Aproveitamento de residuos agroforestais como fonte de biogas e compost

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Tese de doutoramento UDC / 2020

UNIVERSIDADE DA CORUÑA

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AUTORIZA

A Óscar Arias Vázquez a presentar a memoria titulada "**Aproveitamento de residuos agroforestais como fonte de biogas e compost**", que foi realizada baixo a miña dirección no Laboratorio de Enxeñaría Química na Facultade de Ciencias para optar ao grado de Doutor pola Universidade de A Coruña.

E para que conste aos efectos oportunos asina a presente en
A Coruña, a 24 de xullo de 2020.

Asdo. **Manuel Soto Castiñeira**

AGRADECEMENTOS

Non tiña claro se engadir este apartado mais a súa ausencia poderíase interpretar dun xeito que non me agradaba. Si teño claro que, chegado este momento e na forma de agradecementos ou máis vaidosamente na de adicatoria, ámbalas dúas terían unha única protagonista. A miña mai. O que agora remata, tomou folgos logo de ler unha nova no xornal *El Progreso de Lugo*. Na miña vila. Concretamente, na cafetería que hai diante da oficina de Correos. Apenas un pequeno paragrafo, na esquina inferior esquerda dunha das súas páxinas internas abondou para que todo empezase. Case sen lembrar da última vez que pisara a Universidade.

Dende entón, perdín conta das veces nas que teño lembrado daquela mañá. O que agora remata non deixa de ser outra cousa que o resultado dun continuo exercicio de malabares baixo o que conciliar unha tesa coa miña vida profesional e persoal. A miña maior recompensa viría dada no caso de que algún dos contidos que aquí se presentan supuxesen unha inspiración, por leve que esta fose, para outros por vir ou que xa están, no agromo de iniciativas para mellorar o escenario e atenualas actuais eivas do noso sector primario.

Sen ánimo de me extender moito, agradézolle a Manolo a dirección deste traballo e desatoar os non poucos partados e situacións que non podía resolver. Tamén, especialmente, e sen gardar relación, o que fixeches aló por decembro de 2017. Nos principios era máis dependente e recordando aqueles momentos, quero recoñecer a axuda e implicación do persoal do servizo de préstamo interbibliotecario da UDC así como animar ao estudantado a aproveitar o seu bo facer. Nesta viaxe e retrospectivamente, non podo esquecer as conversas con Helena. Tampouco ao amigo e compañeiro Pulgar. A Esther. A Henrique. A Raquel. Yuyixito. A Ruth tamén por botarme unha mau cando o precisei.

Por último y por supuesto por esto mismo, lo más importante, a la Señorita Sheila. Debo confesarte que todo el tiempo que te dije que pasaba con Claudio y el loro, no era del todo cierto. Las páginas que vienen a continuación me llevaron mi tiempo. Imposible decírtelo ahora porque dirías que soy un mentiroso. Prefiero que te hagas mayor y llegado el momento, y si algún día llegas a leer lo que ahora te dejo, sonrías. De la misma manera que lo estoy haciendo yo ahora.

En Sarria, a setembro de 2020.

RESUMO

En Galicia o uso forestal representa aproximadamente 2/3 da superficie total. A súa elevada produtividade ocasiona importantes cantidades fitomasa, en moitas ocasións sen valor comercial e susceptible de ser valorizada. Ao tratárense de materiais cunha elevada proporción de C, avaliouse a súa participación en compostaxe engadindo xurro de gando porcino, vector de auga e N, para impulsar o proceso. Ademais integráronse por primeira vez lodos resultantes da fabricación de taboleiros de fibra de media densidade (MDF) como aditivo a co-compostar. Os estudos ampliáronse coa avaliación de produción de biometano a partires da dixestión anaerobia destes lodos e das augas de proceso da industria de taboleiros MDF.

Os resultados acadados confirman a súa aptitude para seren transformados baixo as dúas técnicas (compostaxe e dixestión anaerobia) , subliñando factores a ter en conta para mellorar a eficiencia dos procesos. A investigación procurou a búsqueda de sinerxías entre distintos fluxos de residuos do sector agrogandeiro galego. Os beneficios acadados traduciríanse nunha vía de xestión distinta á aplicación directa ao solo das dexeccións gandeiras líquidas, da valorización dos residuos da industria forestal, e unha redución do combustible no monte co gallo de reducir o risco de incendio forestal.

RESUMEN

En Galicia, el uso forestal representa aproximadamente 2/3 de la superficie total. Su alta productividad proporciona cantidades significativas de fitomasa, en muchas ocasiones sin valor comercial y susceptible de ser valorizada. Al tratarse de materiales con una elevada proporción de C, se evaluó su participación en compostaje añadiendo purín de ganado porcino, vector de agua y N, para impulsar el proceso. Además, se integraron por primera vez lodos resultantes de la fabricación de tableros de fibra de densidad media (MDF) como aditivo de co-compostaje. Los estudios se ampliaron con la evaluación de la producción de biometano a partir de la digestión anaerobia de lodos y el agua de proceso de la industria de tableros de MDF.

Los resultados obtenidos confirman su aptitud para ser transformados mediante las dos técnicas (compostaje y digestión anaeróbica), subrayando los factores a tener en cuenta para mejorar la eficiencia de los procesos. La investigación buscó encontrar sinergias entre diferentes flujos de residuos en el sector agroforestal gallego. Los beneficios logrados se traducirían en una vía de gestión distinta a la aplicación directa al suelo de las deyecciones ganaderas líquidas, la recuperación de residuos de la industria forestal y la reducción de combustible en los montes gallegos con el fin de reducir el riesgo de incendio forestal.

ABSTRACT

In Galicia, forestland represents approximately 2/3 of the total area. Its high productivity provides significant amounts of phytomass, often unmarketable and capable of being valued. As they are predominantly materials with a high C proportion, their participation in composting was evaluated by adding pig slurry, acting as water and N vector, to boost the process. In addition, sludge resulting from the manufacture of medium density fiberboard (MDF) as a co-composting additive was integrated for the first time. Studies were extended with the evaluation of biomethane production from anaerobic sludge digestion and raw wastewater resulting from the MDF tableboard industry.

The results obtained confirm its suitability to be transformed by the two techniques (composting and anaerobic digestion), underlining the factors to be taken into account to improve the efficiency of the processes. The research aimed to find synergies between different waste streams in the Galician agroforestry sector. The benefits achieved would be translated into a different management route to the direct application to the soil of liquid livestock dejections, the recovery of forest industry wastes and the reduction of forest phytomass in the Galician forestalnd in order to reduce the risk of wildfires.

0. Índice e limiar.

0.1. Índice.

CAPÍTULO I.

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0.2. Limiar.

A xestión de residuos segue a ser un desafío ao que se enfrontan os gobernos. Nos seus respectivos ámbitos e en materia de dispoñibilidade de recursos, as diferentes Estratexias de Economía Circular avogan por cambios de modelo de consumos liñais por outros circulares baixo os que pechar os ciclos de materia orgánica.

En Galicia, unha terceira parte da súa poboación está concentrada preto das súas principais sete cidades. A restante atópase desordeadamente espallada en entidades de carácter rural o semirrural fortementemente vencelladas co espazo agrario e forestal, usos maioritarios no seu territorio. Ata mediados do século XX existían importantes ligazóns entre ambos espazos ao punto que a contorna forestal complementaba ao agrario de múltiples xeitos. Dende entón o gradual abandono de terras viu acompañado pola redución do número de explotacións agrarias, concentración das producións gandeiras e desaparición de usos ancestrais de aproveitamento da matogueira. A superficie adicada a cultivos foi reemplazada espontáneamente polo mato ou destinada á plantación con especies forestais, en boa medida ao abeiro da Directiva EU 2080/92 de forestación de terras agrarias. No escenario actual, a superficie forestal en Galicia representa case o 70 % segundo o IV Inventario Forestal Nacional, namentres que a superficie agraria útil ten descendido ata as 50.000 ha durante o periodo que separa os dous últimos censos agrarios actualmente dispoñibles (1999 y 2009).

A preponderancia do espazo forestal e abondosa acumulación de fitomasa contribúe de xeito significativo ao secuestro de carbono, mitigando os efectos do cambio climático. Porén este efecto é contrarrestado en Galicia pola cíclica ocurrencia de incendios forestais, arrasando anualmente miles miles de hectáreas de superficie arborada e matogueiras.

A elevada produtividade do monte galego representa unha oportunidade para a obtención de fitomasa con escaso ou nulo valor comercial. Nos últimos anos e entre as especies de frondosas, existe un interese crecente dos propietarios forestais polo castiñeiro, capaz de ofrecer rendas anuais por medio do froito, ou a final de quenda coa corta da árbore en forma dunha madeira moi aprezada pola súa excelente calidade. O mantemento destas plantación e a recoleción do froito, nalgúns lugares realizada mecanizadamente, propicia a acumulación de biomasa forestal residual (en forma de restos de poda, outizos, follas e especies adventicias).

Esta fitomasa forestal, pode ser considerada como un combustible susceptible de arder sen control. A súa xestión é acometida pola Lei de montes de Galicia de diferentes maneiras a fin de reducir a súa abondosidade ou xeito na que se dispersa no medio forestal. Esta lei encomendou específicamente á Xunta de Galicia a promoción de políticas relacionadas coa compostaxe e a eficiencia enerxética. No que respecta ao compost, ata o momento non se levou a cabo ningunha iniciativa, ao tempo que se estimulou o enfoque enerxético a través da Estratexia Integral para Promover a Biomasa Forestal 2014-2020. O seu obxectivo é activar unha industria asociada á recuperación enerxética da biomasa forestal con fins térmicos, aspirando a obter un descenso anual do 14% no consumo de combustibles a base de petróleo, recursos dos cales Galicia é moi deficiente.

O obxectivo principal desta tese é o estudo de usos alternativos á combustión da materia orgánica mediante procesos de biodegradación. Persíguese que o C secuestrado pola vexetación non pase novamente a atmosfera mediante a súa combustión, pechando os ciclos da materia orgánica pola súa incorporación ao solo por medio da fertilización ou enmenda. A compostaxe constitúe unha posibilidade tecnolóxica de baixo custo para tratar esta biomasa. O deito de tratarse de materiais cunha elevada proporción de C convida á integración doutros substratos que contribúan a equilibrio da relación C / N das mesturas e favorecer así este proceso.

As dexeccións animais constitúen candidatos ideais polo seu elevado contido en N. Entre elas, as que se presentan fundamentalmente en forma líquida debido a que a compostaxe representa un proceso exotérmico que precisa auga para manter a actividade dos microorganismos. O gando porcino é unha das principais especies explotadas en Galicia con importantes concentracións localizadas. A diferencia do gando bovino, a ausencia dunha base territorial cultivable asociada á explotación e a continua diminución da superficie agraria útil, fan necesario o suxerir métodos alternativos de xestión distinta á habitual aplicación directa ao solo como fertilizante.

Ademáis, estodouse a dixestión anaerobia das augas de proceso e lodos resultantes da fabricación de taboleiros de fibras de media densidade. Galicia é un produtor relevante deste tipo de taboleiros e previamente non se tiñan avaliados estes materiales con este fin. Durante o proceso de fabricación xérase unha cantidade importante destes residuos que non son valorizados e incrementan os custes de produción. Investigouse a participación do lodo en procesos de compostaxe para obter un produto biotransformado capaz con posibilidades de ser retornado ao solo, pechando así o ciclo monte-industria. Adicionalmente avaliouse a súa biometanización e o das augas procedentes da fabricación dos taboleiros co obxectivo de obter enerxía renovable, reducindo a dependencia enerxética dunha industria electro-intensiva e reducindo os custos de xestión, tanto do logo como das augas residuais.

As experiencias levadas a cabo resúmense a continuación, sucesivamente expostos como Capítulos da tese:

Inicialmente a investigación centrouse na biomasa forestal, resultante das operacións silvícolas de mantemento e recoleción do froito dunha plantación nova de castiñeiros (**Capítulo 1**). Avaliouse a súa potencial compostaxe en contedores 340 L, actuando o xurro porcino como aporte de N e auga. O lodo procedente dunha planta de depuración de augas de proceso da fabricación de taboleiro MDF integrouse como aditivo. Deseñáronse ensaios con distintas proporcións dos materiais para testar as diferenzas. A intensidade do proceso en tódolos casos foi inferior fronte a unha mestura testemuña facilmente degradable, con diferenzas de 10-15 ºC no pico da fase termofílica. O ensaio composto unicamente por fitomasa forestal non superou a fase mesofílica nas condicións de ensaio, mentras que a adición de lodo reduxo considerablemente as perdas de N. Obtívose un compost con elevado contido en nutrientes, baixa condutividade eléctrica e contido en metais pesados, podendo ser reincorporado na fertilización forestal.

O **Capítulo 2** afonda na compostaxe dos materiais indicados, incrementando o volume das mesturas ata os 2 m^3. Investigouse o efecto do tamaño da matriz procurando acadar a etapa termofílica no ensaio composto pola fitomasa do castiñeiro e o xurro porcino. Incorporouse a fitomasa da matogueira como novo axente estruturante e unha nova variable, a compactación, para avaliar o seu efecto sobre a intensidade do proceso. Para maximizar a cantidade de xurro empregado, procedeuse a reducir, por simple oreado, a humidade dos materiais sólidos empregados. Os ratios de consumo de xurro variaron entre os 1.8 y 2.5 l por kg de materia seca da fracción sólida. O incremento de volume das matrices propiciou a fase termofílica no ensaio composto pola fitomasa dos castiñeirais (nesta ocasión composta por follas e ourizos). Nesta mestura e a que contiña o lodo, acadouse a hixienización do material por baixo dos límites marcados polo R.D. 506/2013 de produtos fertilizantes. A compactación incrementou significativamente a temperatura do proceso, constituindo unha sinxela alternativa para variar as condicións do proceso.

O **Capítulo 3** avaliou o parámetro da demanda biolóxica de osíxeno (DBO_5), habitualmente empregado en augas residuais, como medio para determinala estabilidade do compost. Trátase dun sinxelo método alternativo a outros máis sotisficados que requiren persoal e equipo especializado. Para elo empregáronse mostras de compost da fracción orgánica dos residuos sólidos urbanos procedentes de dúas plantas a escala industrial, de composteiros domésticos e de residuos agroforestais estudados nos Capítulos precedentes. Os resultados comparáronse cun procedemento respirométrico e o test de autoquecemento, indicadores empregados habitualmente na lexislación sectorial (residuos e fertilizantes). Os índices obtidos coa DBO_5 correlacionáronse cos estándares de referencia. Comparativamente con estes, o limiar de estabilidade estableceuse en 25 mg O_2 gSV^{-1} de DBO_5.

A integración do lodo da industria de taboleiros MDF en procesos de compostaxe supuxo o primeiro intento documentado ata o momento empregando esta técnica. O **Capítulo 4** procurou avaliar a dixestión anaerobia como alternativa de tratamento que podería, ademáis de reducir custes de xestión, proporcionar biometano. A investigación exténdouse ás augas de proceso que dan lugar a este lodo, tamén inexploradas ata o momento con este fin. Estas augas son tratadas na actualidade aplicando, de manera secuencial, un tratamiento físico-químico e outro de tipo biolóxico. Avaliouse o potencial biolóxico de metanización así como o seu tratamento anaerobio tanto para a agua de entrada e salida do tratamento primario, como para o lodo. Para elo establecéronse experimentos batch cunha única ou múltiples alimentacións. A toxicidade metanoxénica para a auga sen tratar e o lodo require dilucións, producindo respectivamente 4.0 y .5 l de CH_4 por litro de auga. A agua resultante do tratamento primario non presenta toxicidade pero o rendemento descende ata 0.7 l de CH_4 por litro de auga. A simple sedimentación mellora os rendementos obtidos producindo ademais unha eliminación do 82% dos sólidos en suspensión, evitando a obstrución dos dixestores e mellorando o seu tratamento anaeróbico en unidades continuas.

Os Capítulos 1 e 2 abordaron a compostaxe como técnica capaz de xestionar e transformar residuos agroforestais. O **Capítulo 5** centrouse na disertación relativa as condicións que deben acadar os composts para poder ser aplicados directamente ao solo en Galicia. A ausencia dunha norma que regule específicamente a fertilización dá lugar a un espazo no que conflúen normas que tanxencialmente regulan a materia. O denominador común na maioría dos casos é a xestión de residuos. A investigación subliña diferenzas entre a norma estatal de fertilizantes e a autonómica, que aborda a xestión de lodos así como otros residuos orgánicos, na que a propiedade fertilizante do produto transformado queda nun segundo plano. Na maioría dos casos, a carga de N, a materia seca, ou o binomio N-P e metais pesados, determinan a máxima cantidade que pode ser aplicada ao solo. Entre outras consideracións, sublíñanse situacións relevantes como a necesaria observación do Código de Boas Prácticas na Agricultura para os composts comerciais mentras que para os estercos é optativa en tanto non se teñen declarado zonas vulnerables a nitratos en Galicia.

0.3. General abstract.

Waste management remains a challenge that governments face. In their respective areas and in terms of resource availability, the different Circular Economy Strategies advocate changes in the model of linear consumption by other circulars under which the cycles of organic matter would be closed.

In Galicia, a third of its population is concentrated near its main seven cities. The rest is disorderly spread throughout rural or semi-rural entities strongly linked to the agricultural and forestry space, the majority of uses in its territory. Until the middle of the twentieth century there were important links between both areas to the point that the forest environment complemented the agrarian in many ways. Since then, the gradual abandonment of land has been accompanied by a reduction in the number of farms, concentration of livestock production and the disappearance of ancestral uses of scrub. The area devoted to crops has been spontaneously replaced by scrub or dedicated to planting with forest species, largely under EU Directive 2080/92 on afforestation of agricultural land. In the current scenario, the forest area in Galicia represents almost 70% according to the IV National Forest Inventory, while the useful agricultural area has fallen to 50.000 ha during the period between the last two currently available agricultural censuses (1999 and 2009).

The preponderance of forest space and abundant accumulation of phytomass contributes significantly to carbon sequestration, mitigating the effects of climate change. However, this effect is counteracted in Galicia by the cyclical occurrence of forest fires, destroying thousands of hectares of forestland annually.

The high productivity of the Galician forest represents an opportunity to obtain phytomass with scarce or no commercial value. In recent years and among deciduous species, there is a growing interest of forest owners in chestnut, able to provide annual income through the fruit, or the tree cutting turn in the form of a wood highly prized for its excellent quality. The maintenance of these plantations and the harvesting of the fruit, in some places carried out mechanized, propitiates the accumulation of residual forest biomass (in the form of pruning wastes, burrs, leaves and adventitious species).

This forest phytomass can be considered as a fuel that can burn without control. Its management is undertaken by the Galician Forest Law in different ways in order to reduce its abundance or the way it is dispersed in the forest environment. This law has specifically entrusted the Xunta de Galicia with the promotion of policies related to composting and energy efficiency. With regard to compost, so far no initiative has been carried out, while stimulating the energy approach through the Comprehensive Strategy to Promote Forest Biomass 2014-2020. Its aim is to activate an industry associated with the energy recovery of forest biomass for thermal purposes, aspiring to

obtain an annual decrease of 14% in the consumption of petroleum-based fuels, very scarce resources in Galicia.

The main objective of this thesis is the study of alternative uses to the combustion of organic matter through biodegradation processes. The aim is to ensure that the C seized by vegetation does not re-enter the atmosphere through combustion, closing the cycles of organic matter due to its incorporation into the soil through fertilization or amendment. Composting is a low-cost technological possibility to treat this biomass. The fact of being essentially materials with a high C proportion invites the integration of other substrates that contribute to balance the C / N ratio of the mixtures and thus favor this process.

Animal manure is an ideal candidate due to its high N content. Among them, those that are mainly in liquid form because composting represents an exothermic process that needs water to maintain the activity of microorganisms. Pig cattle is one of the main species exploited in Galicia with important localized concentrations. Unlike cattle, the absence of a cultivable territorial base associated with exploitation and the continuous decrease of the Useful Agricultural Surface Area, make it necessary to find alternative management methods other than their direct application to the soil as fertilizer.

In addition, the anaerobic digestion of process water and sludge resulting from the manufacture of medium-density fiberboard was studied. Galicia is a relevant producer of this type of boards and these materials had not been previously evaluated for this purpose. During the manufacturing process a significant amount of this waste is generated which is not recovered and increases production costs. The integration of sludge into composting processes has been investigated to obtain a biotransformed product capable of being returned to the soil as a fertilizer or amendment, thus closing the forest-industry cycle. In addition, its biomethanization and that of water from wood refining were evaluated with the aim of obtaining renewable energy, reducing the energy dependence of an electro-intensive industry and reducing management costs, both for the sludge and for wastewater.

The experiments carried out are summarized below, successively set out as Chapters of the thesis:

Initially the research focused on forest biomass, resulting from silvicultural practices and fruit harvesting operations of a new chestnut plantation (**Chapter 1**). Its potential composting in 340 L composters was evaluated, watering with pig manure thus adding N and water. Sludge from a process water treatment plant from the manufacture of MDF board was integrated as an additive. Trials with diverse proportions of materials were designed to avaliate results. The intensity of the process in all cases was lower compared to an easily degradable control mixture, with differences of 10–15 ºC at the peak of the thermophilic phase. The test composed solely of forest phytomass did not pass the mesophilic phase under the experienced conditions, while the addition of sludge considerably reduced the N losses. A compost with high nutrient content, low electrical conductivity and heavy metal content was obtained, making it possible to be returned to forestland as a fertilizer.

Chapter 2 deepens in the composting of the indicated materials, increasing the composting mixtures to 2 m^3. The effect of matrix size was investigated trying to reach the thermophilic stage in the trial composed by chestnut phytomas and pig manure. Shrub phytomass was incorporated as a bulking agent and a new variable, compaction, to evaluate its effect on process intensity. In order to maximize the amount of the pig manure used, the moisture content of the solid materials used was reduced by simply gilding. Water consumption ratios ranged from 1.8 to 2.5 l per kg of dry matter in the solid fraction. The increase in volume of the matrices led to the thermophilic phase in the test composed of chestnut phytomas (this time composed of leaves and burrs). In this mixture and the one containing the sludge, the sanitization of the material was achieved below the limits set by RD 506/2013 of fertilizer products. Compaction significantly increased the process temperature, constituting a simple alternative to varying process conditions.

Chapter 3 evaluated the parameter of the biological oxygen demand (BOD_5), commonly used in wastewater as a technique to determine the compost stability. This is a simple alternative method to more sophisticated ones that require specialized staff and equipment. For this purpose, compost samples of the organic fraction of urban solid waste from two plants on an industrial scale, from domestic composters and agroforestry waste studied in the preceding Chapters were used. The results were compared with a respirometric procedure and the self-heating test, indicators commonly used in sectoral legislation (wastes and fertilizers). The values obtained with BOD_5 were correlated with the reference standards. Compared to these, the stability threshold can be set at 25 mg O_2 gSV^{-1} of BOD_5.

The integration of sludge from the MDF board industry into composting processes was the first documented attempt to date using this technique. **Chapter 4** aimed to assess anaerobic digestion as an alternative treatment that could reduce management costs and provide biomethane. The research was extended to the process wastewaters, source of the sludge, also unexplored so far for this purpose. These waters are currently treated by applying, sequentially, a physical-chemical and a biological treatment. The biological potential of methanation as well as its anaerobic treatment was evaluated for both the inlet and outlet water of the primary treatment, as well as for the sludge. To do this, batch experiments with a single or multiple feeds were established. Methanogenic toxicity to untreated water and sludge requires dilutions, producing respectively 4.0 and .5 l of CH_4 per liter of water. The water resulting from the primary treatment has no toxicity but the yield drops to 0.7 l of CH_4 per liter of water. Simple sedimentation improves the yields obtained, also producing an 82% elimination of suspended solids, avoiding the obstruction of digesters and improving their anaerobic treatment in continuous units.

Chapters 1 and 2 addressed composting as a technique capable of managing and transforming agroforestry waste. **Chapter 5** focused on the dissertation on the conditions that must reach the compounds to be applied directly to the soil in Galicia. The absence of a norm that specifically regulates fertilization gives rise to a space in which norms that tangentially regulate this issue converge. The common denominator in most cases is waste management. The research highlights differences between the spanish state standard of fertilizers and the galician one, which addresses the management of sludge as well as other organic waste, in which the fertilizer property of the processed product is in the background. In most cases, the N load, the dry matter, or the NP binomial and heavy metals, determine the maximum amount that can be applied to the soil. Among other considerations, relevant situations are highlighted such as the necessary observation of the Code of Good Practice in Agriculture for commercial composts while for manure it is optional as long as no nitrate vulnerable areas have been declared in Galicia.

CAPÍTULO I

INTRODUCIÓN E OBXECTIVOS

1. INTRODUCIÓN.

1.1. SOSTIBILIDADE FORESTAL E XESTIÓN DE RESIDUOS.

Ao longo da historia o ser humano serviuse do medio para o seu desenvolvemento. Accións como a transformación do solo, o emprego da auga ou enerxía foron indispensables para a súa evolución. Na Conferencia das Nacións Unidas sobre o Medio Humano celebrada en 1972 recoñeceuse unha transformación do ambiente a unha escala sen precedentes, con evidencias de perigosos niveis de contaminación, trastornos nos procesos naturais da biosfera e esgotamento de recursos insubstituíbles, chamándose a atención sobre os límites do crecemento económico para un futuro non moi afastado. Case medio século despois, a Unión Europea segue a admitir que a extracción e emprego indiscriminado dos recursos alteran negativamente os ecosistemas que os proporcionan, ocasionan consecuencias graves para o estado do ambiente e minguan a dispoñibilidade de recursos claves a escala mundial (Agencia Europea de Medio Ambiente, 2015). Así, nun escenario globalizado e baixo proxeccións de incrementos de poboación próximas aos 9.700 MM de habitantes no ano 2050 (UN, 2019), en pouco tempo acadarase o pico de produción de recursos vitais que foron explotados exponencialmente nun período, en termos relativos, moi breve. Tal pode ser o caso do petróleo (Hubbert, 1949) ou o fósforo (Cordell *et al.*, 2009) con custes de extracción directa e exponencialmente proporcionais á dispoñibilidade do recurso (Figura 1.1).

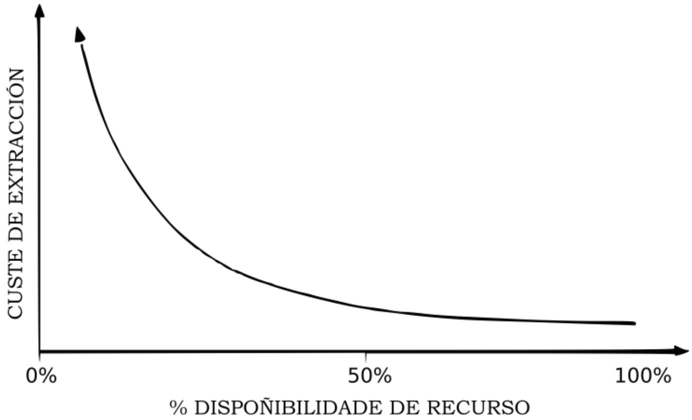

Figura 1.1. Relación entre custes de extracción dos recursos non renovables e a súa dispoñibilidade. Fonte: Redibuxado a partir de Meadows (2009).

En relación á circulación de nutrientes, Rockström *et al.* (2009) presentaron evidencias de que os ciclos do N e P téñense visto gravemente afectados nos últimos tempos ata límites dificilmente sostibles, chegando a definir os procesos humanos como "válvulas xigantes" que transforman millóns de toneladas de N atmosférico en formas reactivas. Hoxe en día o ciclo destes dous nutrientes é obxecto de preocupación no ámbito da Unión Europea de xeito que as súas estratexias ambientais a medio-longo prazo buscan unha xestión máis eficiente e sostible (DOUE, 2013).

Baixo un marco global de ininterrompido deterioro do ambiente e a progresiva toma de conciencia, dende a década dos 70 empezan a xurdir as primeiras normas encamiñadas á eliminación de presións sobre a biosfera. Na actualidade a atención xa non só se centra na preservación da calidade e conservación do medio natural senón que apunta aos novos escenarios xerados ao redor das interaccións entre a sociedade e o ambiente. Especialmente no que atinxe á eficiencia no emprego dos recursos, con tendencias que integren as preocupacións ambientais dun xeito máis sistémico na sociedade e na economía (Freyling *et al.*, 2014).

En Europa o Primeiro Programa de Acción en materia ambiental data do ano 1973 estando en desenvolvemento o Sétimo Programa de Acción (2014-2020). Baixo o título "*Vivir ben, respectando os límites do noso planeta*", o Sétimo Programa pretende reenfocar as clásicas visións temáticas ambientais (solo, auga, biodiversidade, aire, etc.) e derivalas cara un enfoque integral do ambiente como capital natural, termo xa recollido na Carta dos Solos do Consello de Europa en 1972, e conceptualizado como a base da economía humana e provedor de servizos ecosistémicos (Agencia Europea de Medio Ambiente, 2015).

