. Figure 3.15 shows the calibration curve of a measurement plate with a measurement range from 2260 to 138 ou·m$^{-3}$.
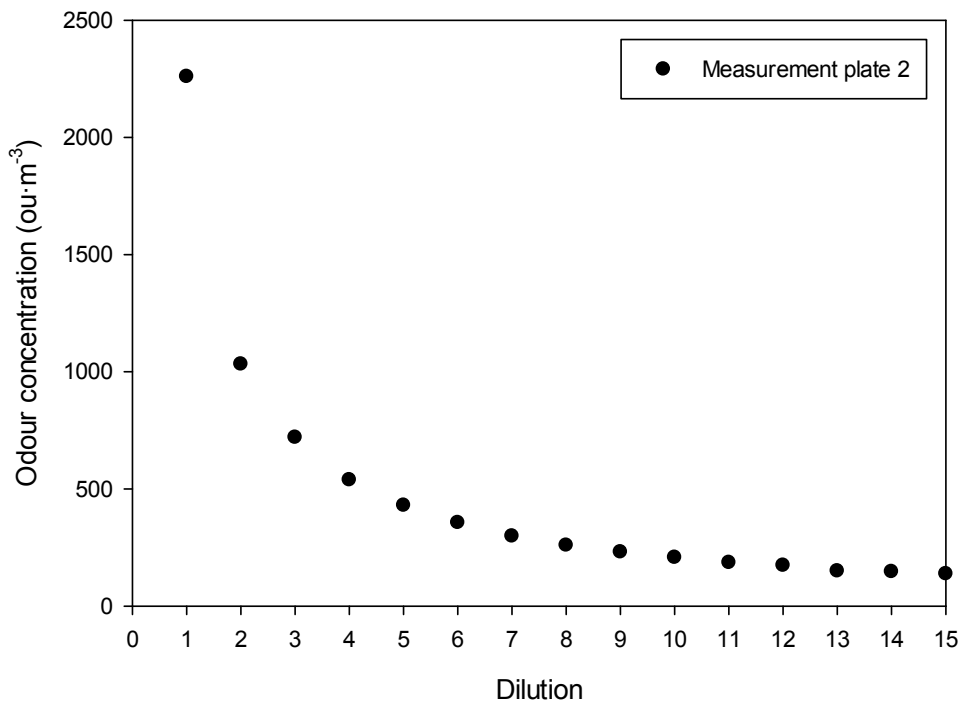


**Figure 3.15.** Example of a measurement plate's calibration curve with a measurement range from 2260 to 138 ou·m$^{-3}$.

The odour concentration analysis of the samples were performed in duplicates by the same panellist during the same day of sampling in a closed, well-ventilated room, leaving 10 minutes between analyses.

### 3.3.6. VOC characterization

The distribution of the VOCs present in the gaseous emissions generated during the composting and biodrying of SS was determined by thermal desorption gas chromatography mass spectrometry (TD-GC/MS), using the equipment showed in Figure 3.16.



**Figure 3.16.** TD-GC/MS system used for VOCs characterization.

Firstly, a liquid VOCs custom mix solution with a concentration of 4000 mg·L$^{-1}$ was prepared with 35 standard compounds (>98 % purity, Sigma-Aldrich Química SL, Madrid, Spain) in pure methanol. These 35 standards, which are presented in Table 3.1, were considered as representative of VOCs found in the gaseous emissions from SS composting processes. Briefly, to prepare 25 mL of the 4000 mg·L$^{-1}$ VOCs mix solution, the specific volume of each standard was calculated and added to a volumetric flask with pure methanol. From the VOCs custom mix solution, seven dilutions were prepared for calibration. 1.5 µL of a liquid standard dilution were loaded onto an adsorbent tube via a calibration solution loading rig (Markes International, Inc, CA, USA) and flushed with pure He at a flow rate of

100 mL·min⁻¹ during 3 minutes to fully evaporate the VOCs and be retained by the sorbent bed. Immediately, the tube was analysed and the process repeated for each liquid standard dilution to obtain the specific calibration curves.

**Table 3.1.** VOCs standards used for the GC/MS calibration.

| Family | Compound | Family | Compound |
|---|---|---|---|
| Alcohols | 1-butanol | Carboxylic acids | Butanoic acid |
| | 1-hexanol | Esters | Ethyl butanoate |
| Aldehydes | Benzaldehyde | | Ethyl pentanoate |
| | Isovaleraldehyde | Ethers | 2-butoxyethanol |
| | Hexanal | Halogenated HC | Tetrachloroethene |
| | Octanal | Ketones | 2-butanone |
| | Decanal | | 2-pentanone |
| Alkanes | Hexane | Nitrogen-compounds | Pyridine |
| | Heptane | | Triethylamine |
| | Decane | Phenols | Phenol |
| | Methylcyclohexane | Sulphur-compounds | DMS |
| Aromatic HC | Benzene | | DMDS |
| | Toluene | Terpenes | α-pinene |
| | Ethylbenzene | | β-pinene |
| | Xylene | | Limonene |
| | Styrene | | Eucalyptol |
| | Indole | | p-cymene |
| | Skatole | – | – |

To proceed with the analyses, desorption of the VOCs trapped in the sampling adsorption tubes was performed using a UNITY-2 Thermal Desorber (TD) (Markes International, Inc., CA, USA). The sorbent tubes were heated at 290 ºC for 8 minutes while flowing high purity He at a flow rate of 50 mL·min⁻¹ to desorb the VOCs onto a cold trap at -10 ºC. Afterwards, the cold trap was heated up to 305ºC at a 40ºC·s⁻¹ rate for 5 minutes to desorb the VOCs trapped and to inject them into the chromatographic column. The split ratio used during all the analysis process was

1:10 in order to adjust the resolution of the chromatogram and to avoid column overloading. Then, the gas was directed to the chromatographic column through a transfer line heated at 250 ºC to prevent condensation. VOCs analysis was performed using an Agilent 7820 Gas Chromatography (GC) coupled to an Agilent 5975 Mass Spectrometer (MS) (Agilent Technologies, Inc., CA, USA). The chromatographic column used for VOCs separation was a DB-624 capillary column (60 m x 0.25 mm x 1.4 µm, Agilent Technologies, Inc., CA, USA), using a He gas flow rate of 1 mL·min$^{-1}$ as carrier gas. The temperature program for the GC oven was an initial isothermal stage at 50 ºC during 2 minutes, then a first temperature ramp to 170 ºC at a 3 ºc·min$^{-1}$ rate, followed by a second ramp up to 280 ºC at a 8 ºC·min$^{-1}$ rate. The GC/MS interface and the transfer line to the MS were maintained at 280 and 235 ºC, respectively, during the whole analysis. Finally, the mass spectra is obtained by electronic ionization at 70 eV and the MS acquired data in scan mode with m/z interval ranging from 35 to 355 amu (atomic mass unit). The different compounds were identified by comparing the retention times to those of the selected analytical standards and by matching the mass spectra with the Wiley275 mass spectral library available in the GC/MS system. Quantification of the individual compounds was performed using the calibration curves obtained previously. The total analysis process lasts 54 minutes.

With the aim of grouping the different compounds present in each sample into categories or families to facilitate the analysis and discussion of the results, the relative abundance of each specific compound (%) was calculated by dividing the specific compound's area by the total chromatogram's area (Equation 3.3). Then, the compounds were classified into families (alcohols, aldehydes, ketones, terpenes, etc.) and the relative abundance of each family (%) was calculated as the sum of all the relative abundances of the compounds belonging to each family (Equation 3.4).

$$\% \, DMDS = \frac{DMDS \, area}{\sum Chromatogram \, area} \qquad (Eq. \, 3.3)$$

$$\% \, Sulfur - compounds = \frac{\sum Sulphur - compounds \, areas}{\sum Chromatogram \, area} \qquad (Eq. \, 3.4)$$

### 3.3.7. CH$_4$ and N$_2$O analysis

The analysis of methane and nitrous oxide were conducted by means of gas chromatography and the results were expressed in ppm$_v$. The gas chromatograph and the analytical conditions were the following:

- Gas chromatograph: Agilent Technologies 6890N Network GC System.
- Column: Agilent Technologies HP-PLOT W semi-capillary column (30 m x 0.53 mm x 40.0 μm).
- Post-column: Agilent Technologies particle trap (2 m, nº 5181-3352).
- Analytical conditions for CH$_4$:
    - Detector: Flame Ionization Detector (FID).
    - Carrier gas: N$_2$ at 2 psi pressure and split 1:2.
    - Injector temperature: 240 ºC.
    - Detector temperature: 250 ºC.
    - Oven temperature: 60 ºC (isotherm).
    - Run time: 4 minutes.
    - Injection volume: 500 μl.
- Analytical conditions for N$_2$O:
    - Detector: Electron Capture Detector (ECD).
    - Carrier gas: N$_2$ at 2 psi pressure and split 1:2.
    - Injector temperature: 120 ºC.
    - Detector temperature: 345 ºC.
    - Oven temperature: 60 ºC (isotherm).
    - Run time: 6 minutes.
    - Injection volume: 500 μl.

## 3.4. Emission factor determination

### 3.4.1. Full-scale sewage sludge composting plant

The emission factors of each specific pollutant were determined with both the total mass of the pollutant emitted during the process time and a representative activity or index related to the release of the pollutant, such as the mass of waste to be treated, the emitting surface or time units, amongst others, as shown in equation 3.5 (United States Environmental Protection Agency (USEPA), 1995a).

$$EF_i = \frac{m_i}{I} \qquad (Eq.\,3.5)$$

where: $EF_i$ is the emission factor referred to a target pollutant (kg pollutant·$Mg^{-1}$ DM); $m_i$ is the total emitted mass of the target pollutant during the process (kg pollutant); I is the representative activity or index (Mg of DM treated).

To evaluate the odour emissions generated during the composting process, it was necessary to calculate previously the specific odour emission rates (SOER) and the odour emission rates (OER) related to each phase of the process. For each process phase of each treatment strategy (dynamic windrows and curing piles of 4-d and 14-d WRT strategies), an average SOER was calculated with all the individual SOER obtained from each sampling point and then, the OER of each process phase was calculated by multiplying the average SOER by the corresponding total emitting surface, as shown in equations 3.6 and 3.7.

$$SOER = \frac{OC \cdot F_{N_2}}{A_{FC}} \qquad (Eq.\,3.6)$$

$$OER = SOER \cdot A_s \qquad (Eq.\,3.7)$$

where: SOER is the specific odour emission rate (ou·$s^{-1}$·$m^{-2}$); OC is the odour concentration (ou·$m^{-3}$); $F_{N2}$ is the nitrogen flow rate introduced into the FC ($m^3$·$s^{-1}$); $A_{FC}$ is the surface covered by the FC ($m^2$); OER is the odour emission rate (ou·$s^{-1}$); $A_S$ is the total area of the emitting surface ($m^2$).

Finally, to estimate the odour emission factor (OEF) of each process phase for each treatment strategy, the OER were divided by the plant's capacity of each treatment (Mg·d-1), as shown in equation 3.8.

$$OEF = \frac{OER}{I} \qquad (Eq.\,3.8)$$

where: OEF is the odour emission factor (ou·$Mg^{-1}$); OER is the odour emission rate (ou·$d^{-1}$); I is the representative activity or index (Mg·$d^{-1}$).

### 3.4.2. Bench-scale sewage sludge biodrying reactor

In the case of the sewage sludge biodrying reactor, due to its reduced emitting surface, which was covered by the FC, and the fact that high-rate forced aeration through the material was used, the pollutants' emission rates were calculated based on the measured concentration of each specific pollutant and the aeration flow through the reactor at the time of each sampling event (equation 3.9).

$$ER_i = C_i \cdot F \qquad (Eq. 3.9)$$

where: $ER_i$ is the emission rate of a specific pollutant $i$ (mg pollutant·d$^{-1}$); $C_i$ is the concentration of a specific pollutant $i$ (mg pollutant·m$^{-3}$); F is the aeration flow through the reactor (m$^3$·d$^{-1}$).

Once all the emission rates of each specific pollutant were obtained for each sampling day, they were represented against process time. The area below the curve obtained corresponded to the total emitted mass of each specific pollutant during the process studied. Therefore, by dividing these total pollutants' masses by the initial mass of sewage sludge DM introduced in the reactor (DM$_0$-SS), the corresponding emission factors were obtained (equation 3.10).

$$EF_i = \frac{m_i}{I} \qquad (Eq. 3.10)$$

where: $EF_i$ is the emission factor of a specific pollutant $i$ (kg pollutant·Mg$^{-1}$ DM$_0$-SS); $m_i$ is the total emitted mass of a specific pollutant $i$ (mg pollutant); I is the initial mass of sewage sludge DM introduced in the reactor (Mg DM$_0$-SS).

# CHAPTER 4: RESULTS

# 4.1. The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant

Daniel González, Joan Colón, David Gabriel, Antoni Sánchez

**Abstract**

Volatile organic compounds (VOCs) and ammonia are some of the compounds present in gaseous emissions from waste treatment facilities that contribute to odour pollution. In the present work, the effect of the residence time on the biological stability of raw sludge (RS) composted in dynamic windrows and the gaseous emissions generated were studied at a full-scale composting plant, aiming to provide specific pollutant emission factors and to determine their variability depending on the composting time. Waste stability and emissions analysis considered both a first phase where mixed RS and vegetal fraction (RS – VF) is actively composted in dynamic windrows and a second standard curing phase in turned piles, which lasted 31 days. Two windrows were operated at 4 days of composting time while two other windrows were operated simultaneously at 14 days composting time. Increasing the residence time leads to a better waste stabilization in the first composting phase, providing a 50% reduction of the Dynamic Respiration Index. A decrease of the ammonia emission factor was achieved when increasing the composting time (from 168.5 g $NH_3 \cdot Mg^{-1}$ RS – VF $d^{-1}$ to 114.3 g $NH_3 \cdot Mg^{-1}$ RS – VF $d^{-1}$), whereas the VOCs emission factor was maintained for the same process conditions (between 26.0 and 28.0 g C-VOC$\cdot Mg^{-1}$ RS – VF $d^{-1}$). However, an increase of the emission masses of both pollutants was observed (from 0.16 to 0.39 kg tVOCs$\cdot Mg^{-1}$ RS–VF and from 1.21 to 1.60 kg $NH^3 \cdot Mg^{-1}$ RS – VF). Finally, ammonia and VOCs emissions generated at the curing piles were nearly avoided when increasing the composting time of the first phase.

## 4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant

Daniel González, Joan Colón, Antoni Sánchez, David Gabriel

**Abstract**

Sewage sludge management is known to cause odour impact over the environment. However, an information gap exists about odour emissions quantification from different treatment strategies. In the present work, odorous emissions generated in a full-scale sewage sludge composting plant were characterized, aiming at providing specific odour emission factors (OEF) and to determine their variability depending on the composting time. Additionally, characterization of VOCs emitted during the process was conducted through TD-GC/MS analyses. Odour emission and VOCs characterization considered both (1) a first stage where a raw sludge and vegetal fraction mixture were actively composted in dynamic windrows and (2) a second curing stage in static piles. After increasing the composting time, a reduction of 40% of the maximum odour concentration referred to the dynamic windrow stage was estimated, whereas a reduction of 89% of the maximum odour concentration was achieved after turning of curing piles. However, global OEF increased from 4.42E+06 to 5.97E+06 ou·Mg$^{-1}$ RS – VF when the composting time increased. Finally, different VOCs such as isovaleraldehyde, indole, skatole, butyric acid, dimethyl sulphide and dimethyl disulphide were identified as main potential odour contributors. Results obtained are a valuable resource for plant management to choose an appropriate sewage sludge composting strategy to mitigate odour emissions.

# 4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions

Daniel González, Nagore Guerra, Joan Colón, David Gabriel, Sergio Ponsá, Antoni Sánchez

**Abstract**

In the present work, a complete study of the sewage sludge (SS) biodrying technology was conducted at bench-scale, aiming at assessing its performance and providing a valuable insight into the different gaseous emission patterns found for greenhouse gases (GHG) and odorant pollutants. As process key parameters, temperature, specific airflow, dynamic respiration index, final moisture content and Lower Calorific Value (LCV) were evaluated. At the end of the biodrying, a product with a 35.9% moisture content and a LCV of 7.1 MJ·kg$^{-1}$ product was obtained. GHGs emission factor was 28.22 kgCO$_{2eq}$ per Mg of initial mass of dry matter in the SS (DM$_0$-SS). During the biodrying process, maximum odour concentration measured was 3043 ou·m$^{-3}$ and the estimated odour emission factor of the biological treatment was 3.10E+07 ou per Mg DM$_0$-SS. Finally, VOCs were completely identified and quantified. The most abundant VOCs found in the biodrying gaseous emissions were terpenes, sulphur-compounds and ketones.

# CHAPTER 5: GENERAL DISCUSSION

## 5.1. Gaseous emissions from the composting of sewage sludge

### 5.1.1. Consequences of the gaseous emissions generated during the sewage sludge composting

From an environmental to an economical point of view, different consequences can be depicted from the gaseous emission produced during the composting of sewage sludge. Many of them will depend on the characteristics of the composting process itself (type of treatment process and/or facility), whereas others will depend on the physical-chemical characteristics of the wastes to be treated.

Firstly, health risk and workplace safety issues should be considered, especially for those toxic compounds whose concentrations in the gas phase must be maintained and controlled under fixed limits. For example, the Occupational Safety and Health Administration (OSHA) sets a permissible exposure limit (PEL) for ammonia in 50 ppm averaged over an eight hour work day, but NIOSH set stricter limits in a time-weighted average format (TWA) of 25 ppm for eight hour work day and 35 ppm as a short term exposure limit (STEL) (OSHA, 1970). On the other hand, the Spanish Government sets the TWA and the STEL limits for ammonia at 20 and 50 ppm$_v$, respectively (MITRAMISS, 2019). In the case of hydrogen sulphide, OSHA sets 10 ppm TWA and 15 ppm STEL, with an acceptable maximum ceiling concentration of 50 ppm (OSHA, 1970), whereas the Spanish Government sets the TWA and STEL limits at 5 and 10 ppm$_v$, respectively (MITRAMISS, 2019). The control of these regulation limits will affect in a different manner to the economics of the global treatment depending on the kind of treatment strategy. For example, if sewage sludge active composting is performed in closed tunnels, during the charge and discharge operations, the concentrations of toxic compounds can exceed the exposure limits. Consequently, a larger renewal of air will be needed to guarantee a proper and safe environment for workers. This fact will lead to high air extraction flows, thus increasing energy costs of the process.

The reduction of $NH_3$ emissions generated during the composting of sewage sludge is also important to preserve nitrogen content in the final compost, which enrich its fertilizer effect (European Parliament, 2019). As shown in Table 1.1, the Spanish Government proposes in the RD 506/2013 that any compost obtained from

aerobic biodegradation of biodegradable organic materials should present a C/N ratio below 20 to guarantee a minimum nitrogen content. However, as demonstrated by Puyuelo et al. (2011), due to the differences between TOC and BOC, it is important to take into account BOC/N ratios to not overestimate the biodegradable carbon available when formulating initial composting mixtures, what helps into minimizing $NH_3$ volatilization and emission and enhancing nitrogen preservation. In this sense, the preservation of nitrogen in the final compost maximise its economic value and can help to reduce the use of nitrogen-based chemical fertilizer and its associated energetic and environmental production costs.

On the other hand, minimizing VOCs emissions is important since VOCs have been reported to affect the environment in different ways. VOCs have been reported as precursors of tropospheric ozone formation (Horowitz, 2010) and one of the main responsible of odours generated during the sewage sludge composting (Maulini-Duran et al., 2013). Furthermore, some specific VOCs that can be formed and/or emitted during the treatment of sewage sludge such as benzene, toluene or xylenes present toxic or human-health risks, so its control and avoidance should be taken into account (Vilavert et al., 2012).

Another notorious aspect is the odour impact that the gaseous emissions, produced during the sewage sludge composting, can generate over the nearby population. Even though a composting process is considered as an aerobic process, depending on the characteristics of the feedstock and the operational conditions of the process, anaerobic degradation processes can occur, leading to the formation and emission of malodorous compounds such as hydrogen sulphide, organosulphur compounds and organic acids, which present very low odour detection thresholds (Nagata, 2003). However, the aerobic decomposition of organic wastes can also lead to the formation of different odorant compounds such as terpenes and alcohols. The effect that these emissions can have over the nearby environment can vary drastically depending on the characteristics and the location of the treatment facilities. For example, an opened composting treatment plant will present an evident odour impact over nearby population if installed in a location without a previous study of the meteorology of the area in order to predict odour immission concentration. On the other hand, closed composting treatment plants can present

a better control of gaseous emissions due to the capture of all the process' off-gases and its final treatment in gas treatment units such as biofilters or biotrickling filters. However, fugitive emissions derived from opened doors or windows, truck's transit or outdoor opened containers can originate odour nuisance in the nearby neighbourhoods. In this sense, it is important to prevent these fugitive emissions in order to avoid odour impact and the devaluation of the investment done in the final gas treatment unit.

For all these reasons, it is important to have a good knowledge about the gaseous emissions generated during the SS composting process and their variability depending on different process or operational conditions to minimize them to the greater extent and to avoid both workplace and environmental impacts.

## 5.1.2. Evolution of the sewage sludge composting process and its associated gaseous emissions

Sewage sludge composting has been thoroughly studied in the past years in order to understand the dependence of its performance on the different parameters affecting it and to optimize these crucial parameters to perform a proper composting process at full-scale (Gea et al., 2007; Nikaeen et al., 2015; Robledo-Mahón et al., 2019). Moreover, there is good knowledge about the influence of different parameters such as humidity, porosity or oxygen level on the formation and emission of different gaseous compounds at bench-scale (Chen et al., 2010; He et al., 2017; Yuan et al., 2016). However, there is plenty lack of information regarding gaseous emissions generated in full-scale sewage sludge composting processes and its relation with key parameters explaining the evolution of the process.