O Sétimo Programa conta con tres obxectivos temáticos:

1. Protexer, conservar e mellorar o capital natural de Europa.
2. Converter á Unión Europea nunha economía hipocarbónica, eficiente no uso dos recursos, ecolóxica e competitiva.
3. Protexer á cidadanía da Unión Europea fronte ás presións e riscos medioambientais para a saúde e benestar.

A Unión Europea considera que hai indicios de que as economías dos países membros achéganse aos límites ecolóxicos do sistema no que están inmersas, e de que comezan a facerse patentes algúns dos efectos das limitacións de recursos físicos e medioambientais (Agencia Europea de Medio Ambiente, 2015). Por este motivo unha das actuacións prioritarias que promove a política comunitaria en materia ambiental é unha actuación eficiente no emprego destes recursos.

Máis recentemente, o concepto de economía circular ten xurdido con forza. Aínda que con certa carga de ambigüidade, Geissdoerfer *et al.* (2017) defíneno como "*un sistema rexenerativo no que as entradas de recursos e residuos, as emisións e as fugas de enerxía son minimizadas ao desacelerar, pechar, estreitar e reducir os circuítos de materias e enerxía*". Este concepto pode referirse a múltiples temas como os residuos, xestión de recursos, sostibilidade, ecoloxía industrial, ecodeseño producións limpas ou incluso considerarse un obxectivo político (Araujo Galvão *et al.*, 2018).

Idealmente a economía circular consistiría nunha rede de conexións na que non se xerarían residuos, non se acudiría a recursos virxes non renovables e os recursos virxes renovables consumiríanse só nunha taxa inferior á da súa renovación. Porén na actualidade esta utópica visión non sempre é materializable e sobre a circularidade de materiais, poderían considerarse dous ciclos, un de tipo técnico e outro de orixe biolóxico. O ciclo técnico está baseado no emprego de recursos nos que os produtos son deseñados e comercializados de tal xeito que poida ser maximizada a súa reutilización. No ciclo biolóxico, os recursos empregados como materias primas son de orixe biótico e os produtos deberían idealmente poder ser reintroducidos nos sistemas naturais unha vez finalizada a súa vida útil (Breure *et al.*, 2018). Sobre este último aspecto, os residuos orgánicos constitúen unha abundante fonte biomasa que, adecuadamente xestionada, pode ser transformada nunha fonte de nutrientes susceptibles de ser recuperados e devoltos aos solos para acadar a mellora das súas propiedades. Isto é tanto máis importante cando en moitas ocasións a fertilidade química dos solos é restituída con aportes minerais, nalgúns casos non renovables, cunha orixe física moi distante do seu destino final.

O Comité Económico e Social Europeo (DOUE, 2015), no seu Ditame sobre as Implicacións da política en materia de clima e enerxía para o sector agrícola e a silvicultura, pronunciouse por unha estratexia activa para un crecemento sostible e viable da biomasa para a bioenerxía e bioeconomía que garanta rendas elevadas e estables suplementarias para agricultores, propietarios forestais e comunidades rurais. Segundo este Ditame as políticas da Unión Europea deberán:

- Promovela transición gradual para modelos agrarios nos que non interveñan os combustibles fósiles.
- Centrarse en mellorala eficiencia de tódolos sistemas de produción.
- Apoiar un uso máis eficiente dos recursos, incluídos a terra, a auga e os nutrientes.
- Promover un modelo sostible de agricultura e silvicultura de ciclos de produción pechados a fin de impulsala competitividade destes sectores.

No contexto da economía circular, a Unión Europea subliña a importancia de promocionar procesos innovativos na procura de simbioses nos fluxos de materiais (EU, 2015). A presenza de residuos orgánicos procedentes de diferentes sectores produtivos invita a un enfoque sistémico e transversal na súa xestión máis alá de consideracións illadas. A significación deste feito é máis notorio cando a simultaneidade de residuos ten lugar tanto no tempo como especialmente nun espazo xeográfico compartido, repercutindo finalmente nos distintos compoñentes do seu capital natural.

Baseadas sobre procesos biolóxicos, as investigacións contidas nesta tese afondan na valorización e procura de sinerxías entre residuos e biomasa residual resultantes das actividades agroforestais e da industria derivada en Galicia. Entre os beneficios ambientais xerais destácanse:

a. Redución de biomasa forestal combustible presente no monte e xa que logo, do risco de incendio forestal.
b. Alternativa de xestión de esterco distinta á súa aplicación directa ao solo.
c. Proporcionar rendas adicionais no sector primario.
d. Redución de custes para os residuos da industria forestal.
e. Recuperación de nutrientes para o seu uso agroforestal sostible.

1.2. BIODEGRADACIÓN: COMPOSTAXE E DIXESTIÓN ANAEROBIA.

A valorización dos residuos xoga un papel fundamental no marco dunha economía circular. Na actualidade os residuos orgánicos seguen a sufrir un tratamento inadecuado na maioría dos países en desenvolvemento, e incluso nalgúns desenvolvidos, debido a distintas razóns como as restricións en asignacións orzamentarias ou ao insuficiente desenvolvemento de infraestruturas (Wainaina *et al.*, 2020).

En funcións das súas características, estes residuos son maioritariamente aplicados de xeito directo ao solo como fertilizantes, ben dispostos en vertedoiros controlados ou incinerados. Fronte a estas vías, a compostaxe e a dixestión anaerobia constitúen interesantes vías para a súa transformación en valiosas substancias de carácter estable, recuperando os recursos contidos nos residuos e contribuíndo a acadar os obxectivos da economía circular (Füleky e Benedek, 2010; Wainaina *et al.*, 2020).

Estas dúas técnicas aproveitan as poboacións de microorganismos presentes nos residuos para a degradación da materia orgánica, ben en presencia (compostaxe) ou ausencia (dixestión anaerobia) de osíxeno. Multitude de residuos procedentes das actividades humanas, nas súas distintas contornas, son susceptibles de ser transformados por estas vías, que idealmente poden conducir a unha constante recirculación de recursos (Figura 1.2).

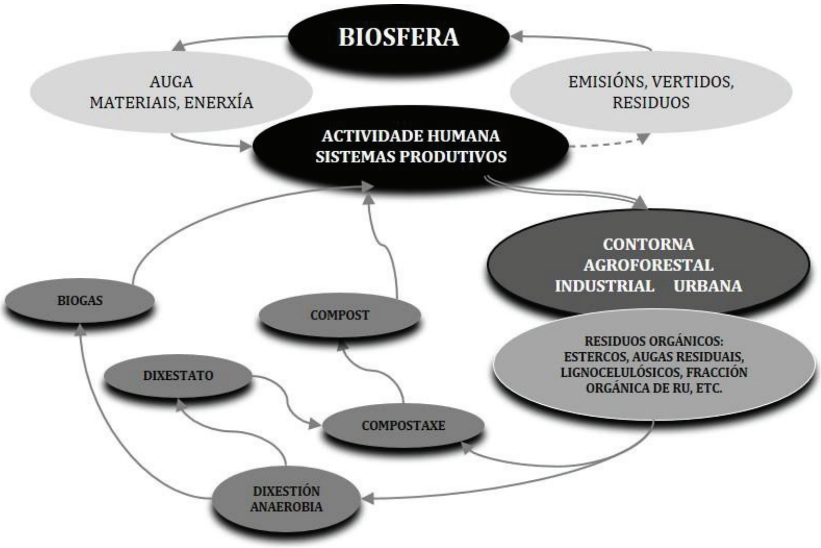

Figura 1.2. Visión sinóptica de interaccións entre a actividade humana e a biosfera, coa intervención de técnicas de orixe biolóxica para reducir o consumo de recursos naturais e a circularidade nos fluxos de residuos orgánicos. Fonte: Elaboración propia para o ámbito desta tese.

A compostaxe transforma os residuos en compost nun proceso durante o cal a materia orgánica é oxidada producindo principalmente CO_2 e H_2O. A dixestión anaerobia produce biogás como fonte de enerxía renovable e importantes cantidades de residuo semisólido, o dixestato, que pode ser integrado conxuntamente con outros residuos en procesos de compostaxe. Estes aportes de materia orgánica ou fertilizantes ao solo diminúen a presión que o ser humano exerce sobre a biosfera para a obtención de recursos non renovables coa mesma finalidade. Outra das principais vantaxes é a desviación de importantes cantidades de residuos que poden acadar os sistemas naturais en formas indesexables ou ser xestionados por outros métodos contrarios aos principios da economía circular, como pode ser a incineración.

1.2.1. Compostaxe. Fundamentos.

A compostaxe é un proceso de descomposición dos residuos orgánicos no que bacterias, fungos e outros microorganismos transforman os materiais orgánicos nun substrato estable chamado compost (Bernal *et al.*, 2017; Figura 1.3). Trátase dun proceso exotérmico que provoca a mineralización e humificación parcial da materia orgánica obtendo, idealmente, un compost libre de fitotoxicidade e patóxenos con certas propiedades húmicas e fertilizantes (Bernal *et al.*, 2009; Haug, 1993). Constitúe unha das técnicas máis axeitadas, dende o punto de vista económico e ambiental, para a xestión de residuos lignocelulósicos e dexeccións gandeiras (Pergola *et al.*, 2017).

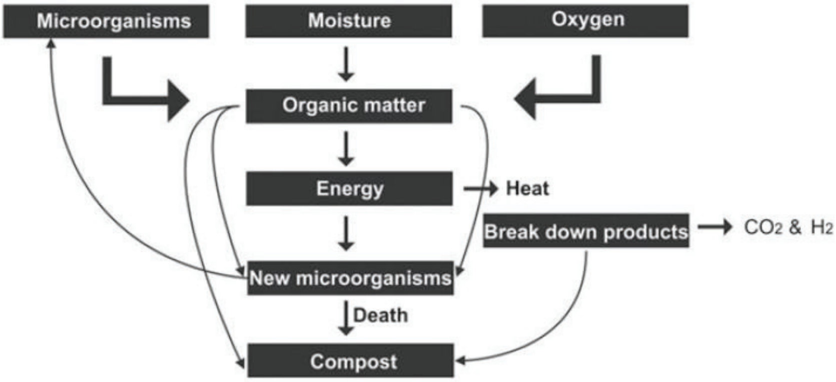

Figura 1.3. Esquema do proceso de compostaxe. Fonte: Maheshwari *et al.* (2014).

Durante a compostaxe identifícanse dúas etapas: a biooxidativa e a de maduración (Figura 1.4). A etapa biooxidativa clasifícase en tres fases en función do perfil de temperatura: mesofílica, termofílica e enfriamento. A actividade dos microorganismos é máxima na etapa termofílica ata acadar unha segunda fase mesofílica na que a temperatura gradualmente descende ata acadar á final de enfriamento (Bernal *et al.*, 2017). A etapa de maduración está caracterizada pola baixa actividade dos microorganismos e unha temperatura constante, próxima aos valores ambientais, e é durante esta fase onde se produce a humificación da materia orgánica (Bernal *et al.*, 2009). A duración desta fase depende de factores varios como a biodegradabilidade da materia prima, a aireación, a relación C/N, o tamaño de partícula (Vesilind e Worrell, 2012).

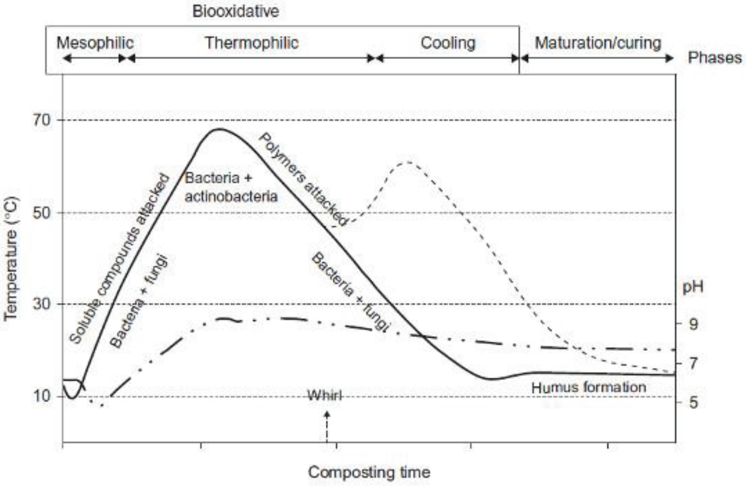

Figura 1.4. Etapas e perfiles de temperatura durante a compostaxe en pilas estáticas (liña continua) ou volteadas (liña descontinua) e evolución do pH (liña punteada). Fonte: Bernal *et al.* (2017).

Os microorganismos implicados na compostaxe son amplamente diversos e se ben son introducidos de maneira natural a través dos residuos, noutras ocasións emprégase o propio compost como inoculante natural (Onwosi *et al.*, 2020; Bernal *et al.*, 2017). Durante a fase mesofílica inicial, de 1 a 3 días de duración, as bacterias mesofílicas e os fungos degradan azucres, aminoácidos e proteínas. Despois, a transformación da materia orgánica ten lugar a maior velocidade e a súa oxidación pode incrementar a temperatura ata os 50-70 ºC. É nesta etapa na que se produce a maior degradación da materia orgánica así como a destrución de patóxenos e sementes (Bernal *et al.*, 2017).

Na etapa de enfriamento, a temperatura baixa polo descenso da actividade dos microorganismos e dá lugar á nova colonización dos mesofílicos adaptados para hidrolizar material lignificado recalcitrante (Bernal *et al.*, 2017). Finalmente na etapa de maduración a temperatura aproxímase á do ambiente, tendo lugar a estabilización microbiana e a humificación (Bernal *et al.*, 2017, 2009).

1.2.1.1. Principais factores que afectan á compostaxe.

Ratio C/N

A relación C/N é unha variable que mide o equilibrio químico da mestura a compostar. Vesilind e Worrell (2012) marcan valores de 20 e 80 como limiares, inferior e superior respectivamente, fóra dos cales a compostaxe non pode producirse. Diversos autores sitúan o rango comprendido entre 20 e 35 (Bernal *et al.*, 2017; Puyuelo *et al.*, 2011). Valores máis elevados ralentizarían o proceso e máis baixos poden incrementar as perdas de N, devalando o poder agronómico do compost (Bernal *et al.*, 2017), motivo polo cal á minimización destas perdas é frecuentemente obxecto de estudo (Bueno *et al.*, 2008; Vázquez *et al.*, 2017).

A consecución dunha relación C/N axeitada conséguese habitualmente coa combinación ou mestura de residuos con diferentes propiedades. Aqueles con elevada proporción de C actúan ademais como axentes estruturantes, xeralmente residuos lignocelulósicos de diferente orixe e natureza (Iqbal *et al.*, 2010; Vassilev *et al.*, 2010) cando a proporción de N é elevada (Guerra-Rodríguez *et al.*, 2001b; Külcü e Yaldiz, 2014). A ratio C/N decrece durante o proceso de compostaxe xa que o carbono orgánico é convertido en CO_2 e o contido de N vaise estabilizando (agás se produzan elevadas perdas de amonio, favorecidas por valores elevados de pH).

pH

Os valores de pH comprendidos entre 6.7–9.0 proporcionan boa actividade microbiana (Bernal *et al.*, 2017) pero o pH da pila de compost varía ao longo do tempo, amosando un descenso inicial para despois aumentar ata as 8-9 unidades, debido á degradación dos ácidos orgánicos e á amonificación. Finalmente logra estabilizarse entre 7 e 9 (Vesilind e Worrell, 2012; Figura 1.4). Valores de pH por riba de 7.0 afectan ás perdas de N (Vesilind e Worrell, 2012). O contido de O_2 e o pH gardan unha estreita relación e así, se o proceso resulta anóxico o pH descende debido á formación de ácidos en condicións anaerobias e sempre e cando o proceso sexa aerobio a pila de compost mantén unha capacidade tampón suficiente como para estabilizar o pH en niveis lixeiramente alcalinos (Vesilind e Worrell, 2012).

Humidade

A humidade é un parámetro fundamental para o desenvolvemento dos microorganismos e para o desenvolvemento das reacccións químicas (Onwosi *et al.*, 2020). Se a mestura está demasiado seca ou conta con demasiada auga, os microorganismos non poden sobrevivir. Contidos inferiores ao 40% e superiores ao 60% son apuntados por Epstein (2011) como posibles limitadores do proceso. Poren o contido de auga necesaria para o proceso depende en boa medida dos materiais a compostar, e valores recomendados por outros autores atópanse fóra deste rango (Bueno *et al.*, 2008; Kim *et al.*, 2017).

Osíxeno

O subministro de oxíxeno durante o proceso de compostaxe depende do sistema empregado. Existen distintos métodos e clasificación de sistemas de compostaxe, sendo clasificados por Füleky e Benedek (2010) en pilas estáticas, ringleiras ou reactores. A aireación en pilas volteadas prodúcese mediante os volteos periódicos, máis necesarios ao comezo do proceso durante o cal a actividade microbiana é máis intensa. En sistemas estáticos o aporte de O_2 prodúcese mediante sopradores. En moitos destes sistemas, a oxixenación tamén se realiza, ou ben vese complementada, pola convención natural que forza a circulación do aire atmosférico a través da matriz en compostaxe, como resultado do gradiente térmico creado.

Para que o osíxeno sexa accesible aos microorganismos, a matriz debe contar cunha porosidade adecuada, e esta, á súa vez depende en boa medida dos materiais a compostar, a súa humidade e o tamaño das súas partículas (Epstein, 2011). Materiais como os lodos ou a fracción orgánica dos residuos urbanos contan cunha elevada densidade polo que son mesturados con axentes estruturantes que corrixen a porosidade, e adicionalmente interveñen no equilibrio da relación C/N e a humidade da mestura final.

1.2.2. Dixestión anaerobia. Fundamentos.

Durante a dixestión anaerobia a materia orgánica é degradada podéndose producir, baixo condicións favorables, biogás e un dixestato (residuo sólido ou líquido resultante de variada composición bioquímica). Unha ampla variedade de residuos poden ser procesados mediante esta técnica (Deublein e Steinhauser, 2010; Van *et al.*, 2019). O proceso ten lugar ao longo de catro fases dominadas por distintos tipos de bacterias: hidrólise, acidoxénese, acetoxénese e metanoxénese (Figura 1.5).

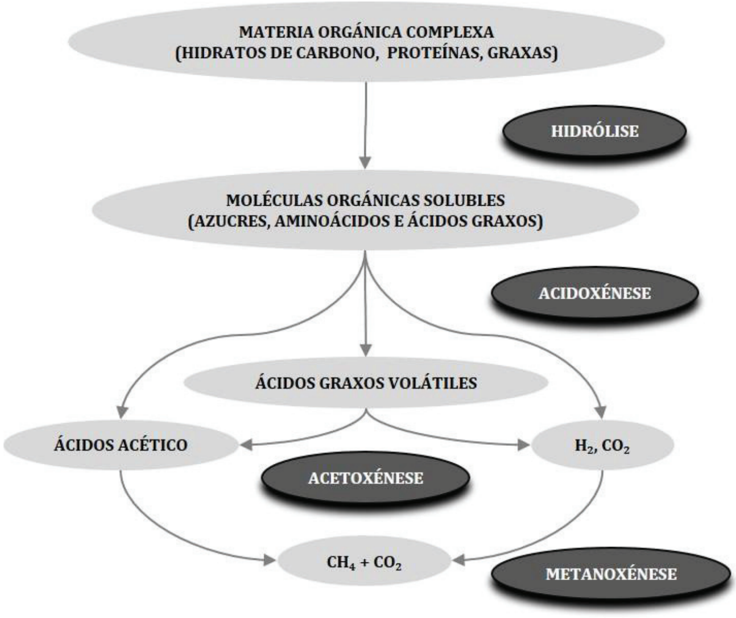

Figura 1.5. Esquema das fases da degradación da materia orgánica mediante dixestión anaerobia. Fonte: Redibuxado dende Gujer e Zehnder (1983).

Durante a hidrólese a materia orgánica complexa insoluble, como lípidos, carbohidratos ou proteínas, é hidrolizada a compostos simples solubles (azucres, aminoácidos e ácidos graxos). Esta etapa está influenciada polo pH, temperatura e o tempo de retención, na que a maior eficacia procúrase en condicións moderamente ácedas, altas temperaturas e tempos de retención relativamente longos (Poh *et al.*, 2015).

Na acidoxénese os compostos simples solubles (produtos finais da hidrólise) son convertidos en ácidos graxos e ácidos orgánicos (acético, propiónico, láctico, butírico, etc.), H_2 e CO_2. O ácido acético ten singular relevancia como precursor para a formación de metano incrementándose a formación dos ácidos graxos volátiles con valores de pH superiores a 5 (Obileke *et al.*, 2020)

A acetoxénese é o paso para converter os ácidos da etapa anterior en acético, sendo de especial relevancia xa que máis do 70% do metano producido durante a dixestión anaerobia procede do ácido acético (Poh *et al.*, 2015).

A metanoxénese é etapa última e máis importante xa que as reaccións determinan a cantidade e calidade do biogás producido. Consiste na produción metano a partires do ácido acético, H_2 e CO_2 xerados nas fases precedentes. Dous grupos de bacterias levan a cabo este proceso: as que degradan o acetato a metano e dióxido de carbono (acetotrópicas) e as que consumen hidróxeno para producir metano (hidroxenotróficas) (Obileke *et al.*, 2020; Poh *et al.*, 2015)

A dixestión anaerobia é un proceso sensible que require distintas tasas de degradación, dependendo das distintas etapas. Mentres que a materia orgánica complexa pode hidrolizar durante días a monómeros, os hidratos de carbono solubles son transformados durante unhas poucas horas.

En función da separación física destas fases, os distintos sistemas de dixestión anaerobia poden clasificarse naqueles nos que todas as fases teñen lugar nun único ou varios reactores. A dixestión anaerobia non depende unicamente no tipo de sistema de dixestión xa que depende das variables de crecemento (temperatura, pH, e nutrientes), o tipo de reactor e parámetros de operación (tempo de retención, concentración e velocidade de carga orgánica a procesar) (Van *et al.*, 2019).

O biogás xerado pode ser empregado directamente para a xeración de electricidade e calor, namentres que o biometano, biogás depurado mediante diversas técnicas ata acadar unha concentración de metano próxima á do gas natural (Angelidaki *et al.*, 2018), pode ser inxectado na rede de gas natural ou empregado como combustible para distintos usos (Figura 1.6).

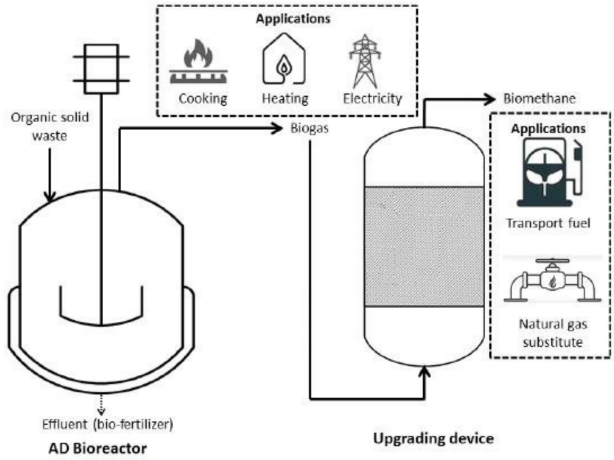

Figura 1.6. Potencial de alimentación, tecnoloxías de conversión e produtos. Fonte: (Wainaina *et al.*, 2020).

A dixestión anaerobia pode ser cuantificada por diferentes parámetros. A relación C/N pode dar unha idea da súa idoneidade para a súa dixestión, propensión á formación de ácidos graxos volátiles ou á inhibición polo amonio. Os sólidos volátiles, DBO ou DQO avalían o seguimento dos dixestores. O tempo de retención hidráulica, a velocidade de carga, ou os sólidos totais poden informar sobre o deseño dos dixestores (Deublein e Steinhauser, 2010; Meegoda *et al.*, 2018).

1.2.2.1. Principais factores que afectan á dixestión anaerobia.

Temperatura

A temperatura é un factor importante ao afectar á estrutura microbiana dos dixestores e a súa flutuación pode provocar desequilibrios asociados á acumulación de ácidos graxos volátiles

(Kougias e Angelidaki, 2018). O proceso de dixestión ten lugar en reactores anaerobios que operan en condicións mesófilas (30 °C – 40 °C) ou termófilas (50 °C – 60 °C) pero habitualmente a unha temperatura constante (±2 ºC).

pH e ácidos graxos volátiles

A produción de biogás sucede nun rango de pH que varía entre 6.0 a 8.5 e valores fóra dese intervalo producen unha forte diminución na produción de metano. Os ácidos graxos volátiles son indicadores do proceso para a monitorización do biogás, e tanto a súa concentración como a relación entre eles pode proporcionar información esencial para detectar posibles desequilibrios (Kougias e Angelidaki, 2018). Cambios nos valores de pH poden correlacionarse con outros parámetros operativos como a abundancia de amoníaco ou eliminación de CO_2 (aumentos de pH), ou a acumulación de ácidos orgánicos (descensos de pH).

Inhibidores

Durante a dixestión anaerobia poden detectarse compostos que, a determinadas concentracións, poden comprometer a produción de biogás ou deteriorar o proceso. Estes compostos ben poden ser substancias tóxicas ou metabolitos intermedios que aparecen durante o proceso. En termos xerais, a inhibición depende da súa concentración, da composición do substrato e da adaptación dos microorganismos ao inhibidor (Deublein e Steinhauser, 2010). Os organismos metanoxénicos son máis sensibles á presencia destes compostos tóxicos (Kougias e Angelidaki, 2018).

A presencia de amoníaco ou fenois son inhibidores frecuentes na dixestión anaerobia (Calabrò *et al.*, 2018; Poirier e Chapleur, 2018) pero poden presentarse outros (Deublein e Steinhauser, 2010): O_2 (os microorganismos metanoxénicos son anaerobios estritos); compostos sulfurosos (os microorganismos redutores do sulfato a sulfuro son dominantes); ácidos graxos volátiles (provocan unha grave acidificación do medio e tamén son inhibidores a concentracións elevada); nitratos (substratos con concentracións superiores aos 50 mg kg^{-1} NO_3-N nos que a denitrificación non fose exitosa antes da metanoxénese); metais pesados (efectos prexudiciais sobre as bacterias a altas concentracións); e outro amplo elenco de substancias (taninos, desinfectantes, herbicidas, insecticidas, surfactantes, antibióticos, etc.). A mesma acumulación de H_2 debe ser evitada pois algunhas reaccións de conversión dos ácidos propiónico e butírico a acético vólvense termodinamicamente inviables.

1.2.2.2. Pretratamentos.

A dixestión anaerobia de residuos agroforestais pode presentar inconvintes como poden ser o baixo rendemento de biogás, baixa calidade dos produtos finais ou variabilidade nas producións (Kainthola *et al.*, 2019). Na práctica a maioría das plantas de biogás seguen estratexias de co-dixestión debido a razóns varias como o baixo potencial de metano, alta concentración de inhibidores (fenois, amonio, etc.) ou dispoñibilidade estacional de substratos específicos (Kougias e Angelidaki, 2018).

Para superar estas dificultades e incrementar a eficiencia do proceso anaerobio, ademais da co-dixestión con outros substratos, existen varias técnicas como a inoculación ou os pretratamentos (Kainthola *et al.*, 2019).

O pretratamentos poden favorecer a súa posterior dixestión (Ariunbaatar *et al.*, 2014; Elliott e Mahmood, 2007; Neumann *et al.*, 2016; Pilli *et al.*, 2015). Soen ser clasificados en mecánicos, térmicos, químicos, biolóxicos ou combinación dos anteriores (Ariunbaatar *et al.*, 2014). A súa eficacia depende en boa medida das características dos substratos (Ariunbaatar *et al.*, 2014) e a bibliografía referencia numerosas experiencias axeitadas ás condicións particulares dos mesmos.

En canto aos residuos lignocelulósicos, os tratamentos térmicos fríos están baseados no incremento do volume da auga. Unha vez conxelada provoca a rotura das paredes celulares da materia orgánica, aumentando a área accesible para a hidrólise encimática polos microorganismos (Rooni *et al.*, 2017). Trátase dun pretratamento de alto consumo enerxético, mais en rexións onde o clima é máis duro preséntase como unha alternativa sustentable fronte a outras tecnoloxías (Anjum *et al.*, 2016; Neumann *et al.*, 2016; Rooni *et al.*, 2017). Rooni *et al.* (2017) indicaron que a temperatura de conxelación non exerce un papel determinante a modo de pretratamento, polo que empregaron ciclos de conxelación (-18ºC) e desconxelación (ambiente). Cada ciclo serviu para incrementar a rotura das estruturas celulares e o acceso das encimas á celulosa. O mellor resultado na eficiencia da hidrólise (+19,2 %) conseguiuse no 4º ciclo, amosando unha boa relación (r^2=0.9) de aumento nos rendementos e o número de ciclos. Dun xeito similar, pero na dixestión de lodos de depuradora, Neumann et. al. (2016) sinalaron incrementos do 52% na produción de biogás.