The gaseous emissions produced by a sewage sludge composting process can have mainly three different origins: the own waste's compounds (such as some volatile hydrocarbons), the gaseous compounds generated by aerobic and/or anaerobic degradation (ammonia or hydrogen sulphide) and the ones generated through chemical reactions (such as ketones or furans). These three formation pathways may appear at different moments of the sewage sludge composting process and their contribution to the global emissions is not normally the same. In sections *"4.1. The effect of the composting time on the gaseous emissions and the*

*compost stability in a full-scale sewage sludge composting plant"* and *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"*, $NH_3$, tVOCs, specific VOC and odour emissions and their relation with the evolution of the sewage sludge composting process in terms of material's temperature and biological stability are presented. Generally, these two sections describe how the emission of $NH_3$ and tVOCs are highly dependent on process and operational parameters such as the composting time, the temperature and therefore the biological activity of the sewage sludge being composted, presenting higher emission rates at higher temperatures, and decreasing as temperature and biological activity decrease. Consequently, odour emissions followed the same tendency, presenting higher odour emission rates at the first steps of the process when material's temperature and biological activity were higher.

By comparing the two different treatment strategies used during the sampling campaigns at the full-scale composting plant (4-d and 14-d WRT strategies), it resulted noticeable the high impact that the first active composting phase's time had on the performance of the global process in terms of temperature and biological stability evolution and, consequently, on the gaseous and odorous emissions generated. Previous to this work, the composting plant operated with a first active composting phase of 4-d WRT, which is in fact a short time before a maturation or curing step of one month. Due to this short active composting time, material's temperature and biological activity did not decreased enough before being sent to the maturation phase, where anaerobic zones possibly formed, enhancing the formation and emission of malodorous compounds during the turning events. The aims of increasing the first active composting phase were to avoid those critical emission situations during the maturation phase and to increase the biological stability of the final compost, even though the global composting process time was increased.

In section *"4.1. The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant"*, $NH_3$ and tVOCs emissions were found to be highly related to the temperature of the material and its biological activity, which has been previously reported by other authors at bench-

scale studies (de Guardia et al., 2008; Pagans et al., 2006a, 2006b; Scaglia et al., 2011). The evolution of the biological stability achieved by the material during the composting process (in terms of DRI) was compared between the two different treatment strategies, and it was observed that by increasing the WRT of the first active composting step from 4 to 14 days, the DRI achieved at the end of the first active composting phase was reduced about a 50%. At this point, it is important to highlight the necessity of having reliable measurements of the biological activity of the material such as the DRI to correctly assess the evolution of the biological activity of the material along the process. The variation in the DRI observed was also reflected in the material's temperature patterns observed in both the dynamic windrows and the curing piles, and it had a direct influence on the gaseous emissions dynamics from both phases. $NH_3$ and tVOCs emission rates tend to increased as material's temperature increased due to the higher biological activity present in the composting material, as presented in Figure 5.1.
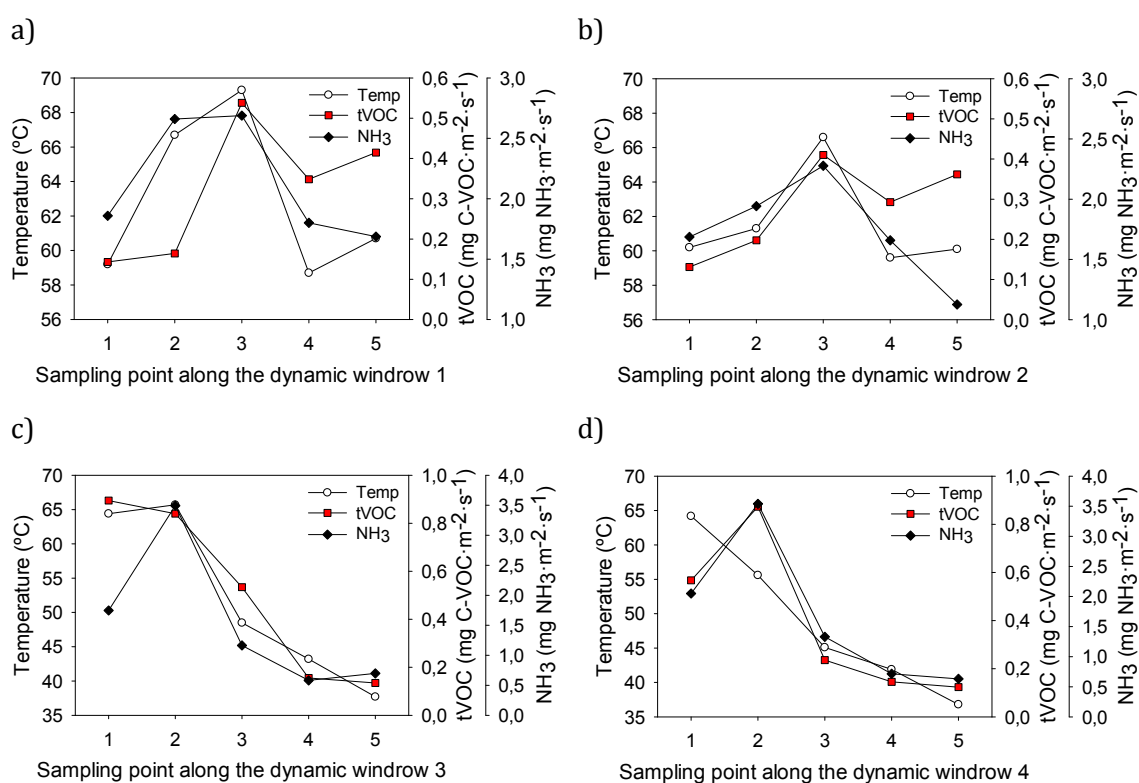


**Figure 5.1.** Evolution of the punctual temperature of the material and the punctual tVOCs and $NH_3$ emission rates along each dynamic windrow. (a) Dynamic windrow 1 (4-d WRT); (b) dynamic windrow 2 (4-d WRT); (c) dynamic windrow 3 (14-d WRT); (d) dynamic windrow 4 (14-d WRT).

As it can be observed, the material at the outlet of the dynamic windrows 1 and 2 (4-d WRT strategy) was still at thermophilic conditions when finishing the first active composting phase due to the high biological activity and the impossibility of microorganisms to biodegrade the easily biodegradable organic matter in this short time. The difference in DRI at the outlet of the dynamic windrows between both treatment strategies discussed before explains this temperature differences and the differences in the emission rates observed for $NH_3$ and tVOCs, what has a direct impact on the performance and the related gaseous emissions during the curing phase.

For the curing phase, significant differences for the emission of both monitored pollutants were observed due to the great difference in the material's temperature at the beginning of the curing step of each treatment strategy (4-d and 14-d WRT strategies), as shown in Figure 5.2.
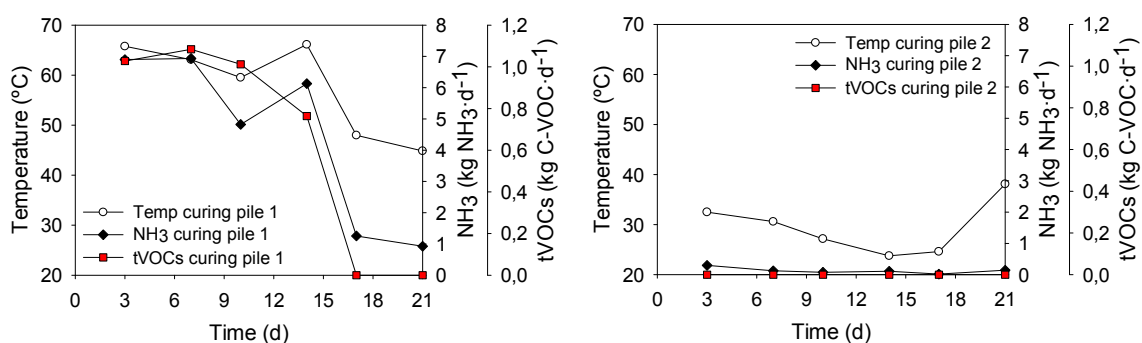


**Figure 5.2.** Evolution of the average temperature of the material and the tVOCs and $NH_3$ average emission rates of each curing pile. (a) Curing pile 1 (4-d WRT strategy); (b) curing pile 2 (14-d WRT strategy).

As it can be observed in Figure 5.2. a and b, the temperature of the curing pile material of strategy 1 remained under thermophilic conditions nearly all the curing phase time in comparison with the temperature of the curing pile material of strategy 2, which never reached thermophilic conditions during this step. This fact is a consequence of the higher biological activity present in the output material from the 4-d WRT dynamic windrows and had a direct influence on the emission of both tVOCs and $NH_3$, being much higher during the curing phase of strategy 1.

In section *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"*, the odour emission

patterns corresponding to both treatment strategies are depicted together with a chemical characterization of the different VOC species present in these gaseous emissions, which is discussed in section *"5.3. Characterization of the different VOCs emitted and its relationship with odour emissions"*. In this section, it was observed that odour emissions followed similar dynamics as $NH_3$ and tVOCs emission, being dependant on material's temperature and biological stability (Toledo et al., 2019b). In fact, Figure 5.3 shows a linear correlation obtained between DRI and odour concentration measured at different moments of the SS composting process for both treatment strategies (4 and 14 days WRT).
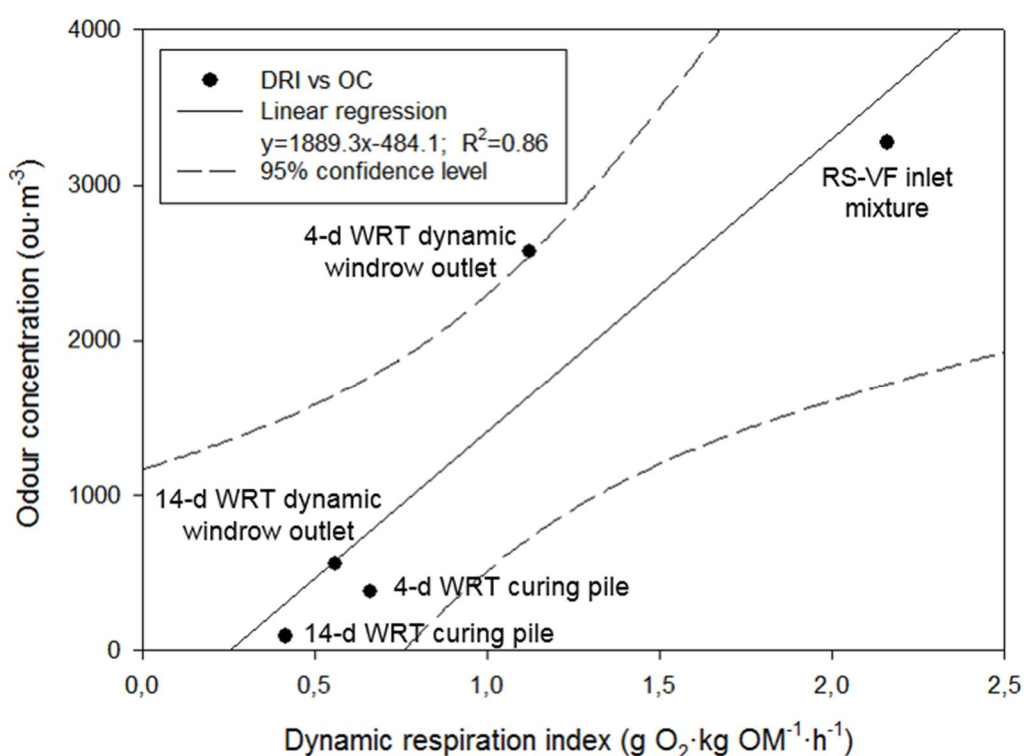


**Figure 5.3.** Correlation between Dynamic Respiration Index (DRI) and odour concentration for different moments of the sewage sludge composting process (data of both treatment strategies).