Noutro extremo dos tratamentos térmicos, Meyer e Edwards (2014) aconsellaron o emprego do microondas e homoxeneización a alta presión para mellorar os rendementos da produción de metano para os residuos da industria da polpa de papel. Sóese marcar o límite de 100ºC para distinguir os tratamentos a baixa e alta temperatura. No caso dos lodos, Meyer e Edwards (2014) indicaron como temperaturas máis axeitadas para o incremento de metano as comprendidas entre os 150-170 ºC, durante un tempo de 10 minutos. Para os compostos lignocelulósicos, Ariunbaatar *et al.* (2014) referenciaron os 160 ºC como o límite a partir do cal os compostos fenólicos son liberados e a conseguinte inhibición da dixestión anaerobia. Ethaib *et al.* (2015) subliñaron diferentes rangos de temperatura en combinación con outros pretratamentos. En xeral, os pretratamentos, térmicos ou outros, recomendados pola bibliografía son específicos para cada tipoloxía de residuo e condicións de operación, resultando que as recomendacións e resultados para un determinado residuo poden non ser axeitados para residuos de aparente similar natureza.

Entre os pretratamentos químicos, os alcalinos aparentan ser os máis axeitados para residuos lignocelulósicos. Isto é debido ao emprego de substancias químicas non contaminantes e non corrosivas, a unhas condicións de operación máis moderadas que as precisas para os pretratamentos con ácidos, e a que os reactivos alcalinos interactúan principalmente con lignina e polo tanto son máis eficientes para a súa eliminación (Kim *et al.*, 2016). Na revisión de Zheng *et al.* (2014) sobre biomasa lignocelulósica expóñense distintos exemplos de pretratamentos alcalinos baseados na adición de Na OH para distintos residuos deste tipo.

Nos pretratamentos biolóxicos, o emprego de encimas modificadoras de lignina ou carbohidrasas parecen os máis axeitados. Así, as encimas que atacan á lignina, tales como as lacasas e peroxidasas, téñense explorado como pretratamento separado antes das probas de potencial de metano para substratos agrícolas ricos en lignocelulosa (Brémond *et al.*, 2018; Widsten e Kandelbauer, 2008).

1.3. FITOMASA FORESTAL E COMPOSTAXE.

1.3.1. Fitomasa forestal residual.

O espazo forestal ten unha especial relevancia en Galicia ao concentrar o 70% da súa superficie (MMAMRM, 2011a) e máis da metade das cortas de madeira de toda España. Os aproveitamentos madeireiros levan asociados a xeración de restos de fitomasa dispersos na área de explotación, con escaso valor comercial e elevados custes de recollida, transporte e amoreado (MMAMRM, 2010a). A eliminación por medio do lume ou o seu abandono no propio monte foron prácticas tradicionais en Galicia, producindo unha serie de riscos e efectos ambientais negativos (Soto *et al.*, 1995; Tolosana *et al.*, 2004):

1. Destrución do solo.
2. Aumento do risco de incendio forestal pola acumulación de combustible.
3. Medio de propagación de pragas ou enfermidades forestais.
4. Diminución do valor paisaxístico e recreativo do monte.
5. En caso de importantes acumulacións nos leitos fluviais, posible deterioro do estado das bacías en épocas de chuvias torrenciais.
6. Dificultade de tránsito de persoas, animais e maquinaria.

Na actualidade, no que atinxe aos aproveitamentos madeireiros a Lei 7/2012 de montes de Galicia (DOG, 2012a) indica que, de forma xeral, a súa execución levará implícita a extracción ou trituración da biomasa forestal residual.

Nos casos da extracción dos restos para o seu posterior aproveitamento, deberase deixar sobre o terreo unha porcentaxe mínima aproximada do 30 % (fraccións máis finas) co fin de non impactar de forma significativa no ciclo de nutrientes do solo (DOG, 2014). A normativa sectorial tamén engade unha visión conservacionista para fomentar a diversidade de especies e ecosistemas, tales como a creación de mouteiras maduras, con especial atención ás frondosas autóctonas, nas que se dean procesos de naturalización, incluso contemplando o mantemento de árbores mortas, sempre que non supoñan riscos de estabilidade do ecosistema, como poderían ser pragas, enfermidades ou incendios (DOG, 2014).

A lei apunta para a biomasa extraída un uso enerxético e a compostaxe. Con respecto á compostaxe, a Lei de montes encomenda ao Goberno de Galicia a promoción de políticas relacionadas co seu fomento. Esta referencia á compostaxe na norma forestal autonómica constitúe unha novidade non previamente contemplada en calquera dos instrumentos normativos e de planificación do Estado: Lei 43/2003 de Montes (BOE, 2003), Plan Forestal Español 2002-2032 (MMA, 2002), Plan de activación socioeconómica del sector forestal 2014-2020 (MAAMA, 2014a), Estratexia Forestal Española (MMA, 1999) ou Estratexia Española para o desenvolvemento do uso enerxético da biomasa forestal residual (MMAMRM, 2010a).

Ata o momento, o impulso autonómico ao fomento da fitomasa forestal residual estivo orientado ao seu aproveitamento con fins enerxético. Así xurdiu a Estratexia Integral de Impulso á Biomasa Forestal 2014-2020 (Xunta de Galicia, 2014) cuxo obxectivo era activar unha industria asociada á valorización enerxética da biomasa forestal con fins térmicos, aspirando a conseguir un descenso anual do 14% no consumo dos combustibles derivados do petróleo, recursos non renovables dos que Galicia é moi deficitaria. A definición de Estratexia Integral obedece máis a un modelo lineal de aproveitamento orixe-destino (biomasa-calor) que a outros máis orientados á diversificación no uso (fertilizantes ou biorrefinaría) ou circulares que contemplen medidas compensatorias das extraccións previstas a medio prazo no monte galego.

1.3.2. Plantacións de castiñeiro.

O castiñeiro (*Castanea*, Fagáceas) é unha árbore presente en Galicia e en todo o hemisferio norte. O xénero está composto, segundo Fei *et al.* (2012), por sete especies distribuídas en Europa (*C. sativa*), América (*C. dentata* e *C. pumila*) e Asia (*C. mollissima* e *C. seguinii* en China e *C. crenata* no Xapón) (Figura 1.7).

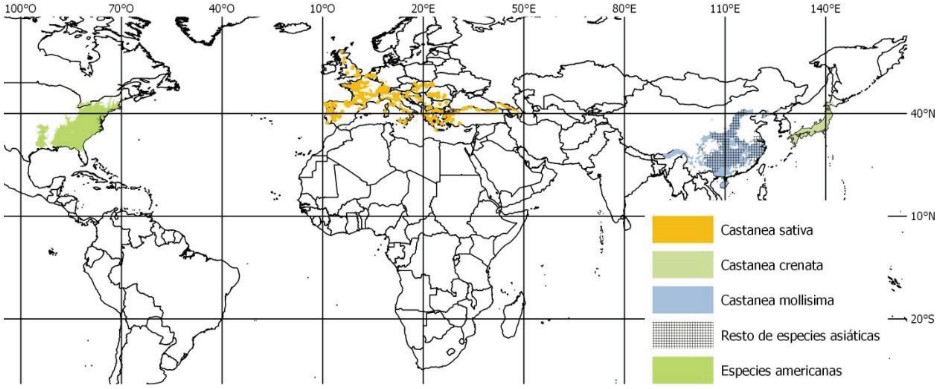

Figura 1.7. Áreas de distribución do castiñeiro (*Castanea* sp.) no mundo. Fonte: Elaboración propia a partires da información de EUROFORGEN (2009), U.S. Geological Survey (1999) e para as especies asiáticas, mapas cortesía de Fei (2012).

Á súa importancia económica e ecolóxica, engádeselle un forte carácter paisaxístico (Bouhier, 1979) e cultural, en boa medida polo ancestral aproveitamento do seu froito (Fei *et al.*, 2012). Outros autores van máis alá, recoñecendo a noutrora estreita relación do ser humano coa árbore e os coñecementos requiridos para manter os soutos nas condicións necesarias para o seu mellor aproveitamento, o que confería independencia económica ás familias (Cherubini, 1981; Fernández de Ana Magán *et al.*, 1998). Así, a comezos do século XVIII en Galicia e outras zonas de Europa, o cultivo do castiñeiro permitía o mantemento dunha alta densidade de poboación e fundamentos de autarquía no medio rural (Conedera *et al.*, 2004; Fernández de Ana Magán *et al.*, 1998).

Hoxe en día as principais masas de castiñeiro, 34.000 hectáreas segundo o Mapa Forestal de España (MMAMRM, 2011b), localízanse nos concellos orientais das provincias de Lugo e Ourense, caracterizados demográficamente, por baixas densidades de poboación, a miúdo coincidentes con índices de envellecemento moi elevados Ao mesmo tempo, o último Inventario Forestal Nacional amosa un incremento no número de pés en Galicia (Figura 1.8) como consecuencia en boa medida das novas plantacións con esta especie.

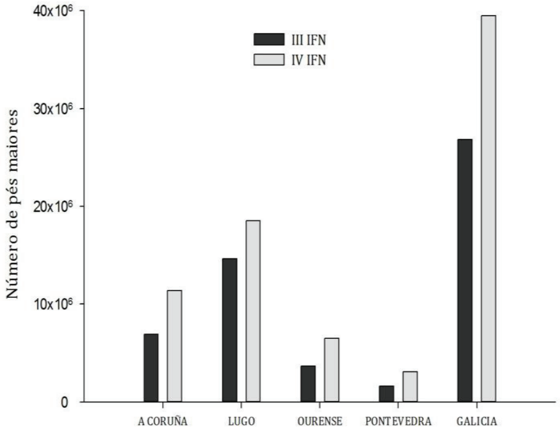

Figura 1.8. Evolución do número de pés maiores de castiñeiro por ámbito entre o III e IV Inventario Forestal Nacional (1997-2007 e 2007-2017 respectivamente). Fonte: Elaboración propia dende datos dos respectivos Inventarios Forestais Nacionais (MMAMRM, 2011a).

Este interese dos propietarios e xestores forestais polo castiñeiro débese ao carácter multipropósito da especie, cultivado principalmente para obter madeira e froito. A súa madeira é de alta calidade e moi prezada cando está libre de defectos (Álvarez-Álvarez *et al.*, 2000; Fernández-López, J. e Alía, R., 2003; Martínez-Alonso e Berdasco, 2015). Ten múltiples aplicacións pola súa durabilidade, resistencia á intemperie e beleza da súa veta: ebanistería, carpintería, construción, cestería, etc. (Santa Regina *et al.*, 1998). En canto a castaña, trátase dun produto con elevadas propiedades nutricionais que pode ser consumida tanto crúa como cociñada. Tradicionalmente o apañado da castaña levábase a cabo de xeito manual (Fernández de Ana Magán *et al.*, 1998), con rendementos medios variables segundo autores: dende 10-15 kg h^{-1} (Bounous e Marinoni, 2010) ata 30 kg h^{-1} (Monarca *et al.*, 2014). Na actualidade a recollida mecanizada ofrece rendementos moito maiores, dende 630 a 1.000 kg h^{-1} (Almeida e Monteiro, 2019; Monarca *et al.*, 2014). As plantacións de castiñeiro e soutos tradicionais poden presentar posibilidades económicas intermedias (cogomelos, mel, a caza, o engorde do gando, etc.) xunto con externalidades ambientais positivas (paisaxe, regulación do ciclo hidrolóxico, regulación de gases de efecto invernadoiro, etc.) (Schabacker, 2015).

Ademais dos tradicionais aproveitamentos, na actualidade diferentes investigacións estanse a levar a cabo na procura de novas aplicacións para a fitomasa residual do souto dentro dos ámbitos farmacéuticos, nutracéuticos, cosmético ou da alimentación humana (Braga, N. *et al.*, 2015). Desta maneira existe un potencial uso das sustancias bioactivas obtidas a partires das follas, ourizo ou cortiza dos castiñeiros con aplicacións na industria alimentaria (Liu *et al.*, 2016; Park *et al.*, 2016; Rodrigues *et al.*, 2015; Yao e Qi, 2016), de biocombustibles (He *et al.*, 2016), médica o farmacéutica (Lyles *et al.*, 2016; Quave, C. *et al.*, 2015; Santulli *et al.*, 2016; Seo *et al.*, 2016), de adhesivos, cosmética (Aires, A. *et al.*, 2016) ou biorremediación (Yao *et al.*, 2016).

A biomasa forestal residual derivada das plantacións de castiñeiro abranguería todas aquelas fraccións resultantes das operacións de mantemento da árbore (tallas de formación e podas) e aproveitamento do froito (follas e ourizos) (Figura 1.9).

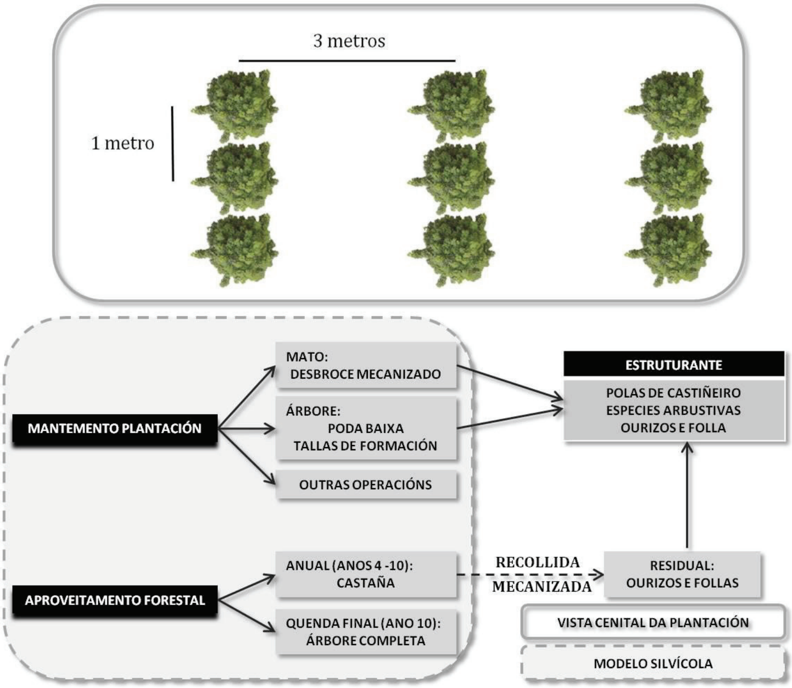

Figura 1.9. Esquema silvícola das plantacións de alta densidade de castiñeiro e orixe do material estrutúrante empregado. Fonte: Elaboración propia para o ámbito desta tese.

Adicionalmente inclúe unha mestura de especies adventicias, cuxa composición resulta moi variable segundo a calidade da estación forestal (Álvarez-Álvarez *et al.*, 2013) e que habería que eliminar ao competiren coas árbores pola luz e os nutrientes do solo.

Este material vexetal residual das plantacións de castiñeiros constitúe un interesante recurso orgánico susceptibles de ser integrado en procesos de compostaxe actuando como material estruturante (Figura 1.10).

Figura 1.10. Biomasa forestal residual das plantacións de castiñeiro: polas novas e mato (A), e ourizo e follas (B). Fonte: Propia, realizadas durante a execución dos traballos.

Experiencias previas de compostaxe foron realizadas por Guerra-Rodríguez *et. al* (2006, 2001a; 2001b). Estes autores indicaron que a compostaxe de follas e ourizos (principalmente ourizos, procedentes dunha industria de procesado da castaña, comunicación persoal) non era posible ao presentaren unha relación C/N demasiado elevada. A este respecto a concentración de N, K e outros elementos da fitomasa do souto depende de factores tales como a estación, a fase do ciclo vexetativo e a dispoñibilidade de nutrientes no solo forestal (Santa Regina *et al.*, 2001), se ben Arrobas et al (2018) atoparon malas relacións entre a fertilidade do solo e a concentración foliar de nutrientes nos soutos do nordeste de Portugal, adxacentes ao territorio galego. En calquera caso, estudos previos amosan que o contido de nutrientes das follas é superior á dos ourizos (Raimundo *et al.*, 2008).

En ensaios de laboratorio, Guerra-Rodríguez *et. al* correxiron a relación C/N coa adición de esterco de polo (2006, 2001a; 2001b), aditivo rico en N. Unha experiencia moi similar foi descrita por Zhang *et al.* (2019), na que ademais de esterco de polo e ovella como aditivos, empregaron urea para acadar o equilibrio C/N, establecendo sinxelos índices para avaliar a madurez do compost de ourizos de castiñeiro. Máis recentemente, Chen *et al.* (2020) propuxeron a adición de esterco e óso de vaca, 55% e 15% respectivamente, para lograr unha maior degradación das fraccións lignocelulósicas e reducir o tempo de compostaxe a 38 días, acadando un compost axeitado para actuar como substrato na propia produción de castiñeiro por semente.

Experiencias levadas a cabo no propio monte foron executadas por Ventorino *et. al* (2013) en Italia, país onde o castiñeiro ten unha especial relevancia. Estes autores empregaron ademais da folla e o ourizo, outros compoñentes como as especies arbustivas do sotobosque e brotes da árbore. A súa intención era intentar simular os procesos de degradación natural nun souto empregando a tal efecto, unha pila dun volume aproximado de 4 m^3, pero ese deseño non conseguiu acadar a fase termofílica.

1.3.3. Matogueiras.

Á marxe das producións madeireiras, os terreos forestais estiveron tradicionalmente vinculados á economía agraria de Galicia ao fornecer colleitas suplementarias de cereal, permitir a alimentación directa do gando así como a obtención de fertilizantes para as terras cultivadas (Balboa, 1990). Con respecto a esta última función, Balboa (1990) subliñou:

> *"…se hai algunha misión que o monte tivera que cumprir con total xeneralidade e á que non se podía subtraer en ningún recuncho poboado de Galicia, esa é a de producir estrume."*

Na súa función de produción de abono orgánico, as especies de mato eran extraídas do monte e logo dun tempo de secado era empregadas como leito para os animais nas cortes, onde se ía mesturando coas dexeccións animais. Progresivamente íanse engadindo sucesivas capas para a renovación da cama, ata que finalmente este material era extraído da corte, dúas ou tres veces ao ano, e empregado como fertilizante nas terras de labor (Balboa, 1990), en ocasións cuns importantes esforzos de traballo manual (Estabrook, 1998). Ao produto transformado aplicábaselle o termo "*estrume*", coincidente coas rexións do norte de Portugal nas que se levaban a cabo as mesmas prácticas (Estabrook, 1998, 2006; 2008).

Na interface agrícola-forestal, existía un equilibrio entre as terras fornecedoras de toxo e outras especies de mato, posteriormente transformadas a estrume, e os espazos laborables que demandaban fertilización se non se quería afectar en maior ou menor medida aos rendementos das colleitas (Balboa, 1990). En Galicia este equilibrio era mantido segundo Bouhier (1984) mediante unha proporción de 1 a 2 ha de monte por cada hectárea de terreo cultivado mentres que Balboa (1990) apunta a 20-40 carros de toxo por cada hectárea de cultivo. En Portugal, Estabrook (1998) subliña a necesidade de 6-8 ha de terreos con mato por cada hectárea de terreo cultivado, se ben o seu traballo desenvolveuse sobre solos pouco fértiles empregando en boa medida especies das ericáceas e cistáceas. As referencias cuantitativas sobre produtividade da fitomasa forestal varía amplamente, sendo en calquera caso as producións nas matogueiras superiores ás rexistradas polo desfronde e a fracción de ourizos nos soutos (Táboa 1.1).

Táboa 1.1. Produtividade anual das principais formacións de matogueira (en Galicia) e de fitomasa residual do souto (en Portugal e Italia). Valores en paréntese representan o rango ou desviación típicas**.**

Fitomasa forestal			**Produtividade (materia seca)**	
			t ha^{-1}	**Referencia**
Matogueiras	Monoespecíficas	Toxeiras con alta densidade	41,17 (11,63 – 94,14)	(Seijas *et al.*, 2009)
		Toxeiras vellas	45 (40 – 50)	(Vega Hidalgo *et al.*, 2001)
		Toxo	20	(Núñez-Regueira, 2004)
		Xesteiras	30	(Núñez-Regueira, 2004)
		Queirogais	15	(Núñez-Regueira, 2004)
	Pluriespecíficas		26,3 (±16,2)	(Viana *et al.*, 2012)
			21,06	(Núñez-Regueira, 2004)
Castiñeirais	Vellos		3,2	(Pires e Portela, 1998)
	Idade media		5,13 (5,47 – 4,78)	(Cutini, 1998)
	Idade temperá		2,64	Santa Regina *et al.*, 1998
			1,71	(Santa Regina *et al.*, 1998)

Dentro das matogueiras, as formacións de toxo acadan as maiores producións en termos de materia seca. Esta especie, endémica en Galicia (García, 2008) e unha das 100 "peores" especies invasoras a nivel mundial (Lowe *et al.*, 2000), constituía a especie de máis grande protagonismo na fertilización de terras na agricultura tradicional (Balboa, 1990). A tal punto que unha das preocupacións do campesiñado era a preservación das reservas de toxo no monte e sempre que fose posible, a súa renovación e aumento mediante sementeira (Bouhier, 1984). A poboación servíase do toxo para ser empregado directamente en verde con fins agronómicos no cultivo das viñas ou para mellorar a estrutura do solo. Ademais da alimentación animal de xeito directo no monte, era recolleito para a produción de forraxes ou mesturado con nabos ou patacas para criar cebóns (Balboa, 1990; Bouhier, 1984). As xestas eran menos valoradas, ao igual que outras especies representativas do medio galego (fentos, uces ou carqueixas) ao produciren estercos de baixa calidade, polo que só eran empregadas á falta doutras alternativas (Balboa, 1990).

Dende as últimas cinco décadas ata os tempos actuais, a área dedicada a cultivos agrarios e pastos reduciuse a unha pequena porción do territorio. Os usos do monte descritos e vinculados aos sistemas agrarios, tan importantes ata mediados do século XX, practicamente desapareceron por mor da despoboación do medio rural, o envellecemento dos seus habitantes e o abandono da actividade agrogandeira (Bouhier, 1984; Estabrook, 2006; López-Iglesias *et al.*, 2013), xerándose unha importante cantidade de biomasa forestal que non ten na actualidade ningún tipo de coidado ou aproveitamento.

Desta maneira, a superficie de Galicia ocupada exclusivamente por mato ascende a 606.588 ha (MMAMRM, 2011a), con predominio do toxo, presente en máis do 60% da superficie de Galicia (Figura 1.11).

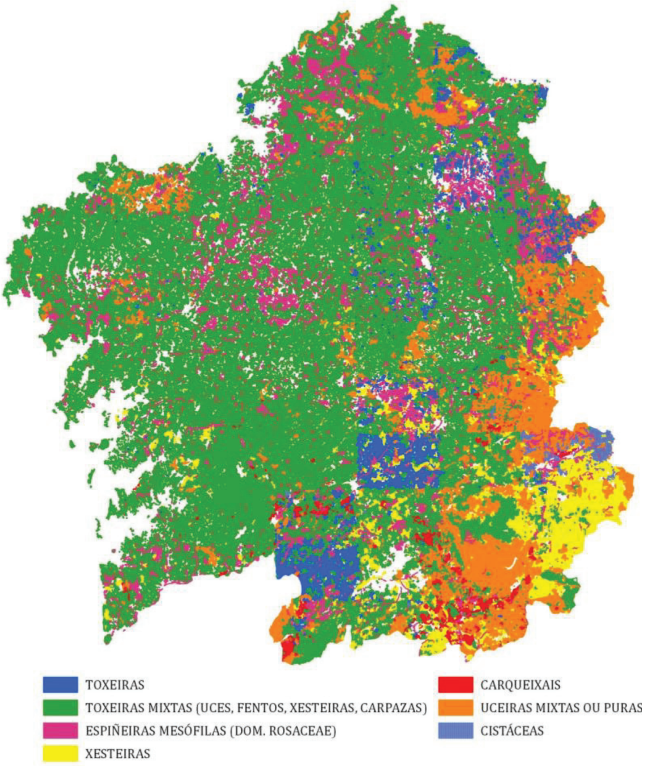

Figura 1.11. Principais formacións de mato en Galicia. Fonte: Propia, dende o Mapa Forestal de España, escala 1:25.000 (MMAMRM, 2011b).

A principal consecuencia ambiental desta situación de abandono de terras e acumulación de fitomasa forestal son os incendios forestais (Estabrook, 2006; López-Iglesias *et al.*, 2013), problema ambiental de primeira magnitude en Galicia (Álvarez-Díaz *et al.*, 2015), a tal punto que na actualidade un total de 197 concellos, representando aproximadamente o 69% do territorio galego (Figura 1.12) están declarados como zonas de alto risco de incendio forestal (DOG, 2007).

Estas zonas de alto risco defínense como superficies onde se recoñece como prioritaria a aplicación de medidas máis rigorosas de defensa contra os incendios forestais ante o elevado risco de incendio, pola súa especial frecuencia, virulencia ou a importancia dos valores ameazados.

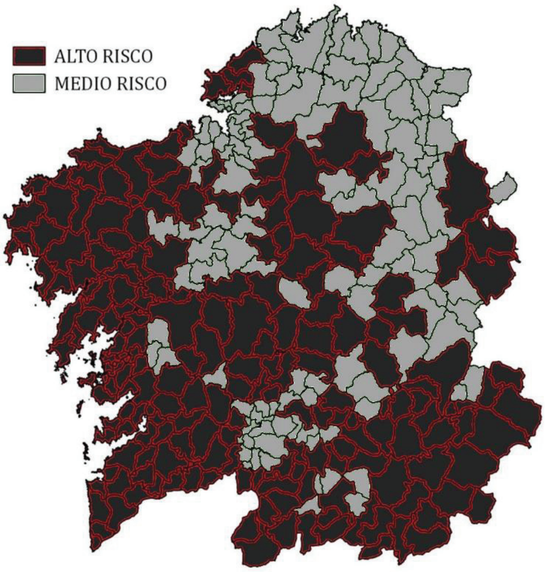

Figura 1.12. Zonificación de Galicia en base ao risco de incendio forestal. Fonte: Redibuxado dende o Anexo I da Orde do 18 de abril do 2007 pola que se zonifica o territorio con base ao risco espacial de incendio forestal (DOG, 2007).

A acumulación de fitomasa forestal e a especial incidencia dos incendios na rexión provocan que anualmente miles de hectáreas sexan queimadas, na súa meirande parte en superficies cubertas por matogueira (Figura 1.13).

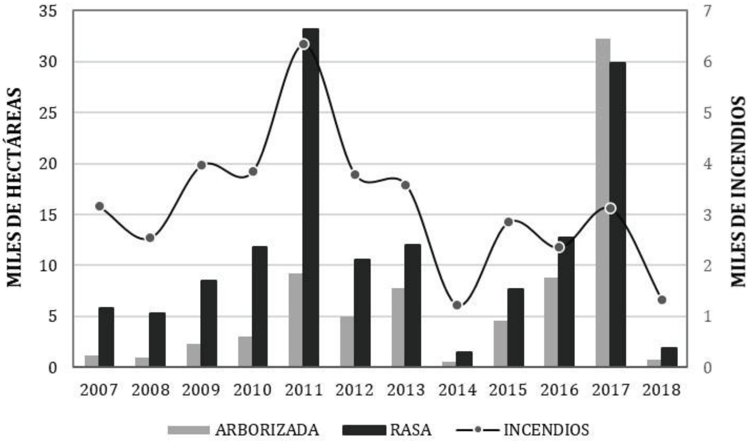

Figura 1.13. Evolución do número de incendios forestais e da superficie afectada en Galicia. Fonte: Instituto Galego de Estatística (IGE, 2019a).

Esta fitomasa forestal constitúe un recurso orgánicos susceptible de seren integrado en procesos de compostaxe, ben por si mesmos, ben como compoñentes con outros aditivos en función dos ratios C/N que presenten os materiais. Esta orientación xa fora suxerida por Bouhier (1984) fronte a acumulación derivada do abandono das antigas prácticas agrarias expostas en apartados precedentes.

A composición química das matogueiras varían en función da calidade do sitio no que habitan e da proporción e composición das súas especies (Núñez-Regueira, 2004; Seijas *et al.*, 2009). A Táboa 1.2 presenta a caracterización de especies arbustivas amplamente distribuídas no noroeste de España, a maioría da familia das leguminosas, ao ser a formación arbustiva maioritaria en Galicia (MMAMRM, 2011a).

O interese destas análises foi o seu potencial uso para a produción de enerxía eléctrica (Núñez-Regueira, 2004; Núñez-Regueira *et al.*, 1994; Soliño *et al.*, 2010, 2009; Viana *et al.*, 2012) e, en menor medida, forraxe para animais de pasto (Bao *et al.*, 1998; Gonzalez-Hernandez e Silva-Pando, 1999; Lambert *et al.*, 1989), azucres destinadas á industria alimentaria e farmacéutica (Ares-Peón *et al.*, 2013; Ligero *et al.*, 2011), e biofibras para a fabricación de taboleiros (Celis *et al.*, 2014; Presenti *et al.*, 2017).

A composición química da matogueira pode condicionar os distintos usos pretendidos. Para a produción de enerxía, límites de N do 0,6% en peso (m.s.) ocasionan problemas de exceso nos límites de emisión (NO_x) (Obernberger *et al.*, 2006) namentres que valores do mesmo elemento superiores ao 1.7% (m.s.) son recomendados para que o pastoreo de animais realice a niveis satisfactorios (Lambert *et al.*, 1989). O Cl e o S poden igualmente comprometer a combustión da matogueira e valores por riba do 0.1% e 0.2-0.3% (m.s.), respectivamente, poden provocar corrosión e emisións gasosas indesexables (HCl e SO_x, entre outros) (Obernberger *et al.*, 2006). Estas situacións fan necesaria a adopción de distintas medidas tecnolóxicas para a depuración dos gases da combustión (Obernberger *et al.*, 2006), suxerindo Viana *et al.* (2012) ensaios demostrativos para as especies de matogueira, sinaladas na Táboa 1.2 para o ámbito local, dada a escaseza de estudos previos para a súa combustión en caldeiras.

Táboa 1.2. Caracterización química (m.s.) das principais especies de mato do noroeste peninsular (celas en branco indican a ausencia de datos; números en paréntese representan a desviación estándar).

Familia	Especie	Nome vernáculo	Ámbito	C %	N %	P (gr/kg)	K (gr/kg)	Ca (gr/kg)	Mg (gr/kg)	S (gr/kg)	Sólidos totais %	Referencia
Hypolepidaceae	*Pteridium aquilinum* L.	Fento	Local	45,4 – 46,7	1,41 – 2,58					0,9 – 3,1	52.4 – 27.5	(Núñez-Regueira *et al.*, 1996)
			Nacional	46,0	1,74							Pérez et al (2014)
Leguminosae	*Genista triacanthos* Brot.	Xesta	Internacional		1,24	1,0	3,4	1,3	0,9	0,9		Estabrook (1998)
	Cytisus scoparius (L.) Link	Xesta	Local	46,2 – 51,1	1,01 – 4,84					0,8 – 2,1	52.4 – 33.3	Núñez *et al.* (1996)
				49,0 – 58,6	1,38 – 2,99					4,2 – 5,0	57,0 – 40,6	Núñez *et al.* (2004)
			Internacional		2 – 3,9							Lambert et al (1989)
	Cytisus multiflorus (L´Her.)	Xesta branca	Local	48,8 (±0,7)	2,05 (±0,65)					< 0,1 (%)	40,8 (±1,7)	Viana et a, (2012)
	Ulex europaeus L.	Toxo arnal	Local	47,0 – 49,7	1,0 – 3,06					0,7 – 2,3	42,5 – 38,0	Núñez *et al.* (1996)
				48,8 – 58,4	0,84 – 2,10					1,7 – 4,8	57,5 – 38,0	Núñez *et al.* (2004)
				48,9 (±0,5)	1,72 (±0,09)					< 0,1 (%)	53,3 (±2,2)	Viana et a, (2012)
				47,8	1,33	0,4	6.80	2,1	0,9	1,25	53,0	(López-López e López-Fabal, 2016)
			Nacional	48,1	2,34							Pérez et al (2014)
			Internacional		1,3 – 1,9							Lambert et al (1989)
	Pterospartum tridentatum (L.) Wilk	Carqueixa	Local	48,8 (±0,3)	0,96 (±0,25)					< 0,1 (%)	53,7 (±1,5)	Viana et a, (2012)
Rosaceae	*Rubus fructicosus* L.	Silva	Local	45,6 – 47,2	1,71 – 2,97					1,2 – 1,6	45,0 – 34,3	Núñez *et al.* (1996)
	Rubus ulmifolius Schott.	Silva	Nacional	46.0	2,24							Pérez et al (2014)
Ericaceae	Genus *Erica*	Carqueixas	Local	46,8 – 52,6	0,61 – 1,91					3,1 – 4,0	55,6 – 39,7	Núñez *et al.* (2004)
	Erica australis L.	Urce vermella	Local	48,1 (±0,5)	0,82 (±0,08)					< 0,1 (%)	41,1 (±0,9)	Viana et a, (2012)
	Erica cinerea L.	Carpaza	Internacional	51,0	1,0							Pérez et al (2014)
			Internacional		0,64	1,6	4,2	2,9	0,9	1,0		Estabrook (1998)
	Erica arborea L.	Uz	Internacional		0,86	0,6	2,0	1,0	0,8	0,6		Estabrook (1998)
	Erica umbellata L.	Carrasco	Internacional		0,90	0,6	1,2	1,6	0,9	0,7		Estabrook (1998)
	Calluna vulgaris (L.) Hull.	Queiroga común	Internacional		0,58	1,0	1,7	2,4	1,0	1,0		Estabrook (1998)

En xeral, todas as especies presentan un alto contido en C, con valores próximos, ou por riba do 50%. O contido en N está no amplo rango do 0.6 – 4.8%, dentro do cal as ericáceas tenden a presentar os valores máis baixos, e ao mesmo tempo os máis altos de C. As especies desta familia están normalmente asociadas aos solos de peor calidade (Webb, 2008) e sobre eses solos a funcionalidade ecolóxica do mato debería prevalecer sobre calquera outro fin baseado na extracción de fitomasa. O xénero *Citysus* parece presentar as maiores concentracións de N, aínda que os valores varían, por un factor de máis de 4 nalgúns casos, entre especies e autores.

En calquera caso, o contido en N das especies de mato en Galicia é superior ao das especies leñosas de coníferas e caducifolias (Obernberger *et al.*, 2006). Segundo Núñez *et al.* (2004) a composición química das especies de matogueira depende das condicións climáticas da área na que habitan, e as variacións dentro desta varían segundo a fracción estudada (follas > tallo > raíces) e a estación do ano, xeralmente maiores na primavera (Lambert *et al.*, 1989; Viana *et al.*, 2012). A estacionalidade para unha mesma localización determina variacións moderadas na composición do mato e este é un factor sinalado por estes autores para unha correcta xestión da alimentación animal e a súa calidade como para uso enerxético. Sen embargo, as flutuacións estacionais do mato non son tan importantes en procesos de compostaxe, nos que a relación C/N é o principal parámetro considerado, o cal pode ser equilibrado con diferentes combinacións de mesturas ou o emprego doutros residuos como aditivos.

O contido de humidade está próximo ao 50% nas diferentes especies. Durante a explotación madeireira, a redución da humidade é unha operación importante e o secado en áreas próximas ao monte pode aumentar a produtividade do transporte nun 50% (Stampfer e Kanzian, 2006). Para fins enerxéticos, a redución da humidade é relevante para incrementar o rendemento enerxético total (Núñez-Regueira, 2004; Pérez *et al.*, 2014), mais dentro do ámbito da compostaxe a importancia radica na maximización da cantidade total doutros materiais a co-compostar para acadar as humidades convenientes na mestura inicial. Na rexión, Núñez Regueira et al (2004) recomendan a instalación de galpóns de secado para minimizar a humidade, indicando que o simple almacenamento da biomasa baixo condicións adecuadas reduce e mantén o valor medio da humidade nun 30%.

En relación á compostaxe con especies de mato, Tighe-Neira *et al.* (2014) subliñaron como oportunidade o emprego do toxo (*Ulex europaeus*) como material de base para procesos de compostaxe ou co-compostaxe con estercos animais. Gómez *et al.* (2009) e Iglesias et al (2009) comprobaron a idoneidade do compost feito a partires de toxo triturado podía actuar como como, respectivamente, substrato de cultivo ou substitutivo da turba ou para a propagación de estaquillas de *Thuja plicata*. Estes autores acadaron máximos de temperatura na etapa termofílica comprendidos entre os 50-60 ºC durante a primeira semana de proceso. Estes valores foron superados por Brito *et al.* (2010) durante a co-compostaxe de toxo coa fracción sólida das dexeccións dunha granxa de vacún, acadando temperaturas de 74ºC ao terceiro día de proceso.

Os traballos de Estabrook, G.F. (2008) en Portugal destacan a utilidade do emprego da xesta como material estruturante e conservación do contido de N nos solos. En experiencias de fertilización empregando xesta e excrementos, dobrábanse as producións de centeo empregando xesta mesturada con excrementos fronte a xesta illadamente debido a unha redución da relación C/N (de 30 da xesta a 20 do estrume) o que favorecía unha maior degradación do material. En referencia a outras especies de matogueira, traballos de Pitman e Webber apuntaron á viabilidade do emprego de compost de fento como substitutivo da turba (2013).

1.4. DEXECCIÓNS GANDEIRAS.

1.4.1. Marco sectorial.

Actualmente a política estatal en materia de residuos agrarios non está directamente enfocada á xestión e aplicación dos estercos. As orientacións do Plan Estatal Marco de Residuos (MAAMA, 2016) pasan pola necesidade de análise e concreción do alcance da aplicación da normativa de residuos aos estercos, resaltando a necesidade de coordinar o réxime xurídico aplicable. A nivel de planificación local existen referencias de modelos de xestión exitosos das dexeccións animais (Dupuis, 2012; Vargas García, 2014) axustados aos condicionantes específicos de cada ámbito territorial.

A Directiva 91/676/CEE relativa á protección das augas contra a contaminación producida por nitratos empregados na agricultura, coñecida como Directiva Nitratos (DOUE, 1991), ten como obxectivo principal o de reducir e previr a contaminación da auga por nitratos de orixe agrario. Se ben as condicións de aplicación de dexeccións como fertilizantes en España limítase ao N, noutros países (Irlanda, Suecia, Estonia, Finlandia, Alemaña, Bélxica, etc.) a carga de P é tamén unha limitación, ben como requirimento legal ou ben soamente a modo de recomendación (EC, 2015).

A Directiva Nitratos impón aos Estados membros a necesidade de identificar dentro do seu territorio as zonas vulnerables á contaminación por nitratos nas que serán de aplicación programas de actuación específicos. Sobre estas zonas marca como referencia o límite de 170 kg de N por hectárea e ano para avaliar como correcta a xestión dos residuos orgánicos na súa opción de aplicalos directamente sobre o terreo. Porén para os primeiros programas de actuación cuadrienais permitíanse límites de 210 kg N ha^{-1} ano^{-1}.

Derivado da publicación da Directiva Nitratos, aprobouse en Galicia o Código Galego de Boas Prácticas Agrarias (DOG, 1999). Este documento recolle recomendacións, de carácter voluntario, para a fertilización con estercos ou xurros de cara a evitar a contaminación nas augas continentais. As referencias en canto ás cantidades máximas de fertilizantes a aplicar, orgánico ou inorgánico, toman como referencia as 170 kg N ha^{-1} ano^{-1}. Porén, a Consellería de Medio Ambiente declarou a non existencia de zonas vulnerables na Comunidade Autónoma de Galicia

(DOG, 2000a) polo que non foron necesarios plans de acción específicos para zonas máis sensibles.

Por outro lado, a Xunta de Galicia elaborou a Estratexia Galega de Xestión de Residuos (DOG, 2000b) para dar unha resposta axeitada a diferentes tipos de residuos configurando para iso plans de xestión específicos, entre eles, o Plan de Xestión de Residuos Agrarios de Galicia (Xunta de Galicia, 2001). O obxectivo principal deste Plan é a adecuada xestión dos residuos xerados na actividade agraria, contemplando, en canto as dexeccións se refire, as seguintes alternativas:

1. Valorización mediante aplicación directa ao solo como fertilizantes.
2. Obtención de compost.
3. Valorización mediante instalacións de tratamento e redución.
4. Valorización enerxética por fermentación anaerobia da materia orgánica.
5. Eliminación por depuración previa vertedura á rede de saneamento ou hidrolóxica.

A elección do tratamento adecuado dependerá da consecución de requisitos tales como a minimización do impacto ambiental, custe económico, máximo aproveitamento dos recursos contidos nas dexeccións, a aceptación social, ou a facilidade de aplicación e mantemento do sistema de xestión.

Os estercos non dispoñen dunha regulación específica. O marco lexislativo contén normas de distintos ámbitos de aplicación e elementos do ambiente a protexer que indirectamente atinxen a estes materiais. En ausencia dunha lectura sectorial transversal, a interpretación de procedementos ou modalidades de xestión resulta a miúdo confusa para o sector produtor (Dupuis, 2012; Ortolano *et al.*, 2009).

A nivel europeo, a Directiva 2008/98 de residuos exclúe ás dexeccións gandeiras do seu ámbito de aplicación cando sexan empregados na agricultura, silvicultura ou na produción de enerxía de maneira que non se perxudique ao medio ou poña en perigo a saúde humana.

Por outro lado, o Regulamento 1069/2009 polo que se establecen as normas sanitarias aplicables aos subprodutos animais e aos produtos derivados non destinados ao consumo humano (DOUE, 2009) engloba ás dexeccións animais dentro da Categoría 2.

Dende un punto vista lexislativo a consideración das dexeccións gandeiras como residuo é función do seu destino e condicións de uso, o que a súa vez determina a aplicación dunha ou outra norma. Así, a efectos normativos, os estercos ou puríns, pode ter distintas consideracións (Táboa 1.2).

Táboa 1.2. Concepto de dexección con respecto á norma e segundo usos contemplados (artigo 2 da Directiva 2008/98 e artigo 13 do Regulamento 1069/2009).

NORMA	CONCEPTO	DEFINICIÓN	USOS
Directiva residuos	Residuo	Calquera substancia ou obxecto que o seu posuidor desbote ou teña a intención ou a obriga de desbotar	Incineración, vertedoiros ou empregados nunha planta de gas ou de compostaxe
Regulamento subprodutos animais	Subproduto animal	Corpos enteiros ou partes de animais, produtos de orixe animal ou outros produtos obtidos a partir de animais, que non están destinados para o consumo humano, incluídos os oocitos, os embrións e o esperma	a) Eliminación como residuo mediante incineración. b) Eliminación ou valorización mediante coincineración. c) Eliminación en vertedoiro autorizado, previo procesado mediante esterilización e marcado permanente do resultante. d) Fabricación de abonos e enmendas orgánicas a introducir no mercado. e) Compostaxe ou transformación en biogás. f) Aplicación á terra sen procesamento previo. g) Ensilado, compostaxe ou transformación en biogás se é orixinario de animais acuáticos. h) Combustible con ou sen procesado previo. i) Fabricación dos produtos derivados mencionados nos artigos 33, 34 e 36, e introduciranse no mercado dacordo con ditos artigos

A existencia dunha superficie agraria dispoñible na que valorizar os estercos como fertilizante desvía a estes materiais do ámbito da Directiva de residuos. En ausencia desta alternativa, o produtor ou gandeiro adquirirá o carácter de produtor de residuos, definido na lei como "*calquera persoa física ou xurídica cuxa actividade produza residuos (produtor inicial de residuos) ou calquera persoa que efectúe operacións de tratamento previo, de mestura ou de outro tipo, que ocasionen un cambio de natureza ou composición destes residuos*". É dicir, a efectos legais tería a mesma consideración que os produtores de actividades industriais ou do sector terciario. Por outro lado, o seu protagonismo como produtor implicaría a súa responsabilidade de xestión en aplicación do principio "quen contamina paga". As alternativas neste caso, en calquera delas debendo acometer os custes e a acreditar documentalmente, serían:

a. Realizalo tratamento dos residuos por medios propios.

b. Encargalo tratamento dos residuos a un negociante, ou a unha entidade ou empresa, todos eles rexistrados conforme ao establecido na Lei de residuos.

c. Entregalos residuos a unha entidade pública ou privada de recollida de residuos, incluídas as entidades de economía social, para o seu tratamento

O Regulamento 1069/2009 foi trasposto ao ordenamento xurídico español mediante o Real Decreto 1528/2012 que establece disposicións específicas para as dexeccións gandeiras entre as que cómpre destacar (BOE, 2012):

1. No que respecta ás condicións aplicables para a produción de compost, considera as dexeccións animais como materia prima apta sen necesidade dunha transformación previa.
2. Autoriza o seu emprego nas terras sen necesidade de procesamento previo, sen prexuízo dos requisitos doutras normas, particularmente as de carácter ambiental, e salvo se considere que exista risco de propagación dalgunha enfermidade transmisible a través de ditos produtos para os seres humanos ou animais.

1.4.2. Dexeccións de gando porcino.

A aplicación directa das dexeccións de porcino sobre o terreo constitúe o método de xestión máis habitual. Estudos levados a cabo a nivel estatal puxeron de manifesto que un 91% das explotacións destinan os xurros como abono en campo sendo este distribuído mediante espallado (MMAMRM, 2010b).

No caso concreto da gandaría intensiva de porcino, o sector experimentou unha profunda evolución nas últimas décadas de tal xeito que a produción de carne ocupa un dos primeiros lugares dentro da produción final agraria española (MMAMRM, 2010b). Esta evolución implicou importantes transformacións ao longo do tempo nun contexto produtivo, sanitario, económico e ambiental.

Froito desas transformación no ano 2000 publicouse o Real Decreto 324/2000, do 3 de marzo, polo que se establecen normas básicas de ordenación das explotacións porcinas (BOE, 2000) actualizando unha lexislación sectorial naquel entón obsoleta, preconstitucional e non adaptada a nova realidade dese momento. O fin era encamiñar o crecemento do sector respectando a ocupación racional do territorio, o ambiente, a saúde humana e o benestar animal. O seu contido foi recentemente derrogado polo Real Decreto 326/2020 (BOE, 2020) que, no que á xestión de estercos atinxe, admite dúas vías de xestión. A primeira, a valorización agronómica que deberá axustarse ao disposto ao Real Decreto 261/1996, de 16 de febreiro, sobre protección das augas fronte á contaminación por nitratos de orixe agraria. A segunda sería a entrega a unha instalación ou operador autorizado, ou ben ser xestionado dentro da propia explotación segundo o Regulamento (CE) n.º 1069/2009, para a produción de compost ou biogás principalmente.

1.4.3. Explotacións gandeiras en Galicia.

En Galicia téñense experimentado profundos cambios estruturais nas explotacións gandeiras sendo as súas principais manifestacións a redución do seu número, a súa especialización e intensificación nas producións polo incremento do tamaño das explotacións (Xunta de Galicia, 2001). Situacións similares tiveron lugar noutras rexións de Europa (Poláková *et al.*, 2011): Holanda (Bos *et al.*, 2013), Bretaña francesa (Ortolano *et al.*, 2009), Cataluña (Ramsey *et al.*, 2013) ou Italia (Zavattaro *et al.*, 2016).

O gando bovino e o porcino son as principais especies explotadas en Galicia (Figura 1.14a). No caso concreto do gando porcino, durante os dez anos que separan os dous últimos censos agrarios (1999-2009) a redución experimentada do 78% no número de explotacións acompañouse dun descenso do 7% no número de animais (Figura 1.14b). Esta concentración das producións está asociada á xeración de dexeccións animais sobre áreas máis localizadas.

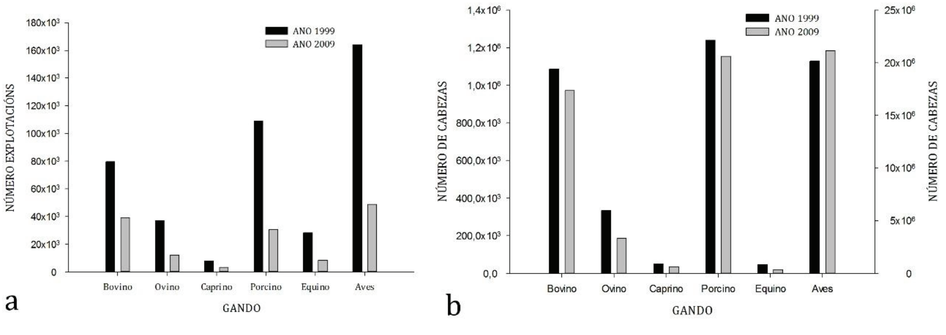

Figura 1.14. Evolución por tipo e capacidade produtiva das explotacións gandeiras galegas (na Figura 1.14b, o eixo dereito correspóndese exclusivamente para as aves). Fonte: Elaboración propia a partires da información dos censos agrarios de 1999 e 2009 do Instituto Nacional de Estatística.

En canto á base territorial, as explotacións son manexadas con frecuencia de xeito intensivo empregando xurros e fertilizantes inorgánicos para incrementar a produción agraria pero ao mesmo tempo os riscos ambientais. Doses anuais de 100 m^3 ha^{-1} de xurro e 1.000 kg ha^{-1} de

NPK 8:24:16 en áreas de gandaría intensiva no interior de Lugo foron sinaladas por Seco-Reigosa *et al.* (2015). Noutras ocasións a sobrefertilización é debida á insuficiencia de capacidade das fosas de xurro para as dimensións das explotacións (López-Mosquera *et al.*, 2005).

En contraposición cos antigos sistemas de produción (López-Iglesias *et al.*, 2013), a moderna gandaría supuxo o tránsito dun modelo de alimentación baseado nos pastos marxinais ou subprodutos da explotación agrícola, a outro no que os animais, criados sen ou con pouco leito, dependen de dietas moi estudadas baseadas en cereais e leguminosas, e pobres en materiais carbonosos (Boixadera, J., 2006).

No sector bovino, a alimentación baséase en boa medida en producións agrícolas obtidas e asociadas á base territorial das explotacións, o que permite un certo grao de autosuficiencia, variable segundo o rendemento das colleitas. Esta base territorial permite por tanto, obter alimento para os animais e adicionalmente, aproveitar as súas dexeccións na súa forma de xestión máis sinxela e barata, a aplicación directa ao terreo da propia explotación como fertilizante.

Poren, no sector porcino a base territorial adquire menor importancia xa que a alimentación dos animais procede integramente de pensos compostos, cuxa produción está deslocalizada ou é allea á explotación. Desta maneira, existe unha menor dependencia da base territorial asociada á explotación para a alimentación animal, manténdose a produción das dexeccións, e xa que logo a súa necesidade de xestión con destino fóra da base territorial.

1.4.4. Distribución das producións.

A forma na que as explotacións e a contía das producións se distribúen xeograficamente é un aspecto importante para avaliar as afeccións ambientais derivadas da súa actividade. Boa parte da produción europea concéntrase en Bélxica, Alemaña e Bretaña francesa, sobresaíndo en España as rexións de Cataluña e Murcia (Figura 1.15).

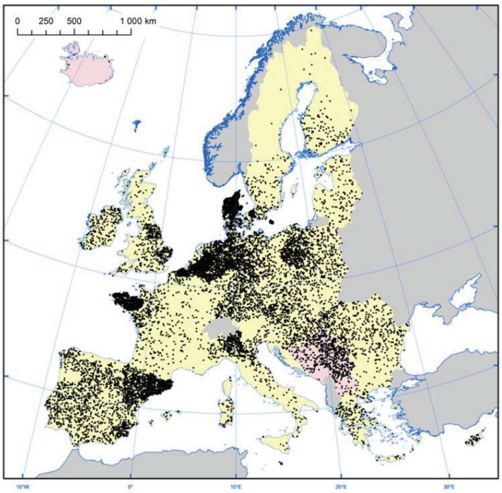

Figura 1.15. Distribución da produción porcina en Europa. Fonte: Eurostat (2013).

Restrinxindo o ámbito xeográfico a Galicia, estimacións da carga gandeira en termos de unidades de gando maior (UGM), confirman que o 56% dos concellos supera as 2 UGM ha^{-1}. Nos restantes distínguense dúas grandes zonas en Galicia, setentrional e oriental, onde se concentran 33 e 49 concellos respectivamente, nos que a carga gandeira é inferior ás 2 UGM ha^{-1}.

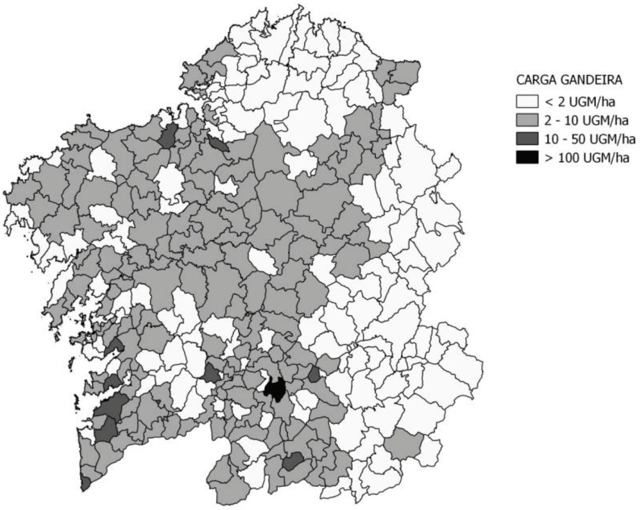

Figura 1.16. Carga gandeira en Galicia (UGM ha^{-1} SAU) para a totalidade de especies. Fonte: Elaboración propia a partir de datos do Instituto Nacional de Estatística (IGE, 2019b) o e relación de explotacións gandeiras en Galicia (Xunta de Galicia, 2015).

Estimacións similares sobre os aportes de N derivada das dexeccións animais das explotacións gandeiras por orientacións zootécnicas revelan amplas diferenzas entre os distintos concellos (Xunta de Galicia, 2015). A Figura 1.17 relaciona os aportes de nitróxeno derivados das dexeccións animais co valor da superficie agraria utilizada (SAU[1]) para cada concello. Tomando como referencia o valor de 170 kg N ha^{-1} subliñado no Código Galego de Boas Prácticas Agrarias (Xunta de Galicia, 1999), só coa produción de porcino, esta cantidade é superada en 19 concellos.

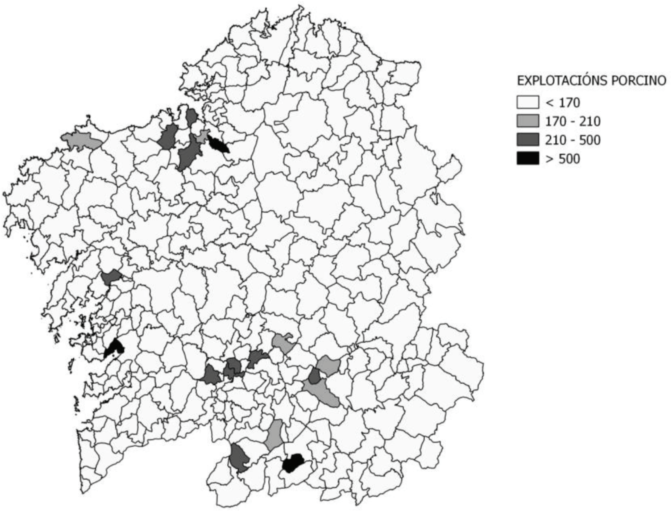

Figura 1.17. Cantidade de N xerado polas explotacións de porcino en Galicia referida á SAU. Fonte: Elaboración propia a partir de datos do Instituto Nacional de Estatística (IGE, 2019b) e relación de explotacións gandeiras en Galicia (Xunta de Galicia, 2015).

Estendendo a análise ao conxunto de explotacións gandeiras, amplíanse as zonas nas que a carga de N de orixe agrario, de seren aplicados na súa totalidade como fertilizante ao solo, pode implicar impactos ambientais negativos (Figura 1.18).

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[1] A SAU comprende o conxunto da superficie de terras labradas (as que reciben coidados culturais con arado, aixada, grade, cultivador, etc.) e terras para pastos permanentes (terras non incluídas na rotación de cultivos, adicadas de forma permanente á produción de herba).