Even though the data presented in Figure 5.3 is not extensive enough, this linear correlation can provide an insight into the evolution of the sewage sludge composting process and its biological stabilisation by measuring the emission's odour concentration. The present data fits with what has been previously observed in terms of temperature evolution and pollutant's emission during the SS composting process studied. Odours produced mainly depended on the presence of

NH$_3$ and VOCs in the exhaust gases, which were emitted in higher amounts during thermophilic conditions, when biological activity was higher. However, deeper study of this relation should be conducted to clearly correlate these two variables, which can be a useful monitoring tool for sewage sludge composting. In this sense, this relation between biological stability and odour concentration has been previously reported during MSW composting (Scaglia et al., 2011).

Different works have proposed the monitoring of the gaseous and odour emissions during composting as a tool to obtain valuable information of the evolution of the process and the quality of the final product (Gutiérrez et al., 2014; Romain et al., 2005; Sironi et al., 2007b; Toledo et al., 2019a). The formation and emission of specific compounds can indicate different problems such as insufficient oxygen content, excessive acidity, deficient initial C/N ratio, low biological activity or low biological stability of the product obtained. In the case of NH$_3$ emission and its high relation with process temperature, it could be used as an indirect monitoring parameter of the biological activity present in the material (Pagans et al., 2006a). On the other hand, odour emissions have been also proved to provide information about the evolution of the biological stability during a composting process, as mentioned before (Figure 5.3) and elsewhere (Scaglia et al., 2011), so its monitoring could be useful too. In this sense, it is clear that during organic matter stabilization processes, odour emissions are strongly related with biological activity of the material. Lately, some studies using e-noses have been presented aiming at online monitoring the odour emissions of different waste treatment processes (Gutiérrez et al., 2014; Sironi et al., 2007b, 2007a). However, the complexity of the gaseous mixtures and the large number of compounds and quantities that can be present in them, amongst other problems, makes that technique hard to implement at full-scale facilities.

## 5.1.3. Characterization of the different VOCs emitted and its relationship with odour emissions

As it has been mentioned before and largely reported elsewhere, VOCs are one of the main group of compounds responsible for odour nuisance present in the gaseous emissions generated during the sewage sludge composting process due to their volatility and low odour detection threshold (Maulini-Duran et al., 2013; Nie et al.,

2019; Schiavon et al., 2017). Their emission during sewage sludge composting is characterized by its uncertainty, its compositional complexity and its periodicity or variability along the process, and hence its characterization becomes a major challenge in order to correlate its emission with its contribution to odour and odour impact. In this sense, many VOCs families have been reported to be present in these emissions, being volatile organic sulphides, terpenes, ketones and carboxylic acids some of the main examples (He et al., 2017; Zhu et al., 2016).

During the study performed in the full-scale sewage sludge composting plant, some differences in the emission of the distinct VOCs families were observed between both treatment strategies in both the dynamic windrow and curing stages. As mentioned in section *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"*, the predominant VOCs families found in the gaseous emissions generated in the first active composting phase were terpenes, organosulphur compounds and ketones, which present similar emission trends for both treatment strategies. However, it is also interesting to know how the presence of different VOCs in a gaseous sample can influence its odour concentration. The seeking of a relation between the concentration of the different VOCs present in a gaseous sample and its odour concentration has been a topic of interest for researchers in the last years, aiming at making more objective measurements of this variable and being able to predict it by VOCs characterization (Blazy et al., 2015; Wu et al., 2015). Different authors have described odour activity values (OAV) as a useful tool to indicate the contribution to odour from individual compounds present in a complex gas mixture by taking into account its concentration and its odour detection threshold (Parker et al., 2012; Sivret et al., 2016). In this sense, Figure 5.4 shows the OAV of the major odour contributors (OAV > 1) quantified in the gaseous samples obtained along the dynamic windrows for both treatment strategies together with the odour concentration measured for each gaseous sample.

a)



b)



**Figure 5.4.** Odour concentration and odour activity values (OAVs) of the major odour contributors quantified in the gaseous samples obtained from the dynamic windrows of both treatment strategies. (a) 4-d WRT dynamic windrow; (b) 14-d WRT dynamic windrow.

It can be observed a slight relation between the evolution of odour concentration measured in each sampling point along the dynamic windrows and the OAV calculated for the VOCs quantified in each sample. The major contributors to odour quantified for both treatment strategies were: skatole at the beginning of the process, which is a typical VOCs related to wastewater treatment and sewage sludge,

due to its very low ODT (0.006 ppb$_v$), butanoic acid, which is a volatile fatty acid typically produced during anaerobic degradation of organic matter with a low ODT (0.190 ppb$_v$), and DMS and DMDS, which are also typical organosulphur compounds produced by anaerobic degradation of sulphur compounds present in sewage sludge. The OAV can be a helpful tool to detect the main odour contributors of a gaseous mixture in order to apply correction or mitigation actions, such as the promotion of real aerobic conditions during composting to minimize or avoid the formation of strong odorants such as volatile fatty acids or organosulphur compounds. Nevertheless, a strong correlation between OAV and odour concentration cannot be depicted from the data presented, and it is even unlike to found reliable correlations of these variables in literature (Wenjing et al., 2015). In this sense, important factors such as the existence of synergistic and antagonistic effects between different odorants present in the gaseous samples, the variability of the physical-chemical characteristics of the waste treated or the fact that not all the VOCs present in a complex gas mixture are normally calibrated in the laboratory are some of the limitations faced when trying to correlate OAV and odour concentration (Hanajima et al., 2010), and explain why these two variables cannot be perfectly correlated (Gallego et al., 2012). Consequently, the use of OAV as an odour concentration predictor can affect in a great extent to the underestimation of odour nuisance.

On the other hand, as shown in section *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"*, a high variance was observed in the gaseous emissions from the curing piles of both treatment strategies. The abundance of some of the main VOCs observed during the first active composting phase such as organosulphur compounds and ketones was reduced during the curing phase because of their rapid formation and emission at the first stages of the composting process (Hort et al., 2009; Schiavon et al., 2017). In contrast, the abundance of more complex compounds such as aldehydes or siloxanes increased at the latter stages of the treatment strategy 2, what can be explained by the fact that these compounds are normally formed from larger organic molecules that need more time to be biodegraded (Smet et al., 1999). However, the increase of siloxanes abundance can be also explained by the fact that some silicoorganic compounds were slowly disaggregated from the chromatographic

column (known as column bleeding). This fact, in addition to a low VOCs emission in quantity and diversity, can cause that a detected compound in a gaseous sample represents a high percentage of the total emission. Figure 5.5 shows the OAV of the major odour contributors (OAV > 1) quantified in the gaseous samples obtained during the curing stages for both treatment strategies together with the average odour concentration measured for each gaseous sample.
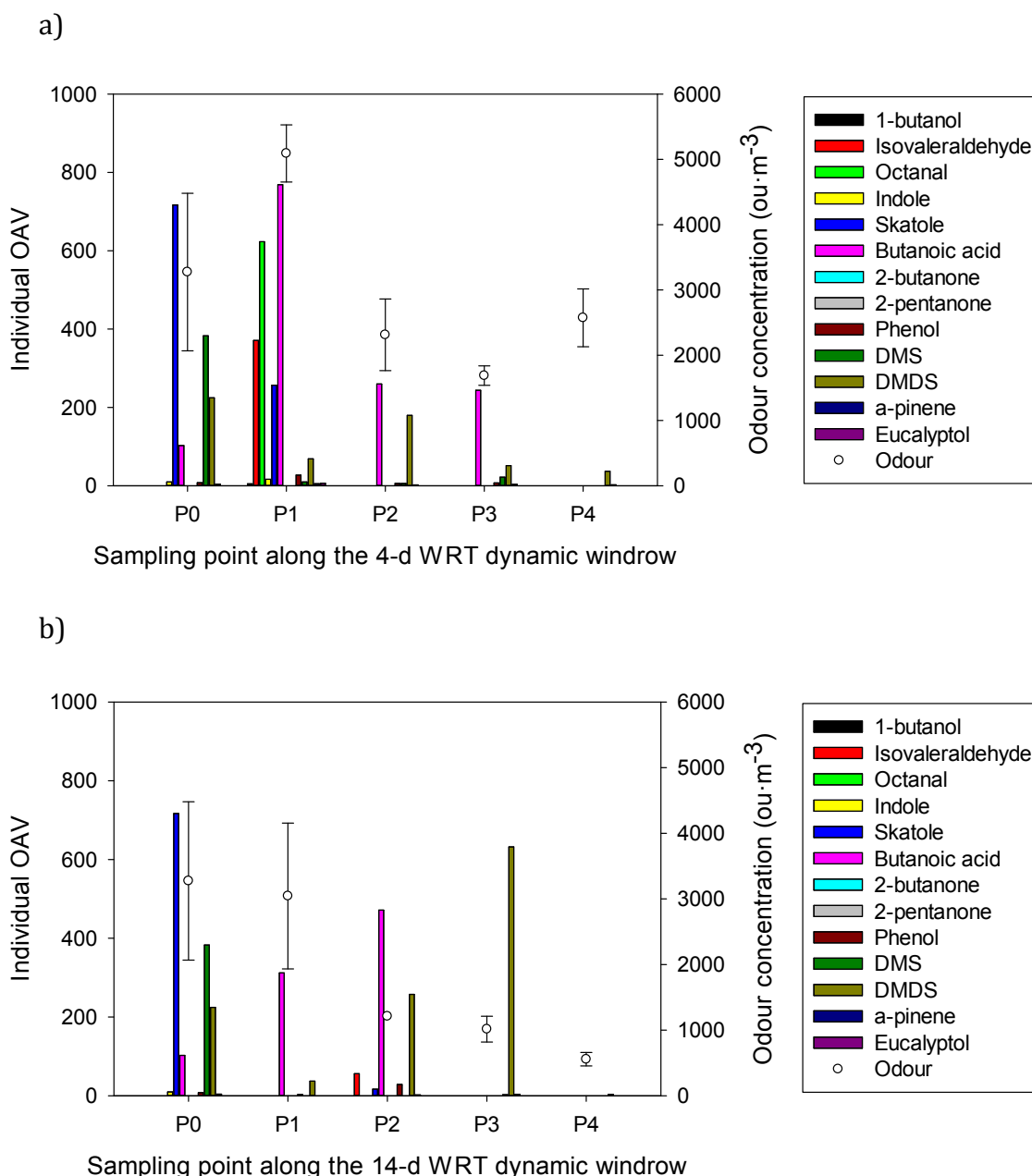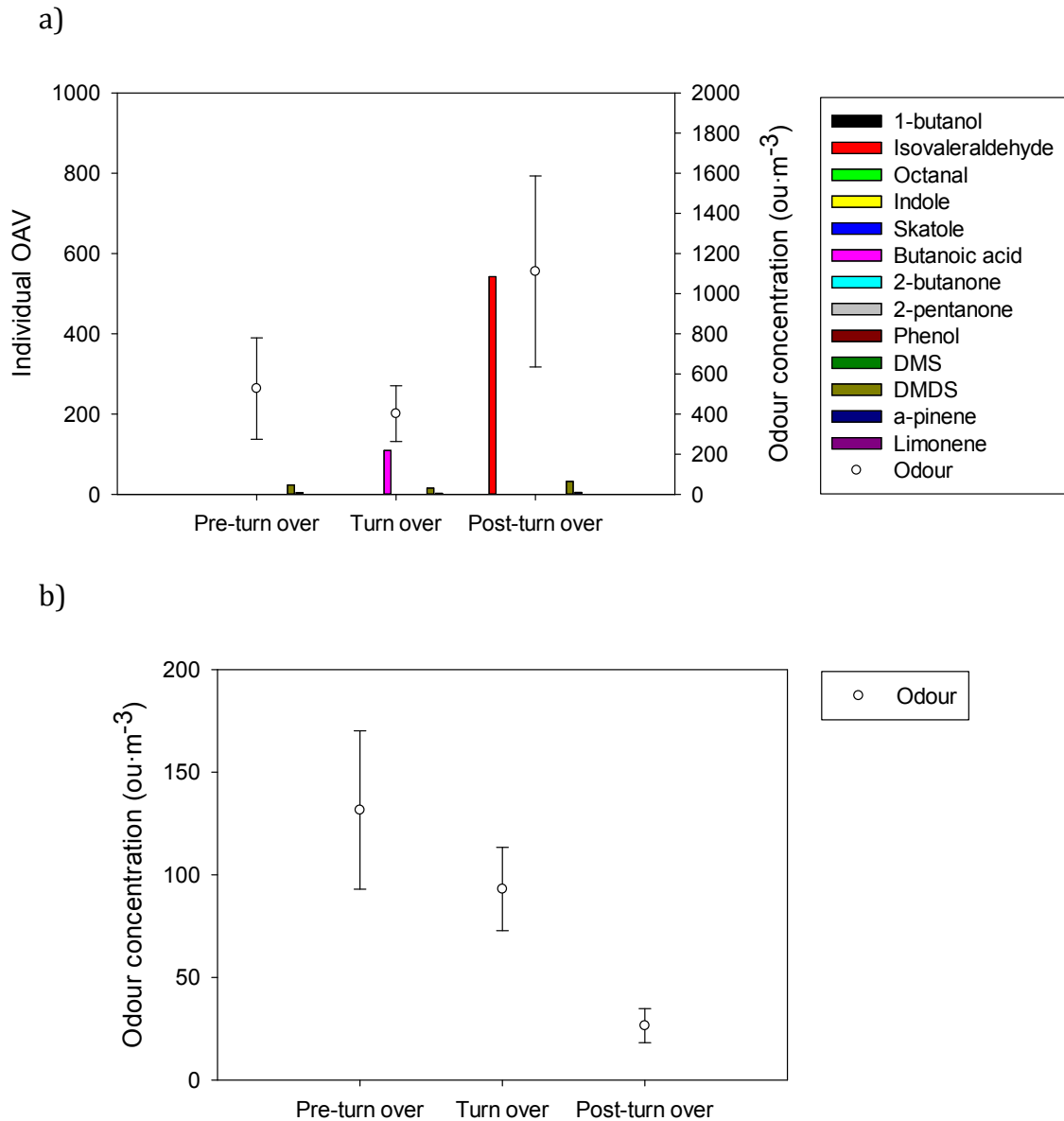
a)