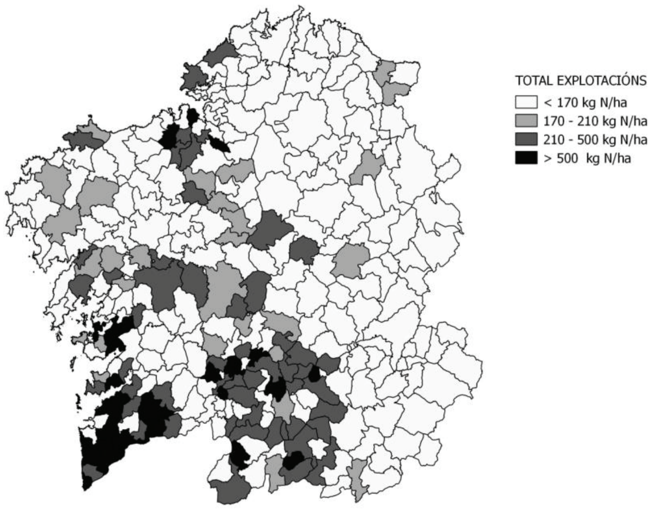

Figura 1.18. Cantidade de N xerado nas explotacións agrogandeiras en Galicia referida á SAU. Fonte: Elaboración propia a partir de datos do Instituto Nacional de Estatística (IGE, 2019b) e relación de explotacións gandeiras en Galicia (Xunta de Galicia, 2015).

En preto dun 25% dos concellos de Galicia, boa parte concentrados ao leste das provincias de Ourense e Pontevedra, xéranse nas explotacións gandeiras dexeccións animais cuxa carga en nitróxeno excede os 210 kg ha^{-1}. En 27 concellos a carga excede os 500 kg ha^{-1}.

Estas referencias non ofrecen resposta a situacións particulares polo que análises pormenorizadas deberían adecuarse ás circunstancias no ámbito local. Así, por exemplo, danse casos como na zona suroeste de Pontevedra (A Guarda, Moaña, Poio, Gondomar, etc.) nos que o problema non radica tanto na concentración da gandería extensiva senón nunha SAU moi reducida sobre a que aplicar as dexeccións como fertilizantes ao solo: 15 hectáreas en Moaña, 17 en A Guarda ou 24 en Poio (IGE, 2019b). Na comarca do Deza, a carga de N segue a ser elevada a pesares de que concellos como Lalín ou Silleda contan cun valor importante de SAU, 14.325 e 7.283 hectáreas respectivamente.

Aos aportes da fertilización animal, habería que engadir os procedentes dos abonos minerais. A fertilización mineral en Galicia acadou un máximo nos últimos anos de 70 kt en 2007. As cargas medias de abonos minerais nitroxenados en Galicia, referidas á SAU media, ascenderon aos 28 kt ha^{-1} nos anos 2005, 2010 e 2014 (Figura 1.19).

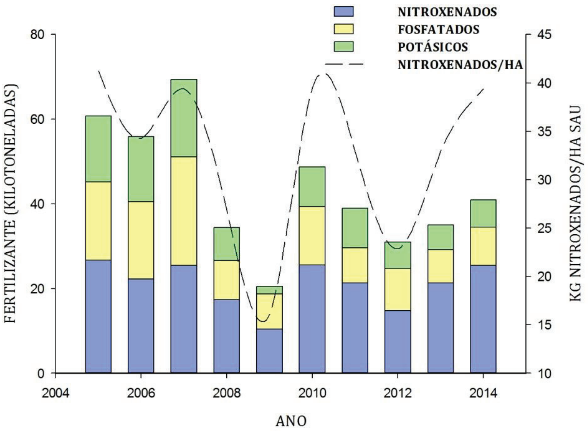

Figura 1.19. Consumo anual de fertilizantes inorgánicos en Galicia e carga media do aporte de nitróxeno mineral referenciado á SAU total en 2009 (no gráfico, o eixo dereito correspóndese coa liña descontinua). Fonte: Elaboración propia a partir de estatísticas estatais (MAAMA, 2014b) e valor da SAU de Galicia tomada do último censo agrario (IGE, 2019b).

A situación descrita contrasta coas estimacións levadas a cabo polo Plan de Xestión de Residuos Agrarios de Galicia (Xunta de Galicia, 2001) no que se considerou que a meirande parte dos concellos eran deficitarios en N tendo en conta as demandas deste elemento polos cultivos (Figura 1.20).

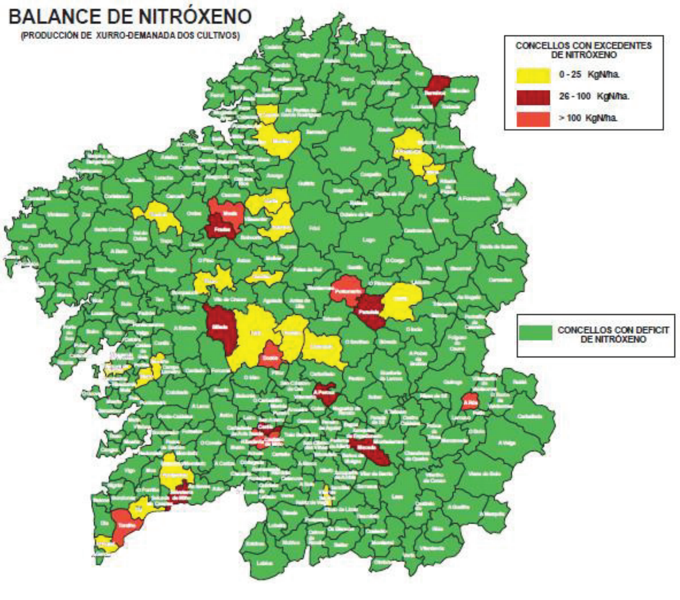

Figura 1.20. Balance de nitróxeno estimado pola produción de dexeccións nas explotacións gandeiras e a demanda dos cultivos en 2001. Fonte: Redibuxado dende o Plan de Xestión de Residuos Agrarios de Galicia (2001).

Naquel momento a meirande parte dos concellos eran deficitarios se ben no período que separa os dous últimos censos agrarios dispoñibles (1999 e 2009), a SAU de Galicia sufriu unha diminución de case 50.000 hectáreas (IGE, 2019b).

A consideración do xurro como residuo depende do posterior destino, o que, no caso da súa aplicación directa ao terreo, á súa vez depende da cantidade de superficie agraria útil a nivel local. Desta maneira a clasificación como residuo xa non depende logo, en boa medida, das propiedades do material senón de circunstancias extrínsecas ao mesmo. Neste contexto, a carga total de nitróxeno e a dispoñibilidade de SAU son variables interdependentes cuxa dimensión está condicionada por unha serie de factores externos (Figura 1.21).

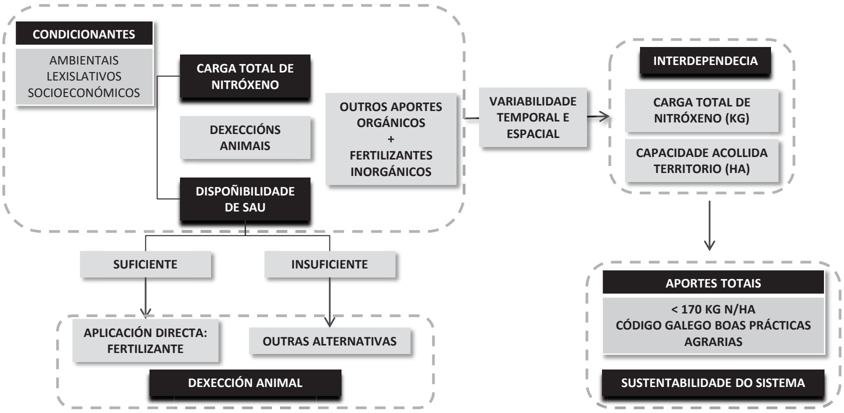

Figura 1.21. Relacións sinópticas na xestión das dexeccións animais. Fonte: Elaboración propia para o ámbito desta tese.

A capacidade de acollida do territorio para a aplicación directa das dexeccións depende do dinamismo do sector primario. A evolución no número e distribución de explotacións incide na produción de esterco e inflúe, pola base territorial asociada a estas, na superficie susceptible de recibir fertilización orgánica. Outros factores a ter en conta para avaliar as relacións de interdependencia serían as tendencias sociodemográficas, políticas agrarias, condicións de mercado para a rendibilidade das explotacións, etc. En definitiva, trátanse de relacións complexas, de carácter non estático, que deben ser avaliadas en función do dinamismo do sistema ambiental, lexislativo, xeoespacial, económico e social do que forman parte.

A situación de sobrecarga gandeira de Galicia é extrapolable a outras zonas de España onde en zonas puntuais acádanse elevadas cargas gandeiras debido a un desenvolvemento das explotacións desordenado e desintegrado do ambiente (MMAMRM, 2010b).

Cómpre prestar especial atención ás dexeccións en forma líquida debido á maior rapidez na que se manifestan os seus efectos no ciclo hidrolóxico, cuestión a ter en conta de maneira singular en Galicia debido ás elevadas precipitacións medias anuais rexistradas comparativamente con outras rexións de España. Diversos autores apuntan a que a transformación experimentada nas últimas décadas polos sistemas agrícolas tradicionais deu lugar a unha progresiva diminución do esterco en detrimento de dexeccións en forma líquida (Dupuis, 2012; Fernández-Marcos e Álvarez-Rodríguez, 2011). Os estercos en fase líquida, e en boa parte a causa do hidrolavado nas granxas, teñen o inconvinte do seu alto contido en auga, o que encarece o seu transporte, sen variar o grao de dilución o contido total dos seus compoñentes (MMAMRM, 2010b).

Nas explotacións intensivas de gando porcino a meirande parte das dexeccións están en forma líquida, 99,29% do total, fronte ao 0,71% que representa a fase sólida (MMAMRM, 2010b). Segundo ata o de agora exposto, existe a necesidade de tratamento destas dexeccións baixo risco de consecuencias ambientais negativas (EC, 2015):

- Contaminación das augas superficiais e subterráneas (NO_3^-, NH_4^+, etc.).
- Acidificación (NH_3, H_2S, NO_X, etc.).
- Eutrofización (N, P).
- Contaminación atmosférica (NH_3, N_2O, NO, polvo, bioaerosoles, etc.).
- Incremento de gases de efecto invernadoiro (CO_2, CH_4, N_2O, etc.).
- Desecación (uso da auga subterránea).
- Perturbacións locais (olores, ruídos).
- Contaminación difusa de metais pesados, pesticidas e substancias tóxicas.
- Dispersión de patóxenos incluíndo aqueles resistentes aos antibióticos.
- Residuos farmacéuticos nas augas.

A Táboa 1.3 recolle unha serie de técnicas dispoñibles (EC, 2015) para mellorar as propiedades dos xurros. Unha estratexia de manexo pode consistir nun único proceso ou na combinación de varios diferentes.

Táboa 1.3. Principais características das técnicas para o tratamento das dexeccións (EC, 2015).

Tecnoloxía	Obxectivo	Principais beneficios ambientais	Principais efectos cruzados
Separación mecánica	Separación e concentración das fases sólidas e líquidas	A fase sólida é mais manexable fóra da granxa, reducindo problemas derivados de excesos de nutrientes, reducindo a acumulación de fósforo e o lixiviado de nitratos	Risco de emisións gasosas. Emisións indirectas de CO_2 debido ao consumo de electricidade.
Aireación da fase líquida/tratamento biolóxico	Descomposición biolóxica da materia orgánica. Eliminación do N amoniacal mediante o gas N_2	Redución de patóxenos e cheiros. Eliminación da materia orgánica biodegradable.	En condicións non óptimas, poden presentarse emisións de CH_4, N_2O e cheiros. Emisións de NH_3 e perda de N no valor fertilizante do xurro cando se combina cunha etapa de nitrificación-denitrificación.
Compostaxe da fase sólida	Obtención dun produto estable, libre de patóxenos, cun baixo contido de humidade e retendo a maioría dos nutrientes iniciais.	Redución importante dos custes de transporte e emisións de CO_2 asociadas debido á redución de masa. Produción dun fertilizante orgánico. Eliminación de patóxenos e redución de cheiros.	Emisións de NH3, cheiros e CH4 durante o proceso
Tratamento anaerobio	Produción de biogás. Mineralización e estabilización da materia orgánica.	Redución da emisión de gases de efecto invernadoiro ao diminuír as potencias emisións de CH_4 e os consumos de combustibles fósiles. Redución dos cheiros, do contido de patóxenos e aumento da hixienización.	Escapes incontrolados de biogás e consecuentes emisións de CH_4. Emisións potenciais derivados do almacenamento do dixestato (CH_4, H_2S, NH_3, N_2O)
Sistema de lagoas anaerobias	Combinación de estabilización do xurro, separación e almacenaxe.	Mellora da calidade das fases sólida e líquida	Emisións altas de CH_4.
Evaporación e secado de dexeccións. Secador de cinto de xurros e dexeccións húmidas.	Concentración de nutrientes e materia orgánica. Redución de volume para un máis doado manexo e transporte.	Produto seco, concentrado, hixienizado e doado de manexar, con concentracións moderadamente altas de nutrientes (N e P).	Concentración de metais pesados que poden limitar a aplicación sobre o terreo do produto. Emisións directas ou indirectas de CO_2, segundo a fonte de enerxía empregada. Alta volatilización de NH_3.
Túnel externo para o secado das dexeccións	Redución das emisións de amoníaco secando as verteduras recollidas polo cinto.	Redución de amoníaco e cheiros.	Consumo de enerxía con emisións indirectas de CO_2.
Acidificación do xurro	Redución das emisións de amoníaco mediante o descenso do pH, coa consecuente retención de amonio (NH_4-N) nas dexeccións.	Redución das emisións de amoníaco. Posible redución das emisións de CH_4.	Emisións de COV e cheiros pola reacción de oxidación debido a adición dun ácido forte.
Desorción (stripping)	Eliminación de amoníaco pola volatilización da fase líquida, co subsecuente recuperación nunha solución ácida como as sales de amonio ou por condensación	Menos contido en N no xurro e consecuentemente máis doado manexo na explotación. Redución de cheiros na aplicación ao terreo. Recuperación de N	Consumo de enerxía con emisións indirectas de CO_2.
Aditivos	Facilitar a xestión das dexeccións. Estabilización e redución no contido de patóxenos	Redución de amoníaco, patóxenos, cheiros e gases de efecto invernadoiro	Alta variabilidade na eficiencia

O documento de Mellores Técnicas Dispoñibles fai referencia á calor residual recuperada doutros procesos, principalmente instalacións mecánicas eléctricas (intercambiadores de calor ou evaporadores, por exemplo). Bonmartí *et al.* (2003) indicaron que a principal limitación para a evaporación do xurro era a existencia dunha fonte calor barata. A inversión e os custes operacionais son altos en comparación con outros sistemas ou técnicas para o tratamento da fracción líquida de xurro de porco, especialmente aqueles que inclúen un proceso evaporativo nalgunha etapa (Melse e Verdoes, 2005). Outros autores (Bonmatí *et al.*, 2003) apuntan á conveniencia de tratamentos previos como a dixestión anaerobia do xurro, para facer o proceso máis viable dende o punto de vista económico. En procesos de compostaxe a calor é producida biolóxicamente como resultado da oxidación aerobia exotérmica da materia orgánica e as instalacións requiren dunha inversión moito menor que os sistemas eléctricos ou mecánicos (Vázquez *et al.*, 2015).

A asociación de fitomasa forestal con xurro de porco en procesos de compostaxe pode converter as matrices en evaporadores naturais de auga. Os fundamentos son similares ás técnicas de xestión de xurro baseadas en técnicas de evaporación contidas no documento da Unión Europea de Mellores Técnicas Dispoñibles para as granxas de porcino intensivo (EC, 2015). A diferencia principal é a orixe das fontes de calor para o proceso de evaporación.

1.5. INDUSTRIA DE TABOLEIROS MDF.

A industria de fabricación de taboleiros con fibra de media densidade asentouse fortemente, con preto de 60 novas instalacións en Europa nas dúas últimas décadas. En Galicia estas instalacións son de considerable importancia ao contar cunha capacidade de produción anual de 997.000 m^3 de taboleiros, aproximadamente o 60% do total de España (Tarling, L. *et al.*, 2016).

Durante a fabricación dos taboleiros, as astelas de madeira son tratadas con vapor a elevada presión e temperatura para debilitar as unións das fibras coa lignina, que serve de aglutinante na madeira. Así as fibras son separadas por fricción con menor custe enerxético. Outras etapas do proceso inclúen o mesturado, formación da manta e prensado. A grandes liñas, o sistema produtivo pode dividirse en tres subsistemas: a preparación da madeira, o conformado do taboleiro e o seu rematado (Figura 1.22).

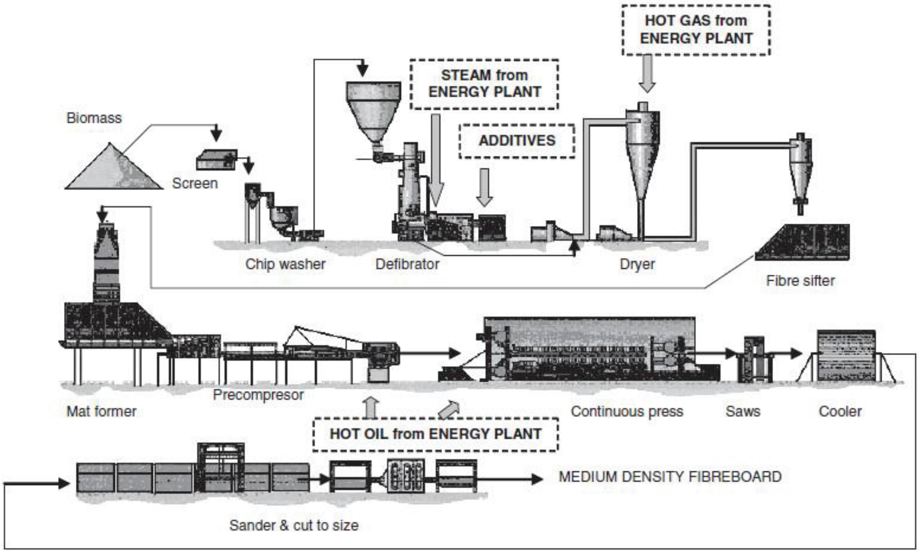

Figura 1.22. Fluxograma da fabricación de taboleiros MDF. Fonte: Rivela *et al.* (2007).

A auga residual procedente deste proceso presenta un pH reducido debido á hidrólise de grupos ácidos presentes na madeira. Outras características son a elevada temperatura, DQO e sólidos en suspensión (Balcik-Canbolat *et al.*, 2016; Ben *et al.*, 2011; Galehdar *et al.*, 2009).

Estas augas residuais son tratadas habitualmente en instalacións propias. A maior parte das fábricas aplican un tratamento primario co obxecto de eliminar a maior parte dos sólidos totais. Seguidamente un tratamento biolóxico aerobio reduce os valores de DQO e DBO_5. A ultrafiltración ou a osmose inversa só teñen lugar cando a auga superficial receptora é especialmente sensible ou cando é posible reutilizar a auga tratada no proceso produtivo (EC, 2014).

1.5.1. Produción de lodos.

Durante a produción do taboleiro xéranse augas residuais cuxa depuración por métodos físico-químicos dá lugar a lodos en cantidades variables, de entre 1,5 A 16 kg de sólidos totais por m^3 de MDF producido (EC, 2014; (Mymrin *et al.*, 2014).

Estes lodos son polo xeral retirados nun tratamento primario (EC, 2014). Na Figura 1.23 amósase o sistema de depuración das augas residuais industriais dunha industria local de fabricación de taboleiros MDF, consistente na aplicación consecutiva dun tratamento primario, de tipo físico-químico, seguido doutro biolóxico aerobio.

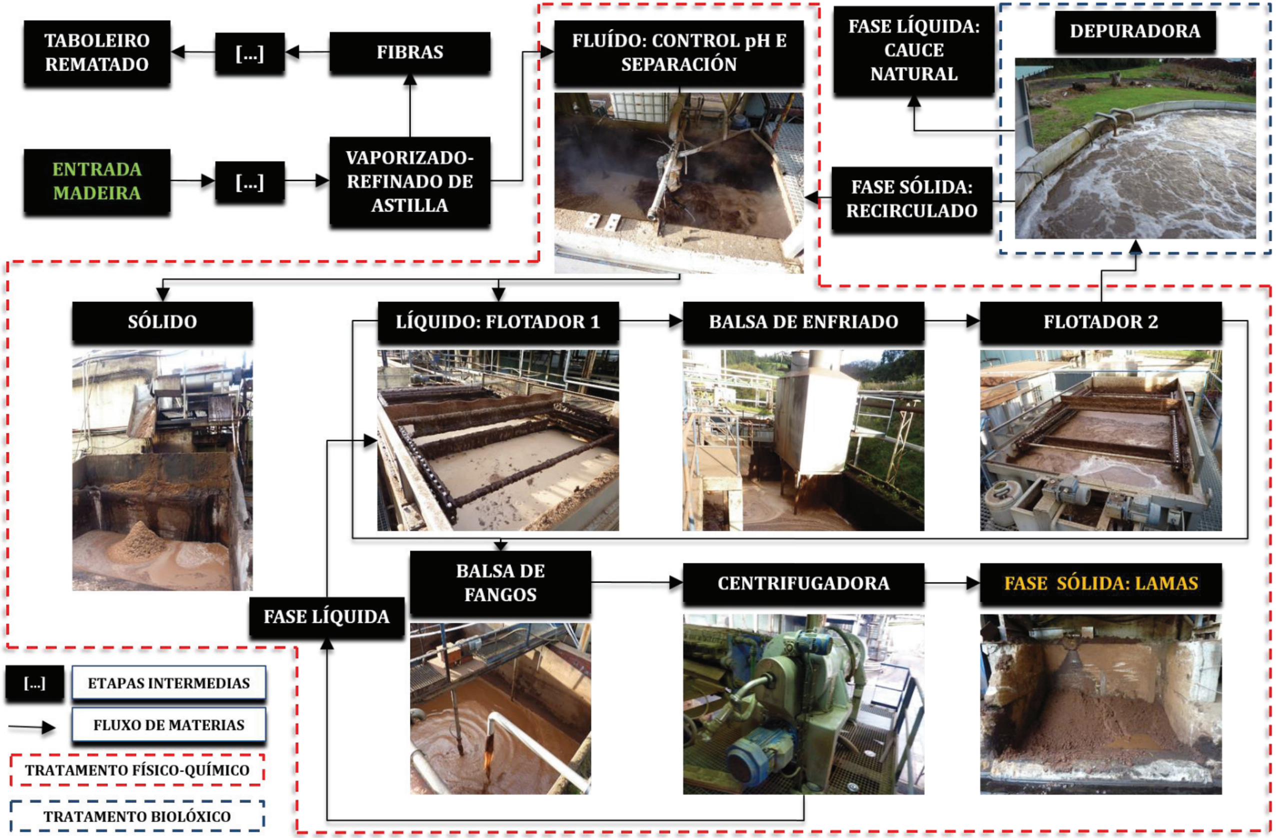

Figura 1.23. Fluxograma do proceso de depuración das augas residuais de industria de taboleiros MDF. Fonte: Elaboración propia para o ámbito desta tese.

O obxecto do tratamento primario é a redución dos sólidos en suspensión e da demanda química de osíxeno aplicando métodos de filtración, coagulación-floculación e flotación ata a obtención das lamas por centrifugado e prensado mediante parafuso senfín.

Inicialmente auméntase o pH, pasando dun valor inicial de 4,5 a outro próximo a 10, mediante a adición de sosa e cal co obxecto de xerar un medio adecuado para os microorganismos no tratamento biolóxico posterior. Nunha primeira balsa prodúcese o desbaste do material máis groso e o material restante entra nun primeiro flotador no que se separa a fracción máis densa, dirixida á balsa de lamas, da corrente líquida, conducida á balsa de enfriamento.

Nesta balsa a temperatura é reducida ata os 29 ºC e posteriormente a auga é derivada a un segundo flotador no que se engade coagulante-floculante. Novamente a fase máis densa é conducida á balsa de lamas e a fracción restante é dirixida a unha depuradora para o tratamento biolóxico secundario, logo do cal, a auga é vertida a un leito próximo. Periodicamente (1-2 veces ao mes) as lamas do tratamento biolóxico son retornadas ao tratamento primario, estimándose un volume aproximado do 5-10% anual con respecto aos lodos xerados no tratamento físico-químico.

O material concentrado na balsa de lamas é centrifugado obténdose unha nova fase líquida que será recirculada no flotador 1 (Figura 1.23), e unha fase sólida que será derivado a un xestor autorizado de residuos externo, alleo á empresa (Figura 1.24).

Figura 1.24. Fotografías das lamas de proceso de fabricación de taboleiro de fibras de media densidade: aspecto xeral (A) e detalle (B). Fonte: Propia, realizadas durante a execución dos traballos obxecto desta tese.

A pesares de que a composición deste residuo sólido é basicamente partículas de madeira e fibras, a súa calidade polo xeral non é suficiente para ser recirculado para a produción de taboleiro MDF (EC, 2014). As actuais prácticas de xestión deste lodo inclúen a incineración nas instalacións da industria (especialmente previo deshidratado), a aplicación ao terreo ou a súa deposición en vertedoiro (EC, 2014). Na literatura científica non existen moitas referencias sobre este material, as súas características e as opcións de manexo. Descartada a posibilidade da súa recirculación na propia industria de MDF pola baixa calidade da fibra, outros destinos potenciais serían o uso como fonte de enerxía en procesos de co-combustión (Skodras, 2004) ou máis recentemente investigouse a súa aplicación como material de construción (Mymrin *et al.*, 2014).

A normativa europea sobre a aplicación de lamas de depuradora en agricultura establece os principios que deben presidir as normativas nacionais na busca dun equilibrio entre os distintos destinos dos lodos e, en particular, o da aplicación en agricultura. Nun esquema de regulación en cascada, as directrices europeas incorporáronse á lexislación estatal e finalmente en Galicia, resultando de aplicación na Comunidade Autónoma o Decreto 125/2012, do 10 de maio, polo que se regula a utilización de lodos de depuradora no ámbito do sector agrario na Comunidade Autónoma (DOG, 2012b). Entre outros, esta norma require un tratamento de estabilización antes da súa aplicación ao terreo como fertilizante. Entre as distintas opcións, a norma destaca a compostaxe e a dixestión anaerobia como técnicas axeitadas para este residuo.

1.5.2. Produción de augas residuais.

Os consumos de auga para a produción de MDF é xeralmente superior con respecto a outros taboleiros de madeira (Raunkjær *et al.*, 2016). Van Asch *et al.* (2016) e Fernandez *et al.* (2001) cuantificaron ratios de consumo de 1.52 e 3 m^3, respectivamente, para a fabricación de 1 m^3 de taboleiro MDF.

A auga residual producida (Figura 1.25) é pobre en nutrientes, rica en extractos, con baixos valores de pH (de 4 a 5 unidades), elevado contido en sólidos (totais e volátiles) e en DQO (Lindemann *et al.*, 2019; Balcik-Canbolat *et al.*, 2016; Ben *et al.*, 2011; Galehdar *et al.*, 2009).

Figura 1.25. Aspecto da auga residual á entrada do tratamento primario. Fonte: Propia para o ámbito desta tese.

A revisión da bibliografía revelou o estudo de diferentes métodos para o tratamento deste tipo de augas. A maioría deles de tipo físico-químico: evaporación (Galehdar *et al.*, 2009), osmose reversa (Portenkirchner *et al.*, 2003), coagulación-floculación (Ghorbannezhad *et al.*, 2016) e outros encamiñados principalmente á redución da DQO, color e sólidos en suspensión (Balcik-Canbolat *et al.*, 2016; Galehdar *et al.*, 2009).

Os tratamentos biolóxicos non son efectivos debido á presenza de compoñentes refractarios e non biodegradables (Balcik-Canbolat *et al.*, 2016; Galehdar *et al.*, 2009), propoñendo Lindermann *et al.* (2019) a recuperación de polifenois ao constituír un subproduto valioso, eliminado ao mesmo tempo unha importante fonte de toxicidade para os microorganismos.

1.6. OBXECTIVOS.

O emprego de técnicas biolóxicas na xestión de residuos de orixe orgánica permite a súa transformación en materias primas dun xeito respectuoso co ambiente. A circularidade destas conversións repercuten positivamente en aspectos tales como a recuperación dos nutrientes contidos nos residuos, a obtención de materia orgánica estable ou de enerxía procedente de fontes renovables non fósiles (Figura 1.26).

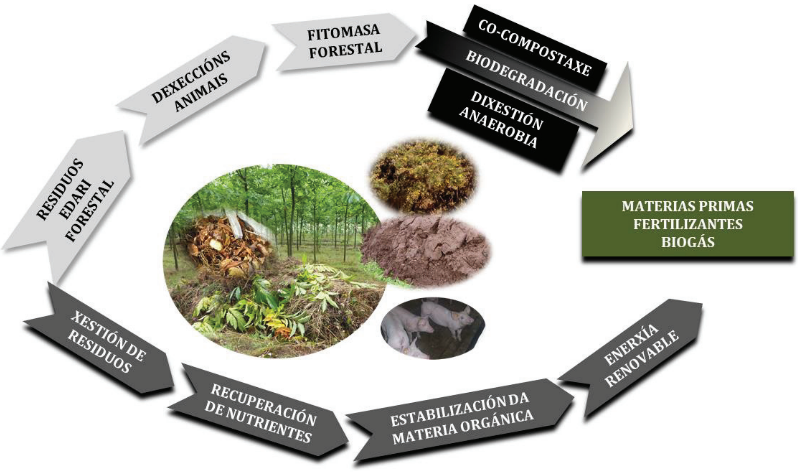

Figura 1.26. Esquema simplificado das experiencias levadas a cabo nesta tese.

O obxectivo desta tese é a aplicación da compostaxe e dixestión anaerobia para a xestión de residuos agroforestais de Galicia, en particular, xurros de porcino, fitomasa forestal residual (procedente de plantacións de castiñeiro e matogueiras) e residuos da industria forestal (augas residuais industriais e lamas do proceso de fabricación de taboleiros de fibra de media densidade).

Os obxectivos específicos son:

1. Integración en procesos de compostaxe dos residuos mencionados: a fitomasa forestal no papel de estruturante e corrección da relación C/N, o xurro de porcino actuando como

vector de auga e N, e co-compostaxe con lamas da industria forestal de taboleiros MDF (Capítulos 2 e 3).

2. O desenvolvemento dun método para avaliar a degradabilidade de composts e residuos orgánicos baseado nos equipos de DBO_5 manómetrico (Capítulo 4).
3. Avaliación da viabilidade da dixestión anaerobia para a obtención de metano a partir das augas residuais e lamas da industria de taboleiros MDF (Capítulo 5).
4. Discusión da idoneidade da normativa sectorial existente relativa á fertilización das terras con residuos orgánicos, no marco da estratexia galega de economía circular (Capítulo 6).

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CAPÍTULO II

COMPOSTING OF PIG MANURE AND FOREST GREEN WASTE AMENDED WITH INDUSTRIAL SLUDGE

Unha versión adaptada deste capítulo foi publicada como:

Arias, O., Viña, S., Uzal, M., Soto, M., 2017. Composting of pig manure and forest green waste amended with industrial sludge. Science of The Total Environment. https://doi.org/10.1016/j.scitotenv.2017.02.118

2. COMPOSTING OF PIG MANURE AND FOREST GREEN WASTE AMENDED WITH INDUSTRIAL SLUDGE.

ABSTRACT

The aim of this research was to study the composting of chestnut forest green waste (FGW) from short rotation chestnut stands amended with sludge resulting from the manufacture of Medium Density Fibreboard (MDFS) and pig manure (PM). Both FGW and MDFS presented low biodegradation potential but different characteristics in granulometry and bulk density that make its mixture of interest to achieve high composting temperatures. PM decreased the C/N ratio of the mixture and increased its moisture content (MC). Three mixtures of MDFS:FGW at volume ratios of 1:1.3 (M2), 1:2.4 (M3) and 0:1 (M4) were composted after increasing its MC to about 70% with PM. A control with food waste (OFW) and FGW (1:2.4 in volume) (M1) was run in parallel. Watering ratios reached 0.25 (M1), 1.08 (M2) 1.56 (M3) and 4.35 (M4) L PM/kg TS of added solids wastes. Treatments M2 and M3 reached a thermophilic phase shorter than M1, whilst M4 remained in the mesophilic range. After 48 days of composting, temperature gradients in respect to ambient temperature were reduced, but the mineralization process continued for around 8 months. Final reduction in total organic carbon reached 35-56%, depending mainly on the content in MDFS. MDFS addition to composting matrices largely reduced nitrogen losses, which range from 22 % (M2) to 37% (M3) and 53% (M4). Final products had high nutrient content, low electrical conductivity and low heavy metal content which make it a valuable product for soil fertilization, right to amend in the chestnut forests and as a pillar of their sustainable management.

Keywords: Forest green waste; Pig manure; MDF sludge; Composting; Chestnut forest sustainability.

2.1. INTRODUCTION.

Nowadays the economies of European countries are approaching the limits of the ecological system in which they are embedded. The effects of the scarcity of resources as well as the environmental impacts from energy, mass losses and emissions are becoming apparent (EEA, 2015). Circular economy and industrial ecology provide new paradigms in which efficient use of resources can be increased and emissions reduced. Integrating the management of farm, forestry and industrial wastes and soil fertility protection can generate new sustainability schemes (Kibblewhite *et al.*, 2012).

Because of the low density of forest biomass generated in many areas of Europe, its collection for energetic or any other kind of exploitation is not economical. Thus, it ends up creating suitable conditions for the spread of forest fires. However, collection viability changes when this biomass is used to solve other problems such as those generated by intensive livestock waste, at least in forested areas close to the location of these farms. In other cases, technological and forest health requirements force the withdrawal of biomass and its subsequent treatment.

In addition to the traditional exploitation of chestnut plantations, e.g. wood, fruit or mixed, recent research emphasize the possibility of obtaining new products with high added value from chestnut forest biomass (Aires *et al.*, 2016; Braga *et al.*, 2015). For this last purpose, chestnut plantations of high density and short rotation are being tested. These new strategies require a periodical collection and removal of plant biomass, during the operations of cultural maintenance of the forest (pruning and thinning of competing weeds and other plant species) and because of efficient mechanized fruit collection (Monarca *et al.* 2014). This creates large amounts of forest green waste (FGW) for which we must find a use. On the other hand, intensive short rotation forest plantations originate a progressive loss of nutrients and degradation of soil properties (Walmsley *et al.* 2009; Abbas *et al.* 2011), which have already been studied by Amorini *et al.* (1998) for the specific case of the chestnut forests (grove). Thus, FGW composting can generate a useful organic amendment to offset the loss of nutrients and organic matter in forest soils.

There are very few researches about composting of materials from the grove. Guerra-Rodriguez *et al.* (2001) studied the co-composting of chestnut leaves and chestnut burr mixtures with solid poultry manure, reaching thermophilic phases and positive results for the final product. More recently, Ventorino *et al.* (2013) conducted an experiment using, in addition to leaves and chestnut burr, other components such as shrub species and tree buds. These authors composted the grove waste in piles of about 5.4 m^3 on site and with no other additives, in order to simulate the natural on site degradation processes. The material to be composted presented a nitrogen content of 0.5% (dry matter basis) and a C/N ratio of 57.8. During 105 days of composting, mesophilic temperatures (27-29°C) were reached, only about 5°C higher than ambient temperature. Guerra-Rodríguez *et al.* (2001) and Ventorino *et al.* (2013) concluded that, if other additives were not added, the composting of chestnut FGW did not reach a complete degradation because the C/N ratio was too high and the composting material never reached the thermophilic phase. In spite of these difficulties, recent researches highlight the interest and sustainability of FGW composting practices. Ventorino *et al.* (2016) studied the lignocellulosic-adapted microbiota and microbial dynamics during the composting of chestnut residues conducted in a natural environment. These authors concluded that this compost could be considered a high-quality end product for solid-based inoculants in crop systems which contributed for a significant reduction of disease in plants. Iglesias-Díaz *et al.* (2009) verified the suitability of compost made from crushed gorse as a substrate for growing, peat substitute or propagation of *Thuja plicata* cuttings. López-López *et al.* (2016) reported that gorse composts exhibit suppressiveness against *Fusarium circinatum* in pine seedlings.

Animal manure and other wastes can be considered as a co-substrate to improve the composting process of FGW. Intensive pig farms produce high volumes of manure (PM) which must be correctly managed from the environmental and economic points of view. Environmental risks involve greenhouse gas emission, saturation of soils, pollution of ground and surface water by nitrates, phosphorus and heavy metals (HM) in soil (Prapaspongsa *et al.*, 2010). On the other hand, farms suffer from increasing costs when pig manure is transported to far farmlands or subjected to conventional technology treatments (Dahlin *et al.*, 2015). The need for low cost and ecological engineered systems therefore arises. However, the high moisture content (MC) of most pig manures (>95%) makes its treatment by composting difficult, although more concentrated manures could be composted by mixing it with amendment and bulking material (Barrena *et al.*, 2011a). Composting approaches to liquid fraction of PM with highly biodegradable organic wastes such as solid fraction of pig manure, sawdust and grape bagasse have been recently proposed (Vázquez *et al.*, 2015a; Cherubini *et al.*, 2015). In fact, due to the negative hydric balance of the composting process, watering the composting material is necessary, which may be carried out with PM (Barrena *et al.*, 2011a). In this way, substantial amounts of PM can be treated by composting, allowing the recovery of nutrients and reducing the volume to be transported to distant crop fields or subjected to further treatment.

Medium Density Fibreboard (MDF) is an engineered wood product made by refining wood into fibres and combining them with wax and resin to form panels by applying high temperature and pressure (Piekarski *et al.*, 2017). The manufacturing industry of MDF settled sharply, with about 60 new facilities in Europe in the last two decades. In Galicia these facilities are of considerable importance with an annual production capacity of 997,000 m^3 of board, approximately 60% of Spain's total (Tarling *et al.*, 2016). This process generates wastewater which treatment by physico-chemical methods results in the generation of sludge, amounts varying from 1.5 to 16 kg of total solids (TS) per m^3 MDF (EC, 2014; Mymrin *et al.*, 2014). Besides possible recovery and application as new building material (Mymrin *et al.*, 2014), current disposal practices of MDF sludge (MDFS) include incineration on the industry site, land application or sanitary landfill disposal (EC, 2014). In some states and regions in Europe, as is the case in Galicia, the agricultural use of MDFS requires previous stabilization treatment. To our knowledge no previous studies on the composting of MDFS have been reported. Thus, we take into consideration the use of MDFS as a co-composting substrate.

In summary, the recollection of chestnut and the maintenance of the chestnut plantations require forest biomass withdrawal. This causes a lost in fertility in the grove, being necessary to give back to the grove an appropriately processed fertilizer. Animal manures are an additional source of fertilizer elements and in many occasions a waste to be processed. The combination of forest waste and pig manure generated in the same area is formulated in this project as a comprehensive solution to solve these two problems and ensure the sustainability of the chestnut grove. A solid waste from the forestry industry is used as an amendment necessary to improve the composting process. Thus, the main objectives of this study are: a) the determination of the biodegradability potential of biomass from chestnut plantations and sludge from MDF production, b) the appropriate ratio of these materials and pig manure to prepare the composting mixture, c) the characterization of the composting process and the final product.

2.2. MATERIAL AND METHODS.

2.2.1. Solid and liquid wastes.

FGW was collected from a short-rotation chestnut (Castanea sp, 3.333 plants/ha, 8 years old) local stand. FGW consisted of a mixture of chestnut leaves (about 20%), chestnut burr (5%), chestnut pruned branches (5%), and undergrowth vegetation (70%) composed of gorse (*Ulex sp.*), bracken (*Pteridium aquilinum*), brambles (*Rubus sp.*), brooms (*Cytisus sp.*) and herbaceous vegetation (*Agrostis sp., Holcus sp*. and others). Undergrowth vegetation and pruned branches were harvested from June to August and chestnut leaves and burr from September to November 2014. FGW was shredded to get a particle size below 10 cm and completely mixed before use. MDFS was obtained from a Galician MDF factory. A fattening pig farm provided the PM, which has been stored in a tank (1000 L) provided of mechanical mixing. Organic food waste (OFW) was obtained from a university canteen and used as reference material for the composting process.

2.2.2. Composters and composting site.

Trials were carried out from December 2014 to September 2015 in Galicia (NW Spain, 43.0438ºN, 8.3268ºW). 340 L composting bins (0.76 x 0.76 m base and 0.80 m height) were used in a covered shed protected from rain. Each composting bin was placed on a concrete surface of 1.20 m^2 delimited by a partition (15 cm height), whose base and walls were treated with an epoxy primer to prevent water infiltration in the concrete. The base had a slope of 5% allowing the drainage and manual collection of leachate that could be generated.

Four duplicate experiments were carried out. The first duplicate M1 received OFW and FGW at a ratio of 1:2.4, and was used as control. Other three different mixtures were prepared at MDFS:FGW volumetric ratios of 1:1.3 (M2), 1:2.4 (M3) and 0:1 (M4). Solid materials were loaded in layers (alternating different materials in M1, M2 and M3 systems) with a thickness estimated to give 5 layers of each material. Each layer was finely watered with PM at a rate below the respective liquid retention capacity, aiming to reach MC close to 70%. Besides, PM was added during the composting process to M2, M3 and M4 when necessary in order to maintain the adequate MC and increase the amount of PM treated.

2.2.3. Monitoring, sampling and analysis.

The composting mixtures were aerated by turning and mixing the whole mass manually. The water content and densities of the different materials and the resulting mixtures were measured twice a month. Temperature and O_2 concentration at three points ranging from 10 to 30 cm depth were measured two to three times a week during the first month and once a week onwards. Interstitial oxygen was measured by a suction probe SON2IN and an oxygen detector ToxiRAE II (Sensotran, Spain). On the days when the material was turned, measures of temperature and O_2

were performed beforehand. The volume of the matrices was measured periodically by measuring the height of the composting material in the composting containers. In addition, the bulk density (BD) of the composting material was obtained by weighing the material occupying a representative volume (usually 10 cm in height, after turning and mixing the matrix) into the composting bin. The average BD before turning can be obtained taking into account the ratio between the total volume before and after turning. However, the differences recorded were low and we only reported here the BD values after turning.

Composite samples (obtained by mixing four grab sub-samples) from the composting matrices were taken periodically and analysed in the laboratory for MC, total solids (TS) and volatile solids (VS). The initial materials and the final composts were analysed for the same parameters as well as for pH, electrical conductivity (EC) and $NH4^+$-N. Analyses were carried out following Standard Methods (APHA, 2005). pH, EC and $NH4^+$-N in solid samples were measured in 1:5 weight:volume water extracts. Besides, elemental composition (NPK and other nutrients), total carbon (C), total organic carbon (TOC) and HM were determined in the initial and final materials. An EA1108 elemental analyser (Carlo Erba Instruments) equipped with an AS200 auto sampler was used for N, C and TOC. Phosphorus and metal concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS Element XR or Element2 from Thermo Electron) after acid digestion with HNO_3. Previously solid samples were air-dried and the solids were finely shredded and mixed. Free air space (FAS) of composting mixtures was calculated as indicated by El Kader *et al.* (2007):

FAS = ([total volume – (dry matter mass/1.6) – (water mass/1.0)]/total volume) x 100;

where mass is in kg and volume in L; it was assumed that the density of dry matter particles was 1.6 kg/L (because the actual value has not been measured) and density of water was 1.0 kg/L.

Germination assays of lettuce seeds (*Lactuca sativa* ‘May Queen’) were carried out as indicated by Zucconi *et al.* (1981) in order to determine the phytotoxicity of the final compost. Twenty seeds were placed evenly on plastic petri dishes lined with filter paper. 4.0 mL aqueous extract of compost were pipetted into each petri dish whilst distilled water was used as control. Compost extracts in distilled water (1:10 w/w) were prepared by shaking the samples mechanically for 2 hours, followed by centrifugation and filtration through 0.45 µm membrane filters. Seeds were incubated in dark conditions at room temperature (20 ºC) for 48 hours. Germination assays were carried out in triplicate. At the end of the assays, the number of seeds germinated was counted and the root length measured. For each treatment, the Germination Index (GI) was obtained as follows:

GI (%) = [(average number of seeds germinated x average root length)treatment] / [(average number of seeds germinated x average root length)control] x 100.

GI is a sensitive indicator of phytotoxicity (Tiquia *et al.*, 1996). Values higher than 80% are considered an indicator of absence of phytotoxicity, while values below 50% indicate phytotoxicity for most crops (Zucconi *et al.*, 1981).

2.2.4. Biodegradability and stability assays.

The respirometric method and the self-heating method were used to determine the biodegradability potential of raw materials and the stability of final products. Respirometric indices have been used to classify organic materials depending on their biodegradability. Barrena *et al.* (2011b) proposed a three level scale of biodegradability: high (>5 mg O_2/g VS h), moderate (2-5 mg O_2/g VS h) and low (<2 mg O_2/g VS h). On the other hand, a threshold ranging from 0.3-1 mg O_2/g VS h is usually accepted to classify compost and organic wastes as stable (Barrena *et al.*, 2006).

Respirometric assays were carried out following the method described by Lasaridi and Stentiford (1998). Approximately 8 g of the fine fraction of compost was dispersed in 500 mL of water amended with buffer, nutrient compounds and allylthiourea. This compost dispersion was subjected to intermittent aeration (45 minutes ON and 15 minutes OFF) and the oxygen consumption was determined (oxygen electrode YSI Pro ODO) during the non-aeration periods. These assays were carried out for at least 20 hours. The parameters determined with this method were the maximum specific oxygen uptake rate ($SOUR_{max}$) and the cumulative specific oxygen consumption over 20 hours ($CSOC_{20h}$). This procedure was adapted for raw solid materials as follows: after carrying out a standard respirometric assay with stable compost (i.e., showing a $SOUR_{max}$ below 1 mg O_2/g VS h, as indicated by Lasaridi and Stentiford, 1998), an amount of 8-16 g of raw material (shredded to <10 mm) was added to the respirometric solution, the pH was regulated to 7.0 and the test was run for a subsequent period of 20 h. A blank was run simultaneously but without raw material addition.

Self-heating potential of compost samples were determined in Dewar flasks of 1.5 L of volume following the procedure indicated by Brinton *et al.* (1995). MC of samples was previously corrected to 60-65%. This procedure was adapted for raw solid materials as follows: shredded (<10 mm) samples were mixed with stable compost at several ratios and the self-heating potential of the mixture was determined. Simultaneously, a control test was carried out with only stable compost.

2.3. RESULTS.

2.3.1. Physico-chemical characteristics of raw materials.

Chemical composition and other characteristics of the raw materials used are given in Table 2.1. Previous studies in regard to MDFS chemical composition were not found (EC, 2014). The high Ca content could be derived from lime addition during physico-chemical treatment of generated wastewater. PM was very diluted, having only a 0.33% of dry matter and 0.16% organic matter on a wet basis. PM content in $NH4^+$-N, total suspended solids and volatile suspended solids was 514, 100 and 80 mg/L, respectively. It also has a low content in nutrient elements and heavy metals, in comparison with previous published characteristics of pig manure in the same region

(Vázquez *et al.*, 2015a). FGW was characterized by its very low BD, of only 0.06 kg/L, and relatively low MC (41%). On the other hand, MDFS and OFW had high BD and high MC. On a dry basis, MDFS was richer in Ca than FGW whilst OFW was richer in P, Ca and P than MDF and FGW but not in Mg. In regard to K, an element of interest to improve fruit production in chestnut plantations, MDFS had the lowest content and PM the highest. On dry weight basis, the content in N was higher in PM followed by OFW and lower in FGW and MDFS. C/N ratio for FGW and MDFS was approximately equal to 27, being similar to recommended values for composting (Onursal and Ekinci, 2017). HM content was low in all solid wastes.

Table 2.1. Chemical composition and other characteristics of raw materials.

	PM	FGW	MDFS	OFW
pH	7.3±0.1	6.2±0.1	7.3±0.1	6.3±0.1
BD (kg/L)	0.990±0.001	0.063±0.019[a]	0.651±0.040[b]	0.594±0.017[c]
MC (%)	99.37±0.01	40.8±0.04	74.8±0.8	76.7±1.9
VS (%)	49.2±0.0	85.3±2.1	66.6±0.1	75.2±3.5
C (%)	14.45±0.70	45.23±0.11	36.63±0.95	45.14±0.07
N (%)	10.60±0.42	1.56±0.02	1.24±0.02	3.38±0.03
TOC (%)	11.79±0.65	41.83±0.14	34.59±0.71	34.50±0.03
C/N	1.11±0.02	26.90±0.27	27.88±0.96	10.20±0.10
Mg (g/kg)	9.9±0.1	2.17±0.03	1.81±0.03	1.60±0.06
P (g/kg)	17.1±0.1	1.21±0.07	2.07±0.03	4.89±0.26
Ca (g/kg)	18.1±0.4	7.78±0.23	21.1±0.02	39.8±0.6
K (g/kg)	67.3±0.9	5.80±0.1	1.94±0.12	15.2±0.8
Cd (mg/kg)	0.157±0.001	0.060±0.003	0.153±0.004	0.064±0.002
Pb (mg/kg)	1.41±0.05	1.53±0.01	3.94±0.11	0.23±0.01
Hg (mg/kg)	0.061±0.002	0.051±0.003	<0.050	<0.050
Cr (mg/kg)	11.4±0.4	6.48±0.11	25.9±1.0	1.42±0.0
Co (mg/kg)	0.80±0.03	1.03±0.04	3.25±0.12	0.14±0.0
Ni (mg/kg)	8.8±0.4	3.6±0.1	18.2±0.6	0.7±0.0
Cu (mg/kg)	165±5	11.1±0.2	12.2±0.3	6.1±0.1
Zn (mg/kg)	1233±5	29.6±0.7	77.9±0.8	16.0±0.3
As (mg/kg)	1.79±0.09	0.39±0.01	2.02±0.14	0.53±0.02
Se (mg/kg)	<1.0	<1.0	<1.0	<1.0

Mean values followed by standard deviation (N = 2, except for BD of solids wastes: [a]N=10, [b]N=8, [c]N=4). pH measured in 1:5 weight:volume water extracts, BD and MC on wet basis, composition on dry basis.

2.3.2. Biodegradability of raw materials.

The self-heating potential of raw materials was determined in Dewar flasks using stable compost as an inoculum and matrix base. The results are shown in Figure 2.1. The maximum increase of temperature of blank assays was 1.9 ºC above ambient temperature. OFW showed the highest self-heating potential reaching thermophilic temperatures for a long period of time. This was followed by MDFS and next by the mixture FGW+PM, whilst the FWG alone showed the lowest self-heating potential. Maximum temperature gradients were 23.5, 16.1, 10.7 and 6.5 ºC, for OFW, MDFS, FGW+PM and FGW, respectively (Figure 2.1). Thus, FGW showed a very low self-heating potential, which was increased by the addition of PM. On the other hand, MDFS showed a medium self-heating potential indicating that this waste needs treatment for further stabilization. In addition, the results suggest that the use of MDFS as a co-substrate could favour a better development of FGW composting process. Compared with the compost stability scale of Brinton *et al.* (1995), FGW would be class V (stable compost), while FGW+PM and MDF would be class IV (moderately stable) and OFW class III (active). However, we must take into account that this scale has been established for compost samples, which is not the case of the raw material analysed here. This is because we are using the self-heating method to explore the biodegradability of raw materials, but a standard procedure and biodegradability scales are not known for this application. Therefore, we must consider the results shown in Figure 2.1 only as relative values for the organic residues studied and under the conditions of the tests performed.

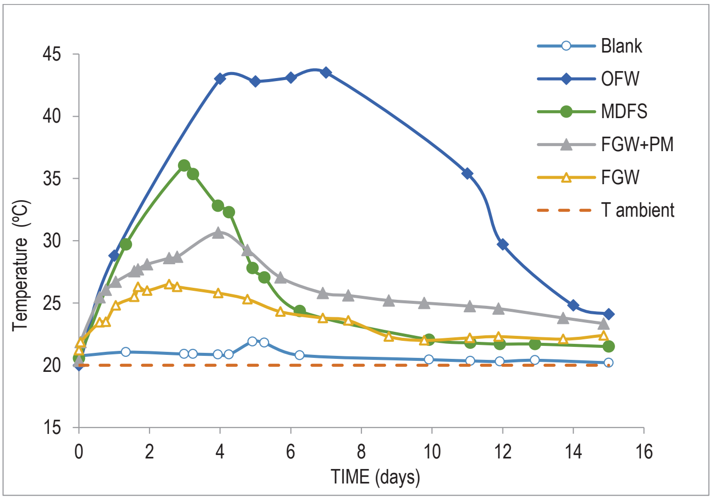

Figure 2.1. The self-heating potential of raw materials in Dewar flasks (stable compost was used as inoculum and matrix base in all assays in proportions 2:1 stable compost-waste in volume).

Results of respirometric assays carried out for these materials were in the same line as those of self-heating assays. While OFW and PM gave $SOUR_{max}$ of 5.4 and 7.1 mg O_2/g VS h, respectively, being classified as a material of high biodegradability, MDFS and FGW showed $SOUR_{max}$ of 2.17

and 0.81 mg O_2/g VS h, respectively, being of low biodegradability with reference to the scale of Barrena *et al.*, 2011b. In addition, the respirometric index for FGW was just lower than the threshold for compost stability (Lasaridi and Stentiford, 1998; Barrena *et al.*, 2006), anticipating a very low composting rate.

2.3.3. Evolution of composting processes.

The amounts of raw materials used in each composting system are indicated in Table 2.2 which also reports the main initial characteristics of the four composting mixtures. MC ranged from 72 to 77%, being higher than the 60% recommended for the composting of pig manure solid fraction and other wastes by several authors (Huang *et al.*, 2006, Ogunwande *et al.*, 2008; Nolan *et al.*, 2011). However, Vázquez *et al.* (2015a) reported adequate composting at MC ranging from 70 to 75%, compatible with large thermophilic periods of 3 to 4 month. Except in M1 systems, leachates were not produced in spite of the addition of PM in different amounts (Table 2.2) and the high MC of the mixtures. M1 leachates were about 3 L (50% of PM added) which were recirculated back to the matrix and then absorbed. The high MC of mixtures M2, M3 and M4 without leachate generation indicated a high capability of both components MDFS and FGW to absorb water.

Table 2.2. Initial amounts of the materials used in each composting system and total matrix characteristics.

Composting system ^{a}	Solid materials added (L)				PM added (L)	Overall matrix					
	FGW	OFW	MDFS	Total		Mass (kg)	Volume ^{b} (L)	BD ^{b} (kg/L)	MC ^{c} (%)	C/N ^{c}	FAS ^{d} (%)
M1	260	110	0	370	6	88	284±0	0.31±0.00	71.5	13.9	72.3
M2	200	0	160	360	32	149	285±4	0.52±0.01	77.2	26.6	52.3
M3	260	0	110	370	36	124	281±5	0.44±0.01	77.5	26.4	59.6
M4	340	0	0	340	29	50	294±0	0.17±0.00	74.5	25.9	84.6

^{a}M1: control with OFW (at 1:2.4 OFW:FGW ratio); M2, M3 and M4: mixtures at MDFS:FGW volumetric ratios of 1:1.3 (M2), 1:2.4 (M3) and 0:1 (M4). ^{b} Measured mean values from the two system replicates. ^{c} Obtained from the amounts of each material added and its characteristics (Table 2.1). ^{d} Calculated as indicated by El Kader *et al.* (2007).

Time profiles of temperature and oxygen in composting material are shown in Figure 2.2. M1 received OFW and FGW at a ratio 1:2.4 and had a C/N ratio of 13.9, lower than recommended values for composting. In spite of this, M1 mixture reached thermophilic temperatures which indicated a successful development of the composting process. The high intensity of biodegradation caused medium oxygen content in the matrix, which progressively increased from 10% to 16% during the first two weeks of composting. After this period, the temperature suddenly decreased to about 15ºC, due to the exhaustion of the readily biodegradable substrate. Besides, ambient temperatures near 0 ºC (about day 20) probably contributed to the rapid temperature decrease.

M2 and M3 mixtures received MDFS and FGW at ratios of 1:1.3 and 1:2.4, respectively, showing C/N ratios of 26.6 and 26.4, respectively (Table 2.2). Profile temperatures were very similar for both mixtures, although with a maximum slightly higher for M3 (49 ºC) than for M2 (44 ºC). Adequate oxygen concentrations were observed during the thermophilic phase, with values of 14% (M2) and 16% (M3). The thermophilic phase lasted only about 10 days, afterwards the temperature decreased to mesophilic values for another 10 days and then to temperatures about 15 ºC, in a similar way to the M1 mixture. Temperature and oxygen profiles for M2 and M3 mixtures suggest a better behaviour of the less concentrated one in MDFS (M3) in comparison to that of higher MDFS concentration (M2). M2 mixture presented a lower oxygenation rate and reached lower maximum temperature.

M4 matrix contained only FGW and PM and reached only mesophilic temperatures, with maximum values of about 22 ºC, and decreasing to about 10 ºC after 20 days of composting. This occurred in spite of a C/N ratio in the optimal range. In this way, the low temperature reached could be related to the low biodegradability of the substrates as well as to the low bulk density and the large particle size which favoured the existence of high porosity and heat loss (Gea *et al.*, 2007; Bernal *et al.*, 2009).