b)



**Figure 5.5.** Odour concentration and odour activity values (OAVs) of the major odour contributors quantified in the gaseous samples obtained from the curing piles of both treatment strategies. (a) 4-d WRT curing pile; (b) 14-d WRT curing pile.

As it can be observed in Figure 5.5, the results obtained from the gaseous emissions generated by (a) curing pile 1 and (b) curing pile 2 show that the relation between odour concentration and the individual OAVs does not fit. As mentioned before, one of the limitations that OAV presents when it comes to correlate it with odour concentration is the lack of some specific VOCs calibration for their quantification. In this sense, it can be observed that in Figure 5.5 (a) just isovaleraldehyde and butanoic acid are present, when the qualitative analysis presented in section *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"* shows that their abundance was lower in comparison to other main VOCs families such as terpenes or ketones. Consequently, it cannot be stated that the increase in odour concentration measured during the third sampling day of curing pile 1 is a consequence of the peak of isovaleraldehyde observed, because as mentioned before, other not quantified VOC and their synergistic or antagonistic effects can affect the final odour concentration measured. On the other hand, the results obtained from curing pile 2 (Figure 5.5 (b)) show a really low odour concentration –close to ambient air odour concentration– and consequently a low VOCs diversity and quantity. In fact, any VOC was quantified in the samples obtained from the curing pile 2 any of the sampling days. So in this case, any kind of relation between OAV and odour concentration can be attributed.

## 5.1.4. Estimation of odour immission at the surroundings of the full-scale sewage sludge composting plant by simple dispersion modelling.

Based on the odour emission data presented in section *"4.2. A systematic study on the VOCs characterization and odour emissions in a full-scale sewage sludge composting plant"* and the meteorological data obtained from a nearby station (Meteoblue, 2019), a simple dispersion model has been applied to evaluate the odour impact on the surroundings of the sewage sludge composting plant in terms of odour immission. The model used is a Turbulent – Gaussian diffusion model, which is a mathematical description of transport and diffusion processes of contaminants based on different factors that influence this dispersion, such as the type of emission and the meteorology, amongst others (Capelli et al., 2013b). The expression defining the dispersion and transport behaviours of a pollutant emitted used for the calculations is presented below (Equation 5.1, Gostelow et al., 2001).

$$C\,(x,y,z) = \frac{Q}{2\pi\sigma_y\sigma_z \cdot u}\left[exp\left(-\frac{y^2}{2\sigma_y^2}\right)\right]\left[exp\left(\frac{-(z-H)^2}{2\sigma_z^2}\right) + exp\left(\frac{-(z+H)^2}{2\sigma_z^2}\right)\right] \qquad (Eq.\,5.1)$$

where: C (x, y, z) is the odour concentration at the coordinates *x, y, z* of the plume (ou·m⁻³); Q is the odour emission rate (ou·s⁻¹); $\sigma_y$ and $\sigma_z$ normal deviations are defined by the atmospheric stability and depend on the distance to the emission point in the direction of the wind (m); u is the wind velocity (m·s⁻¹); H is the effective height of the emission source (m).

Wind speed and atmospheric conditions are the main meteorological variables affecting contaminant's dispersion. Briefly, Gaussian plume models use Pasquill-Gifford-Turner atmospheric stability classes for the characterization of the vertical and lateral dispersion (United States Environmental Protection Agency (USEPA), 1995b), which are divided into six categories from Extremely unstable (A) to Moderately stable (F) depending on the wind velocity and solar irradiation. Atmospheric stability conditions affect directly to the dispersion of contaminants in air, being the most unstable conditions the best scenario for contaminant's dispersion. Depending on the atmospheric stability conditions, the normal deviations $\sigma_y$ and $\sigma_z$ can be calculated using equations 5.2 and 5.3.

$$\sigma_y = 0.15 \cdot a \cdot x^b \qquad (Eq.\,5.2)$$

$$\sigma_z = c \cdot x^d \qquad (Eq.\,5.3)$$

where: *a*, *b*, *c* and *d* are constant parameters defined by the atmospheric stability condition used (A to F), x is the distance from the emission source (m).

Three different meteorological scenarios have been proposed to assess the odour immission at the surroundings of the sewage sludge composting plant for each treatment strategy. The maximum, minimum and average wind speeds registered during August 2017 by the meteorological station of Ariany (Table 5.1) (Meteoblue, 2019) have been used to define the atmospheric stability conditions and hence to estimate the odour immission around the composting facility.

**Table 5.1.** Atmospheric stability scenarios and emission characteristics used for odour impact assessment.

| Wind velocity (m·s$^{-1}$) | Atmospheric stability conditions |
|:---:|:---:|
| 0.28 | Extremely unstable (A) |
| 9.72 | Moderately stable (F) |
| 3.35 | Slightly unstable (C) |
| **Emission characteristics** | |
| OER 4-d WRT strategy (ou·s$^{-1}$) | 455 |
| OER 14-d WRT strategy (ou·s$^{-1}$) | 251 |
| Effective height of the emission source (m) | 3 |

In Europe, some reference values have been published by the authorities of some countries and/or regions in order to regulate and control the odour impact generated by potential activities such as waste and wastewater treatment, animal food production or meat and dairy processing. For example, The Netherlands published the *Netherlands Emission Guidelines for Air*, where a list of maximum immission values for odour concentration are defined depending on the type of activity (Rijkswaterstaat Environment, 2004). On the other hand, the collaboration between the England and Wales Environment Agency, the Scottish Environment Protection Agency and the Northern Ireland Environment and Heritage Service lead to the publication of the Technical Guidance Note IPPC H4 draft *"Horizontal Guidance for Odour"*, where the reference values are classified as function of the type of activity and its odour "offensiveness" (England and Wales Environment Agency et al., 2002). Finally, the Government of Catalonia presented a draft legislative proposal against odour pollution defining the reference values for odour immission depending on the activity developed (Generalitat de Catalunya, 2009). In Table 5.2, some examples of different activities and their reference value are presented.

**Table 5.2.** Odour immission values proposed by different European governmental authorities.

| Activity | Reference | Odour offensiveness | Odour immission value (ou·m$^{-3}$) |
|---|---|---|---|
| Waste Management | 1 | – | 1.5 – 3 |
| | 2 | High | 1.5 |
| | 3 | – | 3 |
| Wastewater treatment | 1 | – | 0.5 – 3.5 |
| | 2 | High | 1.5 |
| | 3 | – | 5 |
| Flavour and fragrance production | 1 | – | 2 – 3.5 |
| | 2 | Low | 6 |
| | 3 | – | 7 |
| Animal fats production | 1 | – | 2.5 |
| | 2 | High | 1.5 |
| | 3 | – | 3 |
| Slaughterhouses | 1 | – | 0.55 – 1.5 |
| | 2 | High | 1.5 |
| | 3 | – | 3 |

1 Rijkswaterstaat Environment (2004)

2 England and Wales Environment Agency et al. (2002)

3 Generalitat de Catalunya (2009)

None of these regulatory documents presents an odour immission limit value for sewage sludge composting or management. However, the most restrictive limit for wastewater treatment activities (0.5 ou·m$^{-3}$) has been adopted to interpret and discuss the results. By applying the model equation, the odour immission concentration at ground level can be estimated at the desired distance of the emission source. In this sense, the distance at which odour concentration is permissible for the different scenarios proposed are presented in Table 5.3.