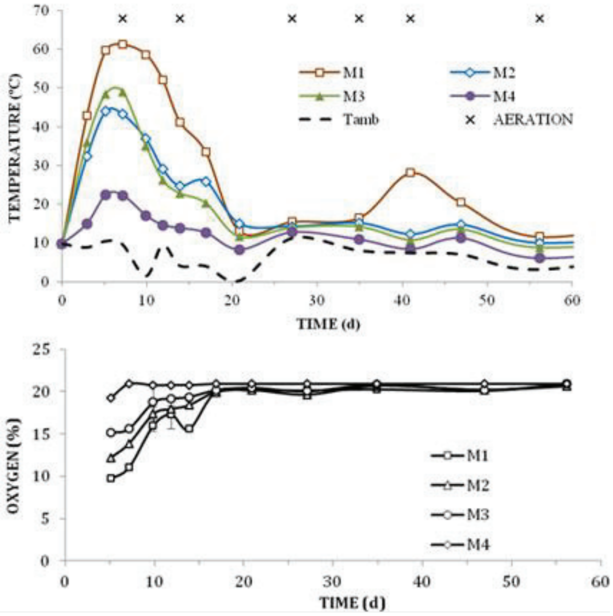

Figure 2.2. Evolution of temperature and of interstitial oxygen in composting matrices.

After 3 weeks of composting, during the period from 21 to 56 days (Figure 2.1), temperatures were low in all mixtures, ranging from 10 to 15 ºC (M1>M2>M3>M4), whilst the gradient above ambient temperature ranged from 2 to 8 ºC. Oxygen ranged from 20 to 21 % in all mixtures, in spite of the high MC. This high oxygen concentration indicated both good aeration conditions provided by the FGW material and low degradation activity. The stability of the mixtures at day 48 was measured in controlled conditions (Dewar flasks assay in lab at 20 ºC). These assays gave maximum temperature gradients of 36.0, 9.0, 6.6 and 6.9 ºC for M1, M2, M3 and M4, respectively. Thus, the M1 material was not stable at that time, corresponding to Rottegrade Class IV (Brinton *et al.*, 1995), whilst the other three materials can be considered completely stabilized (Class I). This was congruent with the temperature profile shown in Figure 2.2.

Since the first days, M1 matrix showed a strong and progressive reduction in volume reaching 59% reduction at day 48 of composting (Table 2.3). In comparison, the other matrices showed lower volume reduction of 4%, 8% and 20% for M2, M3 and M4, respectively. BD remained practically constant during this period (Table 2.3). Thus, the reduction of total mass followed the trend of volume reduction. The MC was high, showing values of 74-75%, and remained practically constant. In spite of the high MC, FAS was high in all mixtures but decreasing in proportion to its content in MDFS. The high FAS value was due to the low BD which is a characteristic of the FGW present in all the mixtures. These high FAS values were maintained throughout the entire composting process (Tables 2.2, 2.3 and 2.5) and explained the fact that aeration was good in all matrices, avoiding anaerobic conditions in spite of the high MC. The variation of organic matter content (as percentage of dry matter) was not detectable during the initial 48 days composting period.

Table 2.3. Evolution of matrix characteristics during the first 48 days of composting.

Composting system	M1	M2	M3	M4
Mean matrix characteristics from 0 to 48 composting days (n=8)[a]				
Mean BD (kg/L)	0.30±0.04	0.38±0.03	0.31±0.02	0.13±0.05
Mean MC (%)	75.0±2.3	75.6±2.5	74.2±4.9	73.7±2.2
Mean VS (% TS)	75.2±1.7	71.6±2.1	73.4±4.3	86.0±2.1
FAS (%)	67.7	64.2	72.7	82.6
Volume and mass reduction at day 48 (n=2) [b]				
Volume (%)	58.9±0.4	3.9±0.8	8.1±0.8	20.3±0.2
Mass (%)	49.7±0.2	6.2±0.2	7.6±0.1	5.5±0.3

[a] Measurements each two weeks approximately (n=4) for each replicate (n=2) of composting system. [b] Mean from the two system replicates.

Between days 60 and 150 of composting, matrix temperature followed ambient temperature (ranging from 7 to 16 ºC) with average gradients of 5.1, 3.3, 2.8 and 0.9 for mixtures M1, M2, M3 and M4, respectively (data not shown). These gradients indicate that biodegradation continued but at a very low rate. Temperature gradients practically disappeared (< 1 ºC) after day 150 (ambient temperature ranging from 17 to 23 ºC), indicating the finalization of the biodegradation process. Oxygen remained high, above 20%, and matrix volume showed a progressive reduction at nearly constant rates with time of 0.09 %/d for M1 and 0.15-0.16 %/d for the other matrices (R^2 >0.95). Other parameters were not monitored during this period, but MC was observed qualitatively. During this period, PM was added to M2 (5 L), M3 (8 L) and M4 (27 L) distributed as necessary in order to maintain MC adequate for the composting process. Total watering ratios reached 0.25 (M1), 1.08 (M2) 1.56 (M3) and 4.35 (M4) L PM/kg TS of added solid wastes. Except for M4, total watering ratios were lower than those reported by Vázquez *et al.* (2015a) for pig manure and biowastes co-composting. The high watering ratios of Vázquez *et al.* (2015a) were attributed to the large heat production from the highly biodegradable biowastes used. However, in the conditions of the present study, other factors such as initial MC of solid wastes and composting time appeared to have a higher effect.

At the end of the process (day 268), the reduction in volume, total mass and other parameters (Table 2.4) largely varied from one matrix to another. M1 matrix, containing the food waste presented the higher loss in all parameters, which was related to the high biodegradability of the substrate and the low C/N ratio. N losses reached in this matrix 71% of its initial content, which is in the upper range of reported values in literature. Typical percentage nitrogen losses during manure composting vary from 5 to 62% of the initial nitrogen content (Bernal *et al.*, 2009) although higher values have also been reported (Ogunwande *et al.*, 2008; Silva *et al.*, 2009). M4 matrix containing only forestry waste and pig manure followed M1 in percentage losses, reaching 55-58 % total solids and organic carbon losses, and 53% nitrogen loses. Losses decreased for all parameters in M3 and mainly in M2 in proportion to its content in MDFS. This means that MDFS was biodegraded in lower extent than the others wastes. Of great interest is the observed reduction of nitrogen losses as the amount of MDFS in the matrix increased. Both M2 and M3 mixtures achieve very good nitrogen conservation, taking into account the long duration of the process.

Table 2.4. Percentage reduction for several parameters at the end of the composting process.

Reduction (%) [a]	M1	M2	M3	M4
Volume	80.7±1.5	37.0±0.1	43.0±1.3	57.0±0.8
Mass	81.9±0.5	45.2±0.2	55.3±0.9	65.2±0.1
TS	75.7±3.1	25.9±1.6	40.0±2.3	54.6±2.7
TOC	78.2±1.5	35.1±0.2	48.3±1.8	57.5±1.0
N	70.6±3.5	21.7±2.0	37.3±2.3	52.7±3.6

[a] Mean from the two system replicates.

After several weeks of composting, it was observed that MDFS in composters M2 and M3 originated small aggregates of spherical or ovoid shape (up to 3 cm in diameter), which were more frequent and of bigger size in M2 than in M3. These particles were resistant to deformation and breakage and consisted of an external dark layer and a light brown core, the last similar to the raw MDFS colour. Respirometric assays of material obtained separately from both layers indicated that the external layer was completely stabilized ($SOUR_{max}$ 0.40 and 0.35 mg O_2/gVS·h for M2 and M3, respectively) whilst the internal core showed a higher biodegradability ($SOUR_{max}$ 1.73 and 1.13 mg O_2/gVS·h for M2 and M3, respectively). At the end of the process, these aggregates accounted for less than 10% (M2) and 5% (M3) of the MDFS added to the composters, thus affecting in a minor extension the stability of final products.

2.3.4. Characteristics of final products.

Chemical characteristics of final composts are shown in Table 2.5. Final composts showed very different characteristics. M1 has a higher content in nutrients (N, P, K, Mg and Ca) than the other mixtures, a lower C/N ratio, lower content in HM, but higher EC. In fact, EC in M1 compost exceeded the recommended values for agronomic use while it was suitable in M2 and M3 mixtures and M4 was close to this threshold of 3 mS/cm (Oviedo-Ocaña *et al.*; 2015). Banegas *et al.* (2007) reported that composts with EC of 8 mS/cm caused negative effects on soil microorganisms activity. All compost showed low respirometric indices but C/N ratio remained high in M2, M3 and M4 due to the low carbon reduction as well as to the losses of nitrogen, as discussed in Section 3.3. However, a clear reduction of C/N ratio occurred in all systems from the starting materials (Table 2.2) to the final materials (Table 2.5). In fact, the C/N ratio for M2, M3 and M4 final products was lower than that reported by other authors for gorse based composts (Iglesias-Díaz *et al.*, 2009; Tighe-Neira *et al.*, 2014).

Table 2.5. Characteristics of final products.

Compost	M1	M2	M3	M4
BD (kg/L)	0.291±0.008 ^{a}	0.454±0.015 ^{b}	0.346±0.078 ^{b}	0.138±0.004 ^{c}
MC (%)	62.0±0.3 ^{a}	69.2±0.4 ^{b}	69.7±0.7 ^{b}	66.5±0.5 ^{c}
pH	6.9±0.1 ^{a}	6.8±0.1 ^{a}	6.6±0.2 ^{a}	5.7±0.1 ^{b}
EC (mS/cm)	5.48±0.35 ^{a}	1.00±0.06 ^{b}	1.09±0.15 ^{b}	3.34±0.30 ^{c}
OM (%)	55.9±0.5 ^{a}	60.1±0.0 ^{a}	59.9±0.4 ^{a}	80.5±7.1 ^{b}
FAS (%)	75.0±0.9 ^{a}	61.0±2.0 ^{a}	69.3±9.3 ^{a}	87.9±0.5 ^{a}
$SOUR_{max}$ (mg O_2/g VS h)	0.25±0.08 ^{a}	0.56±0.15 ^{a}	0.49±0.17 ^{a}	0.21±0.12 ^{a}
GI (%)	53.9±3.1^{a}	97.8±2.6^{b}	87.7±1.4^{c}	34.2±1.0^{d}
NH_4^+ (mg N/L)	114.7±8.5 ^{a}	13.6±0.05 ^{b}	16.3±1.3 ^{b}	72.0±0.5 ^{c}
C (%)	36.1±0.54 ^{a}	33.89±0.11 ^{b}	35.11±0.70 ^{a,b}	41.21±0.46 ^{c}
N (%)	3.26±0.11 ^{a}	1.51±0.04 ^{b}	1.61±0.05 ^{b,c}	2.04±0.05 ^{c}
TOC (%)	33.5±0.25 ^{a}	31.21±0.03 ^{b}	31.85±0.56 ^{a,b}	38.67±0.44 ^{c}
C/N	10.3±0.67 ^{a}	20.62±0.48 ^{b}	19.77±0.31 ^{b}	19.0±1.0 ^{b}

Table 2.6 (continuation). Characteristics of final products.

Compost	M1	M2	M3	M4
Mg (g/kg)	4.3±0.1^{a}	2.5±0.3^{b}	2.6±0.1^{b}	3.0±0.2^{b}
P (g/kg)	6.25±0.03^{a}	2.12±0.03^{b}	1.99±0.08^{b}	1.74±0.18^{b}
Ca (g/kg)	60±1^{a}	21±1^{b}	19±1^{b}	9.0±0.5^{c}
K (g/kg)	28±4^{a}	4.5±0.5^{b}	5.2±0.1^{b}	9.5±1.1^{b}
Na (g/kg)	9.6±0.1^{a}	1.4±0.0^{b}	1.5±0.1^{b}	1.1±0.2^{b}
Cd (mg/kg)	0.15±0.01^{a}	0.152±0.005^{a}	0.147±0.001^{a}	0.071±0.006^{b}
Pb (mg/kg)	2.28±0.24^{a}	4.87±0.79^{b,c}	5.73±0.91^{c}	2.48±0.14^{a,b}
Hg (mg/kg)	<0.05	<0.05	<0.05	<0.05
Cr (mg/kg)	13.7±0.4^{a}	32.6±0.3^{b}	33.5±1.4^{b}	17.3±0.1^{c}
Co (mg/kg)	1.51±0.05^{a}	3.66±0.01^{b}	4.13±0.22^{c}	1.70±0.02^{a}
Ni (mg/kg)	5.7±0.1^{a}	19.5±1.1^{a,b}	24.2±8.2^{a}	6.8±0.0^{a}
Cu (mg/kg)	18.0±2.3^{a}	16.3±1.0^{a}	17.1±0.5^{a}	19.8±0.2^{a}
Zn (mg/kg)	53±1^{a}	102±5^{b}	102±13^{b}	67±1^{a}
As (mg/kg)	1.10±0.0^{a}	1.93±0.08^{b}	4.22±2.85^{a,b,c}	3.42±0.25^{c}
Se (mg/kg)	<1.0	<1.0	<1.1	<1.2

Mean value from duplicate composting bins followed by standard deviation. Values in each row followed by the same letter do not differ significantly ($p<0.05$, one-way ANOVA with pairwise comparison). EC and pH measured in 1:5 weight:volume water extracts, BD and MC on wet basis, composition on dry basis.

Bernal *et al.* (2009) indicated C/N ratios below 20, preferably below 10, as established maturity indices for composts from different sources. However, it is clear that the C/N ratio cannot be considered as an absolute maturity index, since the M1 mixture already had a C/N ratio below 20 before the composting process. Furthermore, a relation between maturity (measured as GI) and C/N ratio did not exist. Therefore, the reduction of the C/N ratio for mixtures M2, M3 and M4 from about 26 to less than 20 should only be considered as a suggestion of compost stabilization but not confirmation. Confirmation of final compost stability was obtained from respirometric assays for M1, M2 and M3 products which showed $SOUR_{max}$ below the stable compost threshold of 1 mg O_2/gVS·h (Lasaridi and Stentiford, 1998).

The content in macronutrients in M2, M3 and M4 final products was high in general but varied depending on the considered element. The content in N, P and K was above 1.5 % N, 0.17 % P and 0.45 % K for M2, M3 and M4 composts. Macronutrients content was in the range of that in composts from other materials such as seaweed and fish waste (Illera-Vives *et al.*, 2015), natural casings waste with sheep manure and dead leaves (Makan, 2015), but lower than that reported by Morales *et al.* (2016) for agri-food sludge compost and by Vázquez *et al.* (2015a) for solid fraction of manure and other biowastes. In Galician forests, the productivity of both the understory and the trees can be limited by low soil fertility as a result of the acidic soil conditions. In order to improve productivity, several studies recommended the use of organic fertilizers such as composted sludge (Mosquera-Losada *et al.*, 2016). Although pH in final products is slightly lower than 7, it is clearly above the pH of most Galician soils and thus a beneficial effect can be expected. On the other hand, the high content in K in final products makes them very interesting to increase fruit productivity in chestnut groves.

HM was low in all mixtures, appearing below the limits of Class A compost for agricultural use in Spain and thus compatible with European Commission organic agriculture (Vázquez *et al.*, 2015b) and Class A+ of the 2001 Austrian Compost Ordinance (Fernández-Delgado *et al.*, 2015). On the other hand, HM content was far below that reported by Guerra-Rodriguez *et al.* (2006) for compost from forest wastes and liquid poultry manure and by Mosquera-Losada *et al.* (2016) for anaerobically digested, composted and pelletized sewage sludge used for forest fertilization. Ni is the metal that reached a high level in comparison with Spanish Class A. This occurred in M2 and M3 composts because of the high content of MDFS in Ni. In general, the content in HM appeared to be in proportion to the content in MDFS of the mixtures although PM significantly contributed to the content of Cu and Zn in M4 compost.

GI values above 80% are considered an indicator of phytotoxicity disappearance (Zucconi *et al.*, 1981) and maturity (Tiquia *et al.*, 1996). M2 and M3 extracts gave 100% seed germination and root elongation of 98% and 88% of control, respectively. Thus, GI of M2 and M3 were 98% and 88% (Table 2.5), respectively, indicating the absence of phytotoxic compounds in these composts. On the other hand, GI for M4 compost was below 50%, indicating that this compost would be phytotoxic for the majority of cultures (Zucconi *et al.*, 1981). M4 extract showed a toxic effect on both germination (60.5%) and root elongation (56.7%). M1 compost showed GI of 53.9, thus exerting moderate phytotoxicity, mainly due to reduced root elongation (57.7%) than seeds germination (93.4%).

Many factors simultaneously influence germination, thus being difficult to determine which factor causes the greatest influence (Tiquia, 2010). Huang *et al.* (2004) reported GI lower than 50% for compost from pig manure and sawdust and suggest that it may be due to a high EC of about 2.5 mS/cm. However, Tiquia (2010) obtained a higher threshold for EC toxicity in hog manure composts with values under 3.4 mS/cm being in the non-phytotoxic or marginally phytotoxic range. Besides, Tiquia (2010) also revealed that ammonium nitrogen was the most important factor causing phytotoxicity of hog manure compost when present at concentrations above 2 g $NH4^+$-N/kg. M1 and M4 composts showed higher values of EC and ammonia nitrogen than M2 and M3, but ammonium concentration (0.57 and 0.36 g $NH4^+$-N/kg for M1 and M4 composts, respectively) was below the threshold of toxicity indicated by Tiquia (2010), whilst EC was close to the toxicity threshold (M4) or clearly higher (M1). Thus, EC could be the factor causing phytotoxicity in M1 compost whilst other factors must contribute to phytotoxicity in M4 compost. Low pH in M4 compost (5.7, Table 2.5) was the main difference among the characteristics of this compost and the other three composts. The optimum pH for lettuce germination is near 7 (Gascó *et al.*, 2016), so the moderately acidic pH might contribute to reduction of the GI of M4 compost. Total heavy metals content in the final products seems not to have a direct relation with GI since M2 and M3 composts present higher values than M1 and M4 composts.

2.4. DISCUSSION.

Forestry cleaning green waste is a very abundant material but it can show very different characteristics. Gorse dominated wastes present high nitrogen content and can undergo thermophilic composting if it is composted in fresh after gridding (Iglesias-Díaz *et al.*, 2009). However, achieving a thermophilic phase is not always guaranteed, particularly when the proportion of tender shoots and young plant parts is scarce, or when the material passed a long period after harvesting. Thus, it is more usual to use forestry green waste as a bulking material in co-composting of animal manures (Tighe-Neira *et al.*, 2014; López-López *et al.* 2016). Guerra-Rodriguez *et al.* (2001) stated that the composting of chestnut burr and leaf litter did not occur because the C/N ratio was too high and the compost never reached the thermophilic phase. However, co-composting of chestnut green waste and poultry manure reached 60 °C in 14 days (Guerra-Rodríguez *et al.*, 2001). Ventorino *et al.* (2013) reported a maximum temperature of 29ºC during composting of chestnut cleaning green waste. Composting times can vary largely from about 3 months to 18 months (Iglesias-Díaz *et al.*, 2009; Ventorino *et al.*, 2016). In our composting systems, the addition of MDFS to FGW clearly increased the maximum temperature and the duration of the thermophilic phase in relation to the composting of FGW. However, even with MDFS amendment, the thermophilic and mesophilic phases were short (about one month or less) and the biodegradation process during these periods was limited to the readily biodegradable fractions. Watering with PM was not sufficient to reach the thermophilic phase during the composting of FGW. However, this result must be considered to be restricted to the use of a much diluted PM, whilst the use of a high loaded PM could increase the composting temperature.

A factor determining the temperature level of FGW composting matrices could be the high FAS derived from the low BD of forestry green wastes. Grinding is a usual pre-treatment to increase BD and reduce FAS (Iglesias-Díaz *et al.*, 2009), but it was usually insufficient because the reduction of the particle size is limited due to practical and economic reasons. Adding MDFS to FGW significantly decreased the FAS of composting matrices, but the obtained values for M2 and M3 mixtures continue to be too high. Increasing MC and physical compacting are other factors that can help in reducing FAS (El Kader *et al.*, 2007). MC was high although below leaching conditions in our experiments and higher MC would not be positive for the composting process. Compacting was not favoured in these experiments, but it could play a positive role in improving composting conditions. A high compaction of composting matrices would increase BD and reduce FAS, thus favouring heat retention. Furthermore, El Kader *et al.* (2007) found that lower FAS significantly reduced ammonia volatilization and nitrogen losses.

As indicated in Section 3.3, the high FAS values throughout the entire composting process helped in avoiding anaerobic conditions. Methane emissions during aerobic composting of organic wastes mostly occur during the thermophilic phase, when oxygen consumption is higher and anaerobic microniches are more probable to be present (Fernández-Delgado *et al.*, 2015). These authors reported that oxygen concentration in pore space should not fall below 10% in order to avoid the presence of anaerobic zones and methane formation. In our systems, oxygen content was always above 10% (Figure 2.2) and thus methane formation can be considered not probable.

The FGW waste used in this study is characterized by its heterogeneity in terms of its composition, predominating the species of bush over the fraction of chestnut tree. Another aspect to consider is that it included all fractions generated in short rotation chestnut plantations. Ventorino *et al.* (2013) also studied the composting of the total waste generated in the forest grove. However, the contents of N and TOC varied substantially as Ventorino *et al.* (2013) reported 0.5% N and 28.9% TOC (C/N ratio of 57.8) whilst our FGW presented 1.54% N and 41.7% TOC (C/N ratio of 27.1). The last C/N ratio was more favourable for composting than the former, and it was still reduced slightly in the composting matrices of our study because of the addition of MDFS and PM. C/N ratio is a parameter that expresses the nutritional balance of the composting mixture, because microorganisms require an energy source (degradable organic-C) and N for their development and activity, being the adequate C/N ratio for composting in the range 25–35 (Bernal *et al.*, 2009). A low C/N ratio such as that of the M1 mixture (C/N of 13.9) required more frequent or intensive turning operations. This coincides with the findings of Onursal and Ekinci (2017) who reported that an initial C/N ratio of 29 (in the range of 12.8 to 37.4) minimized the energy requirement to supply oxygen in composting systems with forced aeration. High MC increases the specific heat of the mixture and high FAS increases the air flux, thus both factors can reduce the temperature level and retard the composting process. However, El Kader *et al.* (2007) reported that reducing FAS lead to lower temperature and lower mass loses. While we are interested in high MC because this implies the treatment of larger amounts of PM, FAS can be reduced by mechanical compacting of the composting matrix. The potential effects of this modification on the temperature level and material conversion are of difficult prediction and will require additional research.

Although variations in nutrient content exist depending on the plant fraction (higher in leaves than in stems) and considered season (generally larger in spring), these were not considered the relevant factors to explain the differences in nutrient content between the FGW of our study and that of Ventorino *et al.* (2013). The differences could probably be due to a higher proportion of biomass of the legume family (*Fabaceae*) in our study, represented by species of the genera *Cytisus* and *Ulex* (gorse), as well as herbaceous species. Encouraging the presence of these species in the chestnut understory would allow us to obtain forestry wastes with higher nitrogen content and composts with higher fertilizer value.

2.5. CONCLUSIONS.

FGW is a very abundant material which can show very different characteristics and composting patterns. FGW in the present study showed a low biodegradation rate which had been increased by amending with MDFS and PM. Mixtures of MDFS:FGW at volume ratios of 1:1.3 and 1:2.4 reached short thermophilic and mesophilic phases of about 3 weeks during which the readily biodegradable fraction of organic matter was effectively removed but the overall material conversion was reduced. After 48 days of composting, reductions were in the ranges of 4-20% (volume) and 5-8% (mass). However, the conversion process continued with reduced gradient temperatures up to 150 days of composting. At the end of the composting process, reductions reached 37-57% (volume), 45-65% (mass), 35-56% (TOC) and 22-53% (N), depending mainly on the content in MDFS. Addition of MDFS to composting matrices largely reduced nitrogen losses as well as phytotoxicity. Nutrients in the final products were above 1.5 % N, 0.17 % P and 0.45 % K and thus similar to nutrient content in compost from other sources. EC was below recommended limit values for agronomic use and HM content was low in all mixtures, appearing below the limits for organic agriculture.

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CAPÍTULO III

CO-COMPOSTING OF FOREST AND INDUSTRIAL WASTES WATERED WITH PIG MANURE

Unha versión adaptada deste capítulo foi publicada como:

Arias, O., Viña, S., Soto, M., 2019. Co-composting of forest and industrial wastes watered with pig manure. Environmental Technology 1–42. https://doi.org/10.1080/09593330.2019.1643411

3. CO-COMPOSTING OF FOREST AND INDUSTRIAL WASTES WATERED WITH PIG MANURE.

ABSTRACT

Co-composting of forest-derived wastes (chestnut forest burr, CST; scrubland biomass, SRB; industrial sludge, MDFS, from the Medium Density Fibreboard production process) watered with pig manure (PM) may constitute a feasible management technique for both solid and liquid streams. PM provided water and improved the carbon to nitrogen (C/N) ratio. Four piles of 1.8-2.4 m^3 were conformed: A (SRB, with compaction bulk density), B (SRB, without compaction), C (SRB and MDFS at a volumetric ratio of 3:1) and D (CST). Thermophilic temperatures were maintained for 8 (B), 16 (A), 28 (C) and 40 (D) days. Stable compost was obtained after 35 (A, B, C) and 48 (D) days. Hygienization was only complete in piles C and D. N losses were higher in piles A (39.3%) and B (33.6%) in relation to C (17.0%) and D (8.9%) which could be attributed to the characteristics of MDFS and CST. Increasing the matrix size from 340 L to around 2000 L led to a higher intensity of the thermophilic phase. Besides, compaction significantly increased temperature during composting. PM was added at ratios ranging from 1.8 to 2.5 L/kg dry matter, being favoured by pre-drying of solid wastes.

Keywords: Forest green waste; shrub; chestnut; MDF sludge; co-composting; compaction.

3.1. INTRODUCTION.

Agriculture, livestock and forestry represent 78% of the total European Union land and play a key role in maintaining the biosphere functionality. In Galicia, north western Spain, these uses rise up to 96.5% of land surface [1] and generate a varied range of wastes. In this context, the persistence of inadequate waste management practices is a matter of concern, while there currently is a demand for sustainable solutions under the EU bioeconomics strategy. In Galicia, forestland occupies 69% of the total land, whilst scrubland itself occupies 21% and generates a large amount of extractable phytomass [1].

Among livestock and forestry wastes, and due to their abundance, this work focuses on chestnut burr and leaves (CST), scrubland phytomass (SRB), pig manure (PM) and a forest industry (Medium Density Fibreboard) sludge (MDFS). New legislative requirements in Galicia demand alternative techniques for management of PM and MDFS [2].

Composting is a process to convert and stabilize organic solid wastes. However, in Galicia current livestock practices led to progressive decreases of solid manure in favour of liquid manure which improperly managed results in environmental problems [3]. Unlike solid manure, liquid manure can be added to composting systems only in limited amounts, serving as a material to correct moisture content (MC) and carbon to nitrogen (C/N) ratio [4,5]. In the same manner, MDFS has been taken into consideration as a co-composting substrate [4]. The experience in the composting of scrubland biomass is focussed mainly on gorse [6,7], and more recently on Scotch broom by vermicomposting [8].

On the other hand, composting phytomass from chestnut plantations received attention by several authors [4,9,10]. Thermophilic temperatures were achieved mainly when chestnut forest biomass is co-composted with animal solid manures (i.e. poultry manure, [7,9]) but not when composted alone [10] or with liquid manure addition [4]. However, Arias et al. [4] reported a short and moderate thermophilic phase during co-composting of forest biomass and MDFS watered with liquid pig manure (PM). This could be due to a significant value of the free air space (FAS) directly correlated to the bulk density (BD) of soil materials. Shredding is a common mechanical technique to modify the BD and FAS rates [6], but in practice its use is conditionated by the availability of resources. The adittion of MDFS resulted in a reduction of the FAS during the bio-oxidative process [4], suggesting that lower rates could improve composting. Thus, an option to lower FAS could be the raising of MC and physical compaction [11]. MC is limited by leaching conditions and the absorbent characteristics of solid materials. Comparative studies on the effect of compaction on forest waste composting have not been previously reported, but it is suggested that its effects could improve the process and especially in the intensity of the thermophilic phase [4]. A high compaction of composting materials would result in a BD increase (and therefore FAS reduction), thus thus promoting the heat conservation within the composting matrices. In this sense, El Kader et al. [11] findings indicated that reducing FAS significantly decreased NH_3 and N losses.

The objectives of the present study are 1) to investigate the effect of matrix compaction on co-composting of forest waste amended with MDFS, 2) to check the effect of thermophilic intensity (temperature and duration) and the type of forest waste on compost biological characteristics, and 3) to determine the amount of PM treated on a forest waste basis. In order to maximixe the final quantity of PM managed, forest wastes were subjected to a prior drying step.