**Table 5.3.** Minimum distance at which odour concentration is below the immission limit of 0.5 ou·m$^{-3}$ for the different scenarios.

| Treatment strategy | Atmospheric stability conditions | Wind velocity (m·s$^{-1}$) | Distance from the emission source (m) |
|---|---|---|---|
| 4-d WRT | Extremely unstable (A) | 0.28 | 152 |
| | Moderately stable (F) | 9.72 | 77 |
| | Slightly unstable (C) | 3.35 | 89 |
| 14-d WRT | Extremely unstable (A) | 0.28 | 109 |
| | Moderately stable (F) | 9.72 | 57 |
| | Slightly unstable (C) | 3.35 | 65 |

The results obtained from this simple simulation show higher immission values at the surroundings of the composting plant for the 4-d WRT treatment strategy, hence the minimum distance at which the odour immission value becomes lower than the odour immission limit value adopted for this treatment strategy. However, the use of more powerful atmospheric dispersion modelling tools such as ADMS, AERMOD or ISC3 will give a better picture of the real odour dispersion of the emission source by using integrated meteorological data for long-time periods and real orographic and topographic data (Capelli et al., 2013b).

## 5.2. Gaseous emissions derived from the sewage sludge biodrying process

### 5.2.1. Evolution of the sewage sludge biodrying process and its associated emissions

Sewage sludge biodrying is a novel technology based on the mechanisms of composting that seeks to remove part of the water content present in sewage sludge and reduce its volume and its biological activity by means of forced high aeration rates together with the metabolic heat generated during the aerobic degradation of the easily biodegradable organic matter (Frei et al., 2004; Villegas and Huiliñir, 2014). The objective of this technology is to obtain a low moisture content product with a considerable LCV that can be lately used as a biomass fuel (Adani et al., 2002).

The sewage sludge biodrying technology has been a topic of interest for related researchers during the last years. From understanding the basic mechanisms of this process (Frei et al., 2004) to optimizing different parameters to improve the performance of the technology (Cai et al., 2013; Zhang et al., 2018; Zhao et al., 2010), different authors have helped to develop this technology. The main objective of this work was not to further optimize the process performance but to fill in the main scientific gap found in literature for this treatment technology: gaseous emissions. However, a follow-up of the performance of the process is needed to link it with the related gaseous emissions generated.

As presented in section *"4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions"*, two different temperature stages (thermophilic and mesophilic) can be differentiate during the SS biodrying process, which are much related to the emission of the different pollutants. For SS composting processes, it has been reported the existing relation between temperature and emission of $NH_3$ (Pagans et al., 2006a), VOCs (Maulini-Duran et al., 2014, 2013) and $H_2S$ (Chen et al., 2010). $CH_4$ emission has been generally linked to the presence of anaerobic zones in the solid matrix due to excessive moisture content, insufficient porosity or inadequate aeration (Amlinger et al., 2008). In addition, the high content of easily biodegradables organic matter can lead to oxygen depletion due to a high biological activity and hence, the formation of

anaerobic areas, promoting $CH_4$ formation and emission. The case of $N_2O$ emission is more complex due to the different formation and emission pathways that can play their own role depending on the characteristics of the solid matrix and the process conditions (Ahn et al., 2011; Moënne-Loccoz and Fee, 2010).

In order to evaluate the relations between the evolution of the process in terms of temperature and the emission of the different pollutants, the percentage of each pollutant emitted during the different temperature stages of the process has been calculated. To do so, the sewage sludge biodrying process has been divided into three main phases: a pre-thermophilic phase, a thermophilic phase (temperature > 41ºC) and a post-thermophilic phase. Even though the pre- and post-thermophilic temperatures are numerically the same, this subdivision is used instead of a mesophilic subdivision to differentiate and determine the percentage of each pollutant emitted at the very beginning of the process and after the thermophilic phase. Table 5.4 shows the percentage of emission of each pollutant (including odour) during each temperature stage of the SS biodrying process.

**Table 5.4.** Distribution of the emission of each pollutant (%) during the different temperature stages of the SS biodrying process.

| Pollutant | Pre-thermophilic phase | Thermophilic phase | Post-thermophilic phase |
|:---:|:---:|:---:|:---:|
| $NH_3$ | 0 | 79.2 | 20.8 |
| tVOCs | 0 | 94.6 | 5.4 |
| $H_2S$ | 0 | 100 | 0 |
| Odour | 1 | 73.1 | 25.9 |
| $CH_4$ | 3.5 | 69.7 | 26.8 |
| $N_2O$ | 10.9 | 36.4 | 52.7 |

The emission of the different pollutants mainly occurs during the thermophilic phase, with the exception of $N_2O$. $NH_3$, tVOCs and $H_2S$ emission are comprised in the thermophilic phase between a 79.2 to a 100%, showing the close relation between the temperature of the sewage sludge and the emission of these compounds along the process (Chen et al., 2010; Maulini-Duran et al., 2013; Pagans et al., 2006a; Yuan

et al., 2016). Consequently, the maximum percentage of odour emission during the sewage sludge biodrying also occurred during the thermophilic phase, as $NH_3$, VOCs and $H_2S$ are the main odorant compounds formed and emitted during the sewage sludge treatment.

In the case of $NH_3$, Pagans et al. (2006a) showed and concluded with a bench-scale study of a SS composting process that a strong relationship between $NH_3$ and temperature existed. This fact was also observed at full-scale in the results presented in section *"4.1. The effect of the composting time on the gaseous emissions and the compost stability in a full-scale sewage sludge composting plant"*, as well as during the SS biodrying process shown in this thesis, in terms of emission patterns and emission percentage during the different temperature stages of the biodrying process. Recently, Zhang et al. (2017) observed the same $NH_3$ emission trend during the SS biodrying process in a full-scale facility, reporting the highest emission rates during the first stage of the process at thermophilic conditions. Moreover, the emission of $NH_3$ is also related with the variation in pH during the biological process, which normally is increased during the thermophilic phase, displacing the $NH_4^+/NH_3$ equilibrium to the $NH_3$ formation and emission.

The emissions of tVOCs and $H_2S$ are shown to be more closely related with the temperature of the solid matrix, being emitted a 95% of the tVOCs and a 100% of the $H_2S$ during the thermophilic phase of the SS biodrying process. Different authors have reported similar situations during the SS composting, presenting the higher tVOC emission during the thermophilic phase of the process. For example, Maulini-Duran et al. (2013) observed the maximum tVOC emission rates during the first three days of a bench-scale SS composting process. On the other hand, Chen et al. (2010) reported how the amount of $H_2S$ formed and emitted was related to the temperature pattern of the material during a full-scale SS composting study, concluding that $H_2S$ is produced mainly during the thermophilic stage and that the maximum $H_2S$ emission rate was found to be at the beginning of the thermophilic phase.

$CH_4$ emissions were also concentrated during the thermophilic phase of the SS biodrying process. However, even though the predominance of $CH_4$ emissions during the high temperature phase, the percentage observed during the post-

thermophilic phase is quite high. This difference can be explained by the fact that $CH_4$ is mainly formed due to the appearance of anaerobic zones around the SS during the biodrying process. These anaerobic spots appear as organic matter is being consumed and the solid matrix losses its structure and porosity, what limits the oxygen transfer and favours the formation of anaerobic zones. Even though high aeration rates were used during the SS biodrying process, the quick oxygen depletion during the high biological activity period could lead to the formation of these anaerobic spots and hence promote the formation and emission of $CH_4$. Nevertheless, as it has been reported in SS composting studies, $CH_4$ is emitted mainly during the high temperature and biological activity periods (Amlinger et al., 2008; Awasthi et al., 2018).

The case of $N_2O$ emission observed during the SS biodrying process is the one that does not follow the typical trend of maximum emission during the thermophilic stage. In this sense, $N_2O$ emissions generated during composting have created controversies and in fact, there is not a general agreement around the scientific community in terms of how is $N_2O$ emitted during SS composting. As explained in section *"4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions"*, the formation and emission of $N_2O$ are referred basically to denitrification and incomplete nitrification processes (Moënne-Loccoz and Fee, 2010). Some works have reported the majority of the $N_2O$ emission during the thermophilic stage of the composting process (Awasthi et al., 2018), whereas others found higher $N_2O$ emissions once the composting process temperature felt down to mesophilic conditions, together with the high ammonia concentration present during the thermophilic stage, what inhibits nitrification (Fukumoto et al., 2003).

To the author's knowledge, this is the very first reported inventory of gaseous emissions generated during a bench-scale SS biodrying process. Even though the emission patterns of typical compounds such as $NH_3$, tVOCs or $CH_4$ are similar to the ones referred to SS composting, it results clear that deeper research is needed in order to better understand the dynamics of pollutant's emissions, the process conditions that most affect them and the evolution of the microbial population

responsible for its formation and emission, what could help in fixing better process conditions to minimize these emissions.

## 5.2.2. Characterization of the VOCs and odour emissions from the biodrying process of conventional sewage sludge

Figure 5.6 shows the evolution of the odour concentration measured in the gaseous emissions generated during the SS biodrying process together with the temperature measurements of the material inside the bioreactor.
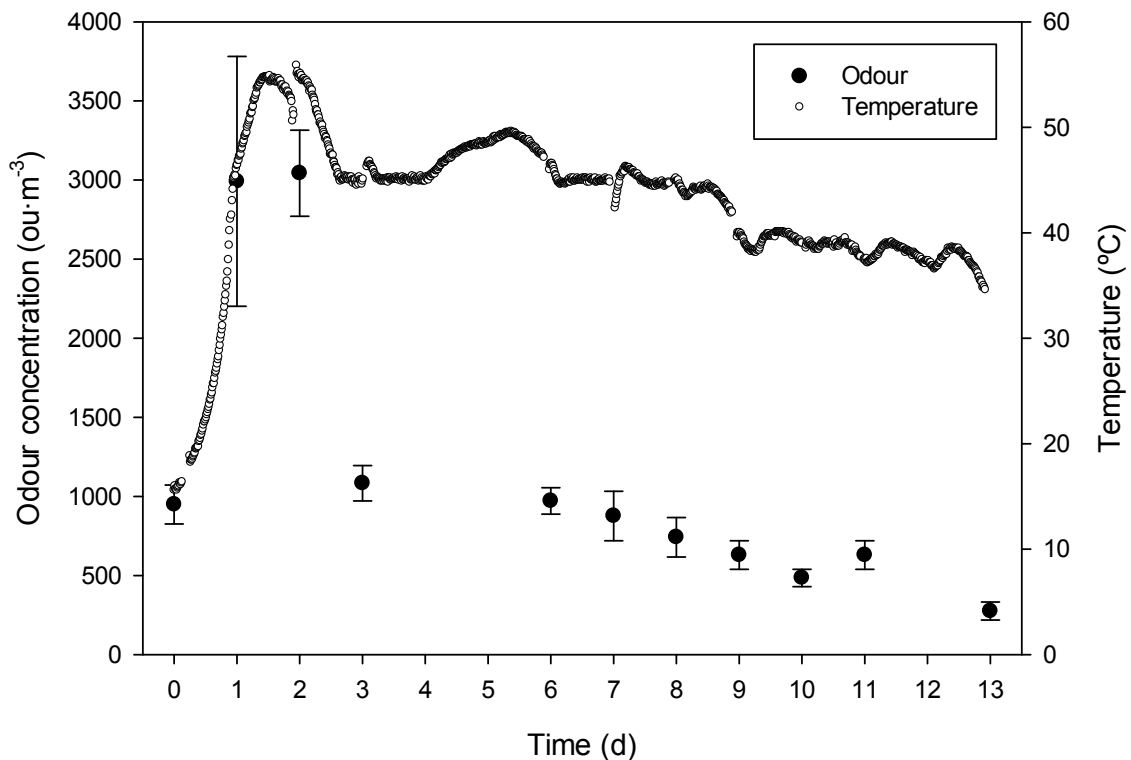


**Figure 5.6.** Evolution of the temperature of the material and odour concentration (ou·m$^{-3}$) measured in the gaseous emissions during the SS biodrying process.

The odour emission dynamics observed in Figure 5.6 are similar to what is reported to happen during SS composting processes (González et al., 2019b; Rincón et al., 2019). Maximum odour concentrations were measured during the thermophilic stage while biological activity is high and easily biodegradable organic matter is being consumed, what leads to the formation and emission of different odorant VOCs, amongst others. Lately, as temperature and biological activity decrease, the emission of those compounds is reduced and hence, the odour concentrations measured in the gaseous emissions are lower. The presence of

different odorant VOC groups such as organosulphur compounds, aldehydes, carboxylic acids and terpenes can explain somehow the variation on the odour concentration measured in the different stages of the SS biodrying process.

As shown in section *"4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions"*, terpenes were the predominant VOCs group (70 – 80%) from the gaseous emissions generated during the whole SS biodrying process. The large abundance of terpenes can be explained by the fact that pruning waste was used as bulking agent during the experiment (Schiavon et al., 2017), with a high 1:3 v/v ratio (SS:PW), as well as that some may appear as intermediate products of aerobic biodegradation of organic matter. The other abundant VOC group found were organosulphur compounds, which during the thermophilic stage presented a 15% abundance over the whole sample. Organosulphur compounds have been reported as typical VOC emitted during the first stages of the biological treatment of SS (Schiavon et al., 2017). As previously mentioned, it exists a clear relation on how the concentration of different VOCs species contributes to the odour concentration found in gaseous emissions. In this sense, the individual OAV of the quantified VOCs have been estimated to present the maximum contributors to odour found in the gaseous samples obtained from the emissions generated during the thermophilic and the mesophilic stages of the SS biodrying process, which are shown in Figure 5.7 (OAV > 1) altogether with the related odour concentration.
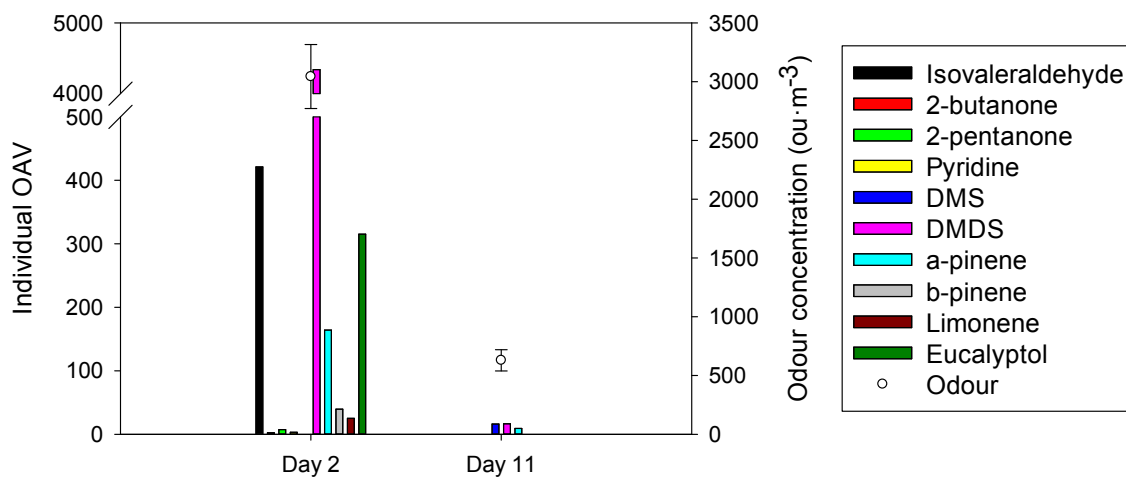
**Figure 5.7.** Odour concentration (ou·m$^{-3}$) and odour activity values (OAVs) of the major odour contributors quantified in the gaseous samples obtained from the SS biodrying process during the thermophilic (day 2) and mesophilic (day 11) stages.

In Figure 5.7 it can be observed that during the thermophilic stage, when biological activity was at its maximum, the odour concentration measured in the gaseous emissions was high –in fact, the highest odour concentration measured during the SS biodrying process–. This moment coincided with the emission of some odorant VOCs such as DMDS (9545.7 ppb$_v$), isovaleraldehyde (42.1 ppb$_v$), α-pinene (2955.5 ppb$_v$) and eucalyptol (3782.9 ppb$_v$), which contributed greatly to odour due to their high concentration and/or low ODT, as it has been previously reported elsewhere (Nagata, 2003; Nie et al., 2019). In contrast, the odour concentration measured in the gaseous emissions of day 11 when the process was at mesophilic conditions and biological activity should be low, was one of the lowest odour concentrations registered during the SS biodrying process, similarly to what has been reported for SS composting processes (Rincón et al., 2019). This low odour concentration fits with the low emission of the different odorant VOCs quantified in the same gaseous sample such as DMS (48.5 ppb$_v$), DMDS (36.5 ppb$_v$) or α-pinene (165.9 ppb$_v$). However, as it has been mentioned before in this thesis, it should be remarked that OAV are taken into account as indicators of the contribution to odour of the individual odorants, but not as a tool to predict odour concentration as it has not been possible to stablish an OAV – odour concentration relationship neither during SS composting nor SS biodrying processes.

**5.2.3. Comparison of the gaseous emissions generated during the biodrying and the composting processes of conventional sewage sludge**

Sewage sludge biodrying has been studied in detail during the last years by different researchers aiming at improving the process by optimizing different operational conditions (Cai et al., 2013; Huiliñir and Villegas, 2015). However, as it has been mentioned in this thesis, no consolidated works dealing with the odour and greenhouse gaseous emissions generated by this technology and its environmental impact are available in literature. Consequently, this last section of the thesis aims to compare the obtained emission factors for the different pollutants evaluated with some of the available literature dealing with gaseous emissions from SS composting to extract some conclusions on how and why they differ. Even though the objectives and operational parameters of each technology are different, SS biodrying process follows the main mechanisms involved in the biodegradation of organic matter are the same, so the pollutant's formation and emission pathways should be similar enough to sustain this comparison.

Table 5.5 shows the emission factors for $NH_3$, tVOCs, $H_2S$ and odour obtained from the SS biodrying process and different emission factors obtained from SS composting literature. In terms of GHG emissions, Table 5.6 shows the emission factors for GHG ($CH_4$ and $N_2O$, expressed in kg of $CO_{2equivalent}$ per Mg of dry matter from SS) obtained from the SS biodrying process and different GHG emission factors obtained from SS composting literature.

**Table 5.5.** Comparison between the emission factors of different odorants from SS biodrying and SS composting processes.

| | Technology | NH$_3$ (kg·Mg$^{-1}$ DM-SS*) | tVOCs (kg·Mg$^{-1}$ DM-SS*) | H$_2$S (kg·Mg$^{-1}$ DM-SS*) | Odour (ou·Mg$^{-1}$ DM-SS*) |
|---|---|---|---|---|---|
| **SS Biodrying** | 100-L reactor | 1.23 | 0.14 | 1.68E-03 | 3.10E+07 |
| **Maulini-Duran et al. (2013)** | 50-L SS composting reactor | 1.33 – 4.12 | 0.66 – 1.00 | – | – |
| **Rincón et al. (2019)** | 300-L SS composting reactor | 2.16 | 1.21 | – | 9.35E+08 |
| **Yuan et al. (2016)** | 60-L SS composting reactor | 0.96 – 3.04 | – | – | – |
| **Han et al. (2018)** | Full-scale SS composting plant | – | – | 0.03 – 0.06 | – |
| **González et al. (2019a, 2019b)** | Full-scale SS composting plant | 25.32 | 6.17 | – | 9.45E+08 |

\* DM-SS: dry matter from sewage sludge.

**Table 5.6.** Comparison between the emission factors for $CH_4$ and $N_2O$ from SS biodrying and SS composting processes.

| | Technology | $CH_4$ (kgCO$_{2eq}$·Mg$^{-1}$ DM-SS*) | $N_2O$ (kgCO$_{2eq}$·Mg$^{-1}$ DM-SS*) | GHG (kgCO$_{2eq}$·Mg$^{-1}$ DM-SS*) |
|---|---|---|---|---|
| **SS Biodrying** | 100-L reactor | 1.27 | 26.95 | 28.22 |
| **Maulini-Duran et al. (2013)** | 50-L reactor | 1.59 – 1.86 | 3.39 – 8.04 | 4.98 – 9.90 |
| **Pan et al. (2018)** | 150-L reactor | 2.93 – 9.70 | 26.36 – 131.63 | 36.05 – 134.56 |
| **Yuan et al. (2016)** | 60-L reactor | 78.17 – 147.47 | 89.30 – 125.05 | 170.43 – 272.52 |

* DM-SS: dry matter from sewage sludge.

As it can be observed, plausible differences exist between the emission factors referred to both SS treatment processes. In general, the emission factors obtained from the bench-scale SS biodrying process are lower than the ones reviewed in literature. These differences come up due to three main aspects.

- Process operation conditions: Even though SS biodrying is ruled by the main mechanisms of a composting process, the aim of the process is totally different so operational parameters such as aeration rate, turning frequency or total process time also differ, which can affect somehow to the total emission of the different pollutants.

- Substrate nature: Although the same kind of organic waste is being treated in the references shown in Table 5.5, the substrate nature and its physical-chemical characteristics may vary, even if they came from similar regions. Pollutant's emission present a high dependence on the characteristics of the main feedstocks.

- Scale of the process: Compared with full-scale processes, it results easier to control and monitor a lab/bench-scale composting or biodrying process, where emission rates are easily measured and temperature and aeration are easily controlled.

Different process parameters can affect the emission of the different pollutants during SS biodrying. For example, low aeration and inadequate moisture content have been reported to increase the emission of GHGs during the SS composting and biodrying processes (Yuan et al., 2016; Zhang et al., 2017), what fits with the lower emission observed in the present SS biodrying process with respect to the reviewed SS composting literature. A recent study on the evolution of the biodiversity present in SS and its relation with $N_2O$ formation and emission during a full-scale SS biodrying process by Zhang et al. (2017) showed that aeration regulation plays an important role in controlling $N_2O$ formation and emission pathways. Yuan et al. (2016) reported the $NH_3$, $CH_4$ and $N_2O$ emission trends and factors during the SS composting in a 60 L bench-scale reactor, showing similar $N_2O$ emission dynamics as the ones reported in section *"4.3. Filling in sewage sludge biodrying gaps: Greenhouse gases, volatile organic compounds and odour emissions"*, where once the material fell into mesophilic conditions, $N_2O$ emission tended to increase. Moreover, it was reported that higher aeration rates reduced total $NH_3$ and $CH_4$ emissions along the SS composting process due to its limitation effect over the material's temperature increase and its oxygen availability's increase, respectively, as it happened during SS biodrying. On $CH_4$ side, it is observed that the higher aeration rate used during SS biodrying helps into minimizing $CH_4$ formation and emission due to a better oxygen availability in comparison to what is observed in SS composting processes, where the formation of anaerobic zones and hence the emission of $CH_4$ is more susceptible to happen. Moreover, as the process is scaled up into full-scale, adequate turning of the material becomes important to avoid compaction and maintain a proper porosity to enhance oxygen diffusion through all the material and minimize the possible formation of anaerobic zones and emission of $CH_4$.

Taking into account that SS composting and SS biodrying are two different SS treatment processes seeking different treatment goals, from this first gaseous emission's inventory referred to SS biodrying, in general it can be stated that the higher aeration rates used, a proper mixing frequency of the material and the shorter time of process are key aspects that helps into minimizing the emission of the typical reported SS composting gaseous pollutants. However, as it has been mentioned before, deeper research into the effect of the different parameters of the

SS biodrying process on the related gaseous emissions is needed to better understand its formation and emission dynamics and to be able to better assess the environmental impact of this SS treatment process.

# CHAPTER 6: CONCLUSIONS AND FUTURE WORK

This thesis fully characterized the gaseous, VOCs and odorous emissions generated during the treatment of sewage sludge by two different biotechnologies, sewage sludge composting in a full-scale plant and sewage sludge biodrying in a bench-scale plant. The main conclusions and the possible future work derived from this thesis are presented below:

## 6.1. Full-scale sewage sludge composting plant

- By increasing the first active composting phase from 4 to 14 days, the sewage sludge composting process was optimized in terms of temperature evolution and biological stabilization of the material. This optimization was clearly observed during the first active composting phase, what could lead to a reduction of the curing phase time to process more material in the same time.

- This process optimization had a direct impact on the gaseous emissions generated during the sewage sludge composting process, minimizing them especially during the curing phase.

- A strong relationship between tVOCs and $NH_3$ emissions and material temperature was observed. Higher pollutant's emissions were observed when the process was at thermophilic conditions, which coincides with higher biological activity.

- The emission factors for $NH_3$, tVOCs and odour emissions referred to the global treatment were obtained for both treatment strategies, showing that by increasing the first active composting phase time, these emission factors were slightly increased. This was a consequence of the composting time increase and thereby the reduction of material treated per time unit during the first phase. However, the emission factors referred to the curing phase were significantly decreased when the first active composting phase time was increased from 4 to 14 days, leading to have lower gaseous and odorous emissions during the critical moment of the turning of the curing material.

- In terms of punctual environmental impact, it has been estimated that the odour immission concentration at a specific distance from the composting plant is lower when increasing the first active composting phase time from 4 to 14 days for each of the three scenarios proposed.

- The VOC inventory obtained from the gaseous emissions generated during the full-scale sewage sludge composting process shows that terpenes, organosulphur compounds, ketones and carboxylic acids were the main VOC groups emitted along the process.

- The contribution to odour of some specific VOC was assessed using the individual OAV. Isovaleraldehyde, butyric acid, DMS, DMDS and α-pinene were found to be the major odour contributors from the gaseous emissions generated during the sewage sludge composting process.

- It has been proven that the $OAV_{SUM}$ cannot be used as an odour concentration prediction tool for sewage sludge composting processes at these conditions due to different influential aspects such as the variability of the feedstocks or the synergistic and/or antagonistic effects between odorants in a complex gas mixture.

- Even though the mentioned benefits that the new strategy could add to the composting process performance, the related gaseous emissions and its environmental impact, its implementation could compromise the economical balance of the composting plant for two main reasons. Firstly, if working with the same facilities, its treatment capacity would be reduced. On the other hand, if the treatment capacity is desired to be maintained or incremented, and investment in reshape and enlargement of the plant should be conducted.

## 6.2. Bench-scale sewage sludge biodrying

- A proper performance of the conventional sewage sludge biodrying was achieved. By applying high aeration rates, moisture content of the material was reduced to a 36% and its LCV was increased to 7.1 MJ·kg$^{-1}$ of product, which is known to be sufficient for self-sustaining combustion, in 13 days of processing.

- The gaseous emissions of the majority of the pollutants evaluated ($NH_3$, tVOCs, $H_2S$ and $CH_4$), as well as odour emissions, were found to happen mainly during the thermophilic phase of the sewage sludge biodrying process.

- On the other hand, $N_2O$ emissions were found during both the thermophilic and the post-thermophilic phases of the process, being higher during the post-thermophilic phase. $N_2O$ emissions highly increased when material's temperature fell below the 40ºC, probably due to the promotion of the $NO_3^-$ denitrification by some denitrifying bacteria present in the sludge at these conditions. However, $N_2O$ formation and emission pathways are something that should be studied in deep in the future.

- The emission factors for $NH_3$, tVOCs, $H_2S$, odour, $CH_4$ and $N_2O$ were obtained, which are valuable information that help comparing different treatment strategies and evaluating its environmental impact.

- Since this is the very first inventory of gaseous and odorous emissions generated during the conventional sewage sludge biodrying process, the emission factors obtained have been compared with already published emission factors from sewage sludge composting processes due to their process similarities. Generally, the emission factors referred to the sewage sludge biodrying were lower than the ones referred to sewage sludge composting. The variations in here can be explained mainly by the differences in operational conditions (aeration rates or process time) and the physical-chemical variability of the feedstocks.

- The VOC inventory obtained from the gaseous emissions generated during the thermophilic and mesophilic phases of the bench-scale sewage sludge biodrying process shows that terpenes were the most abundant VOC group emitted along the process. However, other typical VOC groups such as organosulphur compounds, ketones, alkanes and alkenes were present in these gaseous emissions.

- The contribution to odour of some specific VOC was assessed using the individual OAV. Isovaleraldehyde, DMS, DMDS, $\alpha$-pinene and eucalyptol were found to be the major odour contributors from the gaseous emissions generated during the sewage sludge biodrying process.

## 6.3. Future work

Environmental impact and, especially, odour impact generated by sewage sludge management and treatment are topics of great interest not only for the scientific community but also for local authorities and plant managers/operators.

In terms of sewage sludge composting, this thesis gives an insight into how the gaseous and odorous emissions can be affected by the modification of operational parameters in order to optimize both the composting process and decrease the related environmental and odour impact to the surroundings of the composting plant. There is a widespread presence of lab and/or bench-scale sewage sludge composting studies aiming at providing and characterizing the related emission dynamics and emission factors of different pollutants, but there is a lack of information in terms of gaseous and odorous emissions' inventories at full-scale facilities. In this sense, it is important to keep on enlarging the knowledge about gaseous and odorous emissions from full-scale sewage sludge composting facilities to provide much more robust inventories, which can be very helpful for both local authorities and plant managers/operators when implementing new facilities. Due to the quick globalization occurred during the last decades, which is in fact going on, waste management should be optimized to avoid at the greater extent environmental and odour impact on the population, amongst other critical aspects. Therefore, the improvement of the information referred to gaseous and odorous emissions from different typologies of full-scale sewage sludge composting facilities with different treatment and/or operational strategies should be a line to follow to facilitate the proper implementation of new facilities or to optimize gas treatment strategies in already implemented plants in order to minimize environmental and odour impact.

In reference to sewage sludge biodrying processes, no robust information about gaseous and odorous emissions have been found in literature. Due to the fact that this is the first complete characterization of the gaseous and odorous emissions performed during a conventional sewage sludge biodrying process, it is obvious that much more work needs to be done to fully comprehend the pollutant's emission dynamics, how are they affected by the different operational strategies that can be applied to the biodrying process and which are the best practices to optimize the

sewage sludge treatment to obtain a valuable product minimizing its environmental impact. For example, the optimization of the aeration strategy can be an influential aspect on the reduction of GHGs emissions. On one hand, trying to avoid the formation of anaerobic spots around the material to minimize $CH_4$ emissions. On the other hand, trying to increase the thermophilic phase to minimize the promotion of $N_2O$ formation by denitrification at lower temperatures at the latter stages of the process. Furthermore, the gaseous and odorous emission inventory extracted from this thesis can be integrated with other data from the biodrying process to assess the environmental impact of this technology by means of Life Cycle Assessment techniques, which for sure will be helpful at the time of implementing it at larger scale.

In general, research focused on other typologies of organic wastes such as anaerobically digested sludge, which are also of great interest, and their related environmental impacts derived from their biological treatment, can and should be assessed by using similar methodologies as the ones described in this thesis. Research on this direction could help into increasing the existing knowledge related to gaseous emissions and environmental impact of the different wastes' treatment processes, which would be relevant to improve the treatment strategies applied with the objective of minimizing the associated environmental impacts.

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González, D., Colón, J., Sánchez, A., Gabriel, D., 2018. *Evaluation of the odorous compounds emitted in a full-scale sewage sludge composting plant and its relationship with the biological stability.* Chemical Engineering Transactions, 68, 175-180. Doi: 10.3303/CET1868030.

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González, D., Guerra, N., Colón, J., Gabriel, D., Ponsá, S., Sánchez, A. *A thorough characterization of the gaseous and odorous emissions from the composting of conventional sewage sludge.* Under preparation.

González, D., Colón, J., Sánchez, A., Gabriel, D. *Multipoint characterization of the emission of odorants and greenhouse gases from a full-scale wastewater treatment plant.* Under preparation.

## Conference contributions

González, D., Colón, J., Sánchez, A., Gabriel, D., 2017. *Emisiones gaseosas en procesos de tratamiento biológico de residuos. Caso práctico en una planta de compostaje de lodos de EDAR.* IV Conferencia Internacional sobre Gestión de Olores y COVs en el Medio Ambiente 2017, Valladolid, España (Oral presentation).

González, D., Colón, J., Sánchez, A., Gabriel, D., 2018. *Evaluation of the odorous compounds emitted in a full-scale sewage sludge composting plant and its relationship with the biological stability.* NOSE 2018: 6th International Conference on Environmental Odour Monitoring & Control, Milan, Italy (Oral presentation).

González, D., Guerra, N., Colón, J., Gabriel, D., Ponsá, S., Sánchez, A., 2019. *Assessment of the gaseous and odorous emissions generated during the sewage sludge biodrying process.* 8th International Conference on Biotechniques for Air Pollution Control and Bioenergy, Galway, Ireland (Oral presentation).

## Research projects

Proyecto COPCO: *Estudio de las mejoras en la planta de compostaje de lodos de depuradora de Ariany (Mallorca).* Convenio de colaboración entre la Universitat Autònoma de Barcelona y TIRME S.A (2016 – 2018).

Collaboration in the Horizon 2020 research and innovation programme MSCA-RISE 2014 *C-FOT-CTRL: Developing on line tools to monitor, control and mitigate GHG emissions in WWTPs.* Grant Agreement nº 645769 (2017 – 2019).

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