3.2. MATERIAL AND METHODS.

3.2.1. Raw materials.

Chestnut leaves and burr (CST) were collected in a local 9 years plantation. Collection took place soon after abscission to prevent bio-chemical oxidation or degradation on forest soil. CST were transported to a covered shed where they were air dried and then shredded to a 20-50 mm particle size by using a hand-held forest brushcutter.

Two to three year SRB species (mainly gorse and brooms) were obtained by mechanical cutting from an uncultivated land near the chestnut stand. SRB was transported to a concrete surface located outdoors and shredded with a hand-held forest brushcutter. This material mostly acquired a quite heterogeneous 20-150 mm particle size but containing a small fraction of scraped and ripped thicker chunks (150-700 mm). The shredded SRB was extended on the same concrete surface in a layer of less than 50 cm in thickness, for five non-rainy days. It was mixed manually, at least once a day, in order to lower its MC. During the drying period, the average of daily mean and maximum temperature were 11.1 and 17.8 ºC, respectively, and the average wind speed was 7.8 km/h [12].

A local Medium Density Fibreboard industry provided MDFS. A lorry transported 20 metric tonnes of sludge to the composting site. An aliquot sample was spread on a polyethylene plastic in open air and dried during the same period as SRB by periodic raking up. A nearby intensive pig farm provided the liquid PM, stored in a 1,000 L tank with mechanical mixing.

3.2.2. Composting facilities, pile formation and monitoring.

Composting experiences started in April 2016 on a roofed shed with a waterproof concrete base with also counted with a 2% slope and four manhole pits, 50 cm deep, were built ad hoc. A plastic bucket was placed within the manhole pit to collect possible leachates. During the first two months of composting, mean, maximum and minimum ambient temperature was 14.7 ºC, 20.1 ºC and 9.4ºC on average, respectively. Minimum temperature ranged from 1.9 to 16.5 ºC. Daily rainfall was 2.9 L m^{-2} on average during the period [12].

CST and SRB were independently mixed to get homogenization prior to the formation of the composting piles. Solid materials were weighted in 150L plastic buckets before the pile conformation to know the final volume treated and to calculate bulk density.

Four piles were conformed, namely, A B, C and D. Piles A and B were composed of SRB. After 14 days of process, compaction was applied to pile A in order to increase density. Pile C was conformed by SRB and MDFS at the volumetric ratio of 3:1, disposed without compaction, by adding alternating layers of SRB and MDFS (7 and 6 layers respectively). Pile D was composed of SRB and CST homogeneously mixed at the volumetric ratio of 1:8.7. Once solid materials were piled up, they were initially watered with PM under the liquid retention capacity and, to maintain an adequate MC onwards.

Temperature, oxygen and moisture were monitored during composting. Temperature and O_2 were registered at four points of the composting matrix core two to five times a week during the first two months and with less periodicity onwards. Dräger equipment (detector X-AM) and a thermometer with a HI 935005N probe were used to respectively register gas and temperature values.

The composting material was manually turned and mixed once temperature and oxygen were measured. During turning, representative samples of each pile were extracted by taking four to six subsamples from different points. To estimate volume evolution, the shape of the piles was kept close to that of a regular prism and the surface area and average height were measured periodically.

3.2.3. Biological assays.

The self-heating test was performed in duplicate to test maturity in 1.5 L. isotherm Dewar flasks as indicated by Brinton et al. [13]. Materials were shredded by hand to 10-15 mm size with pruning shears.

The respirometric technique proposed by Lasaridi and Stentiford [14] was used to assess compost stability.

Phytotoxicity tests were evaluated by the germination index [15]. Four replicates of twenty lettuce seeds were incubated on petri dishes as described in Arias et al. [4].

3.2.4. Analytical methods.

The elementary composition of the raw materials and composts, total nitrogen (N), carbon (C) and organic carbon (TOC), were determined with an EA1108 elemental analyser (Carlo Erba Instruments) equipped with an AS200 auto-sampler.

Heavy metal (HM) concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS Element XR or Element2 from Thermo Electron) after acid digestion with HNO3. Samples were previously dried in an oven at 60 ºC for 48 hours and posteriorly finely milled with a RETSCH Cutting Mill SM 300 and a 0.25 mm bottom sieve.

The MC of raw materials and compost samples was determined by drying at 105ºC to constant weight and volatile solids by ignition at 550 ºC for five hours. Ammonium was determined with an ion-selective electrode. *E. coli* and *Salmonella spp* detection were measured following ISO 16649-2 and ISO 6579 standards respectively. FAS of composting samples was determined as indicated by El Kader et al. [11], considering 1.6 kg/L as the BD of dry matter particles.

Final compost characterization was carried out once the process temperature was less than 5 ºC above the ambient temperature. Total and dry weight, C, N and TOC reductions were calculated at the end of composting from mass balances.

3.2.5. Statistical methods.

The suitability of the least-squares fitting method was evaluated by the square of the coefficient of determination (R^2), the statistical F-value and probability (p). One-way and two-way analysis of variance were used to compare sets of data. Data was processed using Microsoft Excel 2016

3.3. RESULTS.

3.3.1. Raw materials. Properties and pile formation.

Raw materials presented different properties (Table 3.1). N content was relatively high for CST, SRB and MDFS. High N content in CST was attributed to a larger proportion of leaves than burrs [16] whereas for SRB was in the range of that reported for gorse [7]. N concentration in SRB was higher than that of CST, but SRB showed lower values for most of the other nutrient elements (i.e. P, K, Mg and Ca, Table 3.1).

Chemical references of MDFS are scarce in literature and values of Table 3.1 are similar to these reported in Arias et al. [4]. Relating CST and SRB, MDFS counted for lower content in Mg and K and higher in P, Ca and Ni, indicating a less balanced composition. Except for Ni in the case of MDFS, HM content of solid materials was generally low.

Table 3.1. Chemical composition of raw materials (d.m. basis).

Parameter	CST	SRB	MDFS	PM
BD (kg/L)	0.049 ± 0.005	0.059 ± 0.008	0.397 ± 0.027	0.997 ± 0.000
MC (%)	19.1± 0.85	13.02 ± 0.17	35.17 ± 1.10	98.99 ± 0.06
VS (%)	88.2 ± 1.1	96.4 ± 0.3	79.5 ± 1.3	60.7 ± 0.5
N (%)	1.11 ± 0.05	1.53 ± 0.07	1.13 ± 0.02	12.83 ± 0.03
C (%)	41.67 ± 1.02	48.03 ± 0.04	42.40 ± 0.06	37.50 ± 0.05
TOC (%)	38.18 ±0.94	42.56 ± 0.03	38.19 ± 0.03	18.75 ± 1.06
C/N (TOC/N)	34.4	27.8	33.8	1.46
Mg (g/kg)	3.37 ± 0.02	1.09 ± 0.02	1.07 ± 0.08	11.6 ± 1.3
P (g/kg)	0.83 ± 0.05	0.61 ± 0.02	1.66 ± 0.07	16.2 ± 1.5
Ca (g/kg)	7.62 ± 0.29	2.88 ± 0.04	28.66 ± 0.10	38.1 ± 1.1
K (g/kg)	6.06 ± 0.07	4.96 ± 0.06	1.38 ± 0.02	128.1 ± 2.8
Na (g/kg)	<0.20	1.57 ± 0.02	1.55 ± 0.03	38.9 ± 1.1
Mn (mg/kg)	970.24 ± 99	244.36 ± 8	484.32 ± 32	478.3 ± 45.8
Fe (mg/kg)	4644.71 ± 341	493.08 ± 23	2628.22 ± 23	1072 ± 140
S (mg/kg)	891.38 ± 56	1119.35 ± 23	1400.64 ± 23	7451 ± 134
B (mg/kg)	24.84 ± 0.6	14.18 ± 0.7	14.33 ± 0.4	435 ± 5

Table 3.2 (continuation). Chemical composition of raw materials (d.m. basis).

Parameter	CST	SRB	MDFS	PM
B (mg/kg)	24.84 ± 0.6	14.18 ± 0.7	14.33 ± 0.4	435 ± 5
Cd (mg/kg)	<0.05	<0.05	0.16 ± 0.01	0.41 ± 0.01
Pb (mg/kg)	2.89 ± 0.20	<1.00	1.94 ± 0.03	1.00 ± 0.20
Hg (mg/kg)	0.06 ± 0.02	<0.05	<0.05	0.03 ± 0.01
Cr (mg/kg)	16.42 ± 0.62	17.15 ± 0.69	30.63 ± 0.36	4.21 ± 0.07
Co (mg/kg)	1.97 ± 0.16	0.31 ± 0.02	1.56 ± 0.08	0.58 ± 0.02
Ni (mg/kg)	7.19 ± 0.16	2.09 ± 0.03	20.52 ± 0.6	10.2 ± 1.3
Cu (mg/kg)	11.07 ± 2.14	6.45 ± 0.88	10.61 ± 1.86	273 ± 18
Zn (mg/kg)	34.47 ± 4.81	25.19 ± 0.51	73.81 ± 2.26	968 ± 70
As (mg/kg)	0.70 ± 0.07	<0.50	1.44 ± 0.08	0.90 ± 0.08
Se (mg/kg)	<1.0	<1.0	<1.0	1.20 ± 0.06

PM presented low to medium values of NH4+-N (1.97 g/L), dry matter content (1.001%), and total and volatile suspended solids (3.5 and 3 g/L respectively). Other properties were a pH close to neutrality (7.2), electrical conductivity of 10 dS m-1 and chemical oxygen demand of 11.1 g O_2/L. Comparatively with the solid materials, on a dry mass basis, PM registered higher values of N, as well as in most nutrient elements and HM. The content of Cu and Zn in pig manure is a worrying issue since their concentrations can be relatively high, impairing the quality of the obtained compost. HM content in PM are in the range of other local pig farms [4,17].

Different initial properties of piles and the varied proportions of materials affected the C/N and the liquid fraction of PM per unit of total solids (L/S) ratio (Table 3.3).

Piles A and B were differentiated by the BD which was higher for pile A after day 14 of operation due to the compaction. Pile C combines MDFS and SRB at a volumetric ratio 1:3.5 and received PM at a higher volumetric ratio but reaching a lower L/S ratio (1.79 L PM/kg dm, Table 3.3) than piles A and B (2.42 L PM/kg dm). The use of MDFS in pile C clearly increased its BD in relation to the other piles, except pile A after compaction. Pile D received mainly CST biomass, a minor amount of SRB and PM at the same ratio as piles A and B.

Table 3.3. Materials used and characteristics of composting piles.

	Added materials						Initial pile				S/L final ratio
Pile	SRB (kg)	CST (kg)	MDFS (kg)	Initial PM (L)	Final PM (L)	Total mass (kg)	Volume (L)	BD (kg/L)	FAS	C/N [b]	(L PM / kg dm) [b]
A	108.16	0	0	92	230	338.16	1830 (842)[a]	0.109 (0.182)[a]	91.0 (85.0) [a]	23.4	2.42
B	108.16	0	0	92	230	338.16	1830	0.109	91.0	23.4	2.42
C	90.14	0	173.72	115	345	608.85	1963	0.193	84.3	26.5	1.79
D	20.2	116.9	0	105	265	402.50	2422	0.086	89.0	26.5	2.46

[a] Considering the effect of compaction. [b] Including the final PM amount added.

3.3.2. Evolution of the composting process.

MC shows a different pattern for piles A, B and C than for pile D (Figure 3.1). PM additions to pile D were large at the starting. Subsequent additions kept MC in the range of 70-76% during the first month and between 64-66% without watering for the next two months. On the contrary, initial MC in piles A, B and C was lower than in pile D, due to a lower water retention of SRB. The early development of thermophilic temperatures in these piles led to a sudden decrease in MC that was compensated with additional PM amounts. As composting evolved, the ability of the matrices of piles A, B and C to retain water increased and rounded 60% at day 30 of composting. Hereinafter water losses were low but sustained over time as the piles reached the cooling phase, pile D keeping humidity in a more sustained way. In comparison to pile B, MC content was lower in pile A after compaction, due to the higher temperatures reached, but remained higher in the long-term, probably due to a lower aeration rate. Leachates were generated and recirculated only in pile C (13 L).

Composting implies the progressive reduction of volume [18], due to the breakdown of organic matter and the self-compaction of the material throughout the process. As shown in Figure 3.1b, volume decrease was high during the first month in pile D, whilst showing an initial period of little variation in piles A, B and C. This behaviour can be related to the MC, indicating that values higher than 50% were required to facilitate self-compaction. On the other hand, volume reduction stopped when the temperature decreased to about 30ºC (see Figure 3.1 and Figure 3.2), probably due to the reduction of the degradation rate because the remaining substrate was more resistant to decomposition [18].

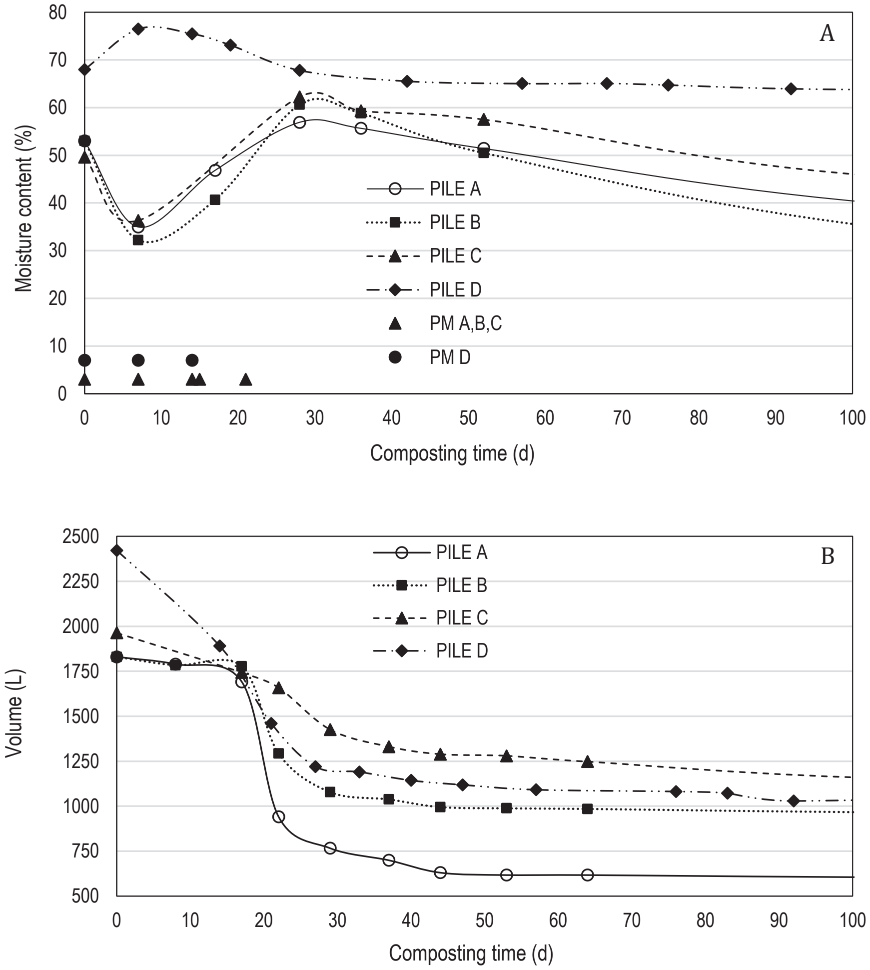

Figure 3.1. Evolution of MC and PM addition episodes (a) and volume evolution (b) for the different composting piles.

Piles A, B and C maintained active composting up to day 41, with temperatures above 30ºC (Figure 3.2). In general, temperature of all the piles increased after turning during the first five weeks. Thermophilic temperatures (higher than 40ºC) were maintained for 28 days in pile C. By comparison, pile B achieved thermophilic temperatures only during 8 days, whilst compaction in pile A increased the time of the thermophilic temperature to 16 days. After six weeks, the temperature of the three piles decreased below 30ºC and progressively approached the ambient temperature. Oxygen never compromised the process, ranging from 15.6 to 20.9 % (Figure 3.2b). In all piles, oxygen content and temperature showed a significant ($R^2>0.4$, $p<0.05$) negative correlation. In general, the lower oxygen levels corresponded to the higher temperatures, indicating a higher biodegradation activity in these conditions.

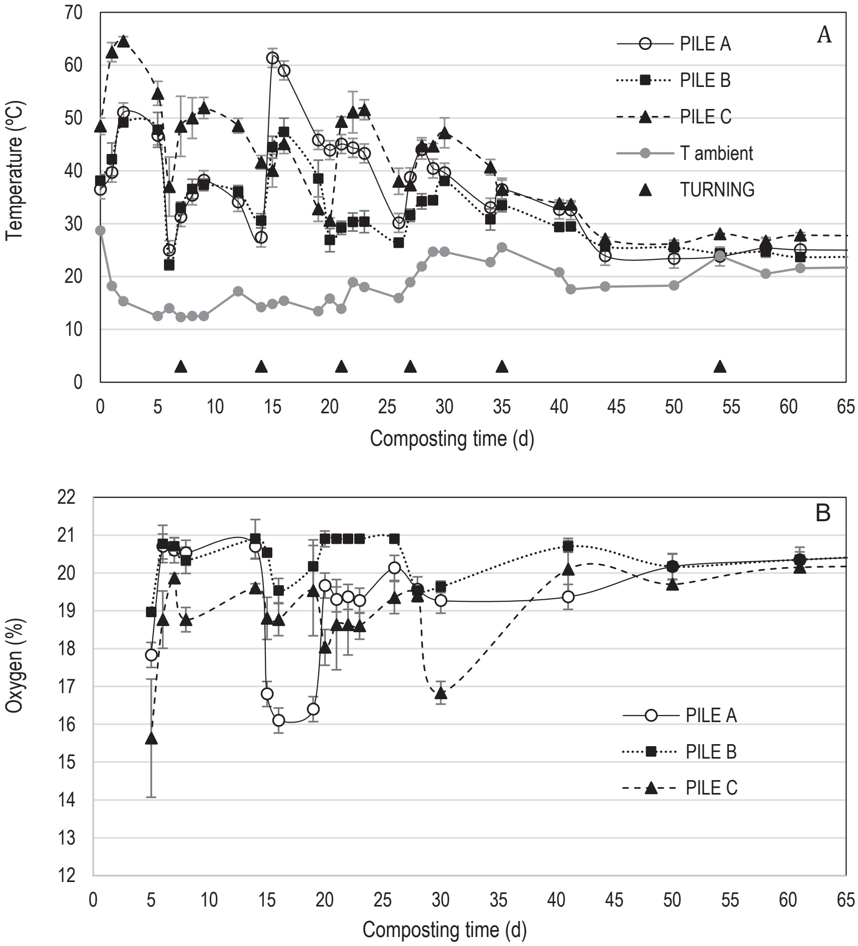

Figure 3.2. Temperature evolution and turning episodes (a) and oxygen content evolution (b) in piles A, B and C (error bars represent standard deviation).

During the first two weeks of composting, piles A and B constituted a replicate system with the same raw materials and composting conditions and showed very similar temperature and O_2 profiles. Piles A and B reached thermophilic temperatures of approximately 50 ºC on day 2. Following, the temperature rapidly decreased, probably because of the drastic reduction of the MC and an excessive ventilation rate. Mean temperatures during the two first weeks of 37.6 ºC (A) and 38.0 ºC (B), and mean oxygen content of 20.0% (A) and 20.2% (B) did not show significant differences (p>0.8). Pile C behaved in a similar way to piles A and B, but showing temperatures approximately 12 ºC higher, reaching mean temperature of 51.8 ºC which was significantly higher than that of piles A and B (p<0.002). In addition, pile C also showed mean oxygen content (18.1%) significantly lower than that of pile A (p=0.03) and B (p=0.06) during the first two weeks.

Temperature in piles A and B increased again once the MC increased above 40% (Figure 3.2a). Furthermore, compaction (day 14) led to a higher increment of temperature in pile A that immediately reached 61.4 ºC (versus 47.4 ºC in pile B). Mean temperatures from day 14 to day 41 were significantly higher ($p=0.003$) for pile A (41.9 ºC) than for pile B (33.4 ºC), which demonstrated the strong effect of pile compaction. During the same period, pile C showed a mean temperature of 41.1 ºC, similar to that of pile A ($p=0.76$). On the other hand, mean oxygen content was significantly lower ($p<0.001$) in piles A (18.7%) and C (18.8%) than in pile B (20.4%). This could be due to the combination of a lower ventilation rate, as FAS was lower in piles A and C (Table 3.3), and a higher biodegradation rate because of the higher temperature.

Due to differences in air temperature and density between the composting matrix pile and surrounding environment, heat and water vapor are displaced by convection from the bottom and side parts of the pile to the top. This caused a vertical stratification of MC, which was more drastic in pile A after compaction. In pile A, the first top 30 centimetres were water saturated by the effect of condensation. This layer was followed by the dry matrix core and finally, the material at the 10-15 cm ground level had a higher MC due to lower temperature and air circulation.

Compared with previous results for co-composting of forest green waste and MDFS [4], increasing the matrix size from 340 L to around 2000 L led to higher intensities of the thermophilic phase probably due to the lower specific surface area in relation to total volume that reduced the dissipation of heat by unit of mass. The composting units used by Arias et al. [4] had a square base and height of, respectively, 75 and 80 centimetres (effective composting volume of 340 L). The height of those systems was higher than 50% of the pile height in the present study, whilst the total mass was only 12 to 24%. Thus, in addition to the matrix size, the matrix shape also favoured heat losses in the study of Arias et al. [4]. Given the effect of the matrix size found, it is suggested that composting of SRB and CST watered with PM at large scale field applications probably would reach and maintain thermophilic temperatures for a longer time these here reported.

Pile D reached thermophilic temperatures during the first week (Figure 3.3a). However, temperature decreased at days 8-12 due to PM addition and excessive MC that reached 76% (Figure 3.1). Even though the high MC, thermophilic temperatures were reached again and kept in the range of 40-51 ºC from day 14 to 54. Mean temperature of pile D during this period (45.8 ºC) was significantly higher and oxygen content (mean value of 14.8 %) significantly lower than those of piles A, B and C (period from day 14 to 41, Figure 3.3b). Thereafter, the temperature decreased and stabilized at approximately 30 ºC for about two months (Figure 3.3a), despite periodical turning. During this period, the temperature gradient was nearly constant at 6-7 ºC over ambient temperature and oxygen content ranged from approximately 19% to 20%. Maintaining this temperature for such a long period could be due to the self-insulating properties of the composting materials which confered certain thermal inertia to the pile. A similar behaviour was reported for gorse composting in steel tanks [6].

As in the case of the other piles, oxygen content in pile D inversely correlated with temperature (R^2=0.51, p=0.000). Minimum values of approximately 10% O_2 were registered coincident with the highest temperature.

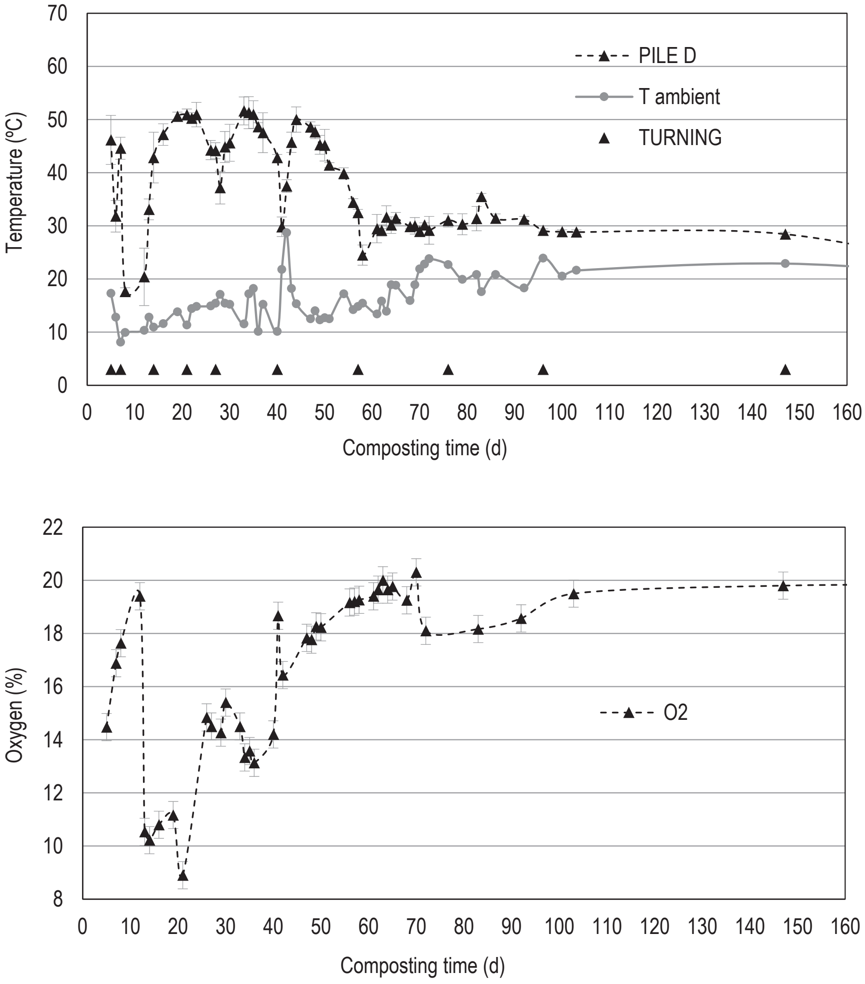

Figure 3.3. Temperature and oxygen (represented in secondary vertical axis) evolution and turning in pile D. (error bars represent standard deviation). Temperature and oxygen (represented in secondary vertical axis) evolution and turning in pile D. (error bars represent standard deviation).

3.3.3. Biological characteristics of compost.

After approximately one month, composting materials were classified as stable according to both self heating and respirometric methods (Table 3.4). Samples reached classes IV (pile A) or V (piles B, C and D), being classified as stable compost according to Brinton et al. [13].

Respirometric assays gave SOUR values below 1 mg O_2/g VS·h for all samples, as well as low AOD_{20h} values. These results confirmed the stability after a moderately brief period of time [20].

Table 3.4. Biological criteria used to evaluate compost quality.

CRITERIA	Composting pile				Legal or recommend limit [Reference]
	A	B	C	D	
Rottegrade, MTG (ºC) and Stability class [a]	10.5 (IV)	9.6 (V)	2.6 (V)	3.2 (V)	Class IV or V [13]
Respirometry, SOUR (mg O_2/g VS·h) [a]	0.60	0.89	0.99	0.96	1.0 (Stable) [19]
Respirometry, AOD_{20h} (mg O_2/g VS)	7.1	9.7	8.8	17.7	Not established
E. coli (mpn/g wet matter) [b]	4.6 x10^3	5.1 x 10^3	6 x 10^2	<2	1 x 10^3 [25]
Salmonella (Present/ Absent in 25 g) [b]	Absent	Absent	Absent	Absent	Absent [25]
Germination index (%)[c]	132.1 ± 1.2	133.1 ± 19.1	110.6 ± 6.3	134.3 ± 27.4	80 [15]

[a] Stability assays were applied at 35 d (A, B, C) and 48 d (D) of process. MTG: maximum temperature gradient, Stability classes: IV: Moderately stable compost, V: Very stable compost. SOUR: Specific Oxygen Uptake Rate. AOD_{20h}: Accumulated oxygen demand in 20 hours. mpn: most probable number. [b] Pathogen indicator were determined at 62 d (A, B, C) and 104 d (D) of process. [c] Germination assays applied at the end of process, at 152 d (A, B, C) and 194 d (D).

Microbiological assays revealed the absence of *Salmonella spp*, and *E. coli* populations in piles C and D below the regulation threshold (Table 3.4). The very low level of *E. coli* in pile D could be due to the longer process time and higher temperature in comparison to the other piles. In spite of the shorter time, the higher process temperature obtained in pile C respect to piles A and B was the main reason for the *E. coli* reduction. On the other hand, different raw materials of piles C and D, MDFS and CST respectively, could improve the hygienization.

GI overcame a 130 value in piles A, B and D, whereas pile C rounded 110 (Table 3.4). Seed germination was similar to that of control (p>0.36), whereas radicle growth was stimulated by the compost extracts in all cases (p>0.05 for piles A, B and C, p=0.08 for pile D). Among composting piles, only pile C compost showed lower stimulation of the radicle growth than the compost from piles A and B.

Absence of phytotoxicity, and maturity is usually considered when GI values are higher than 80% according to Zucconi et al. [15].Nevertheless, Ko et al. [21] found GI above 90% at the active composting stage and proposed values greater than 110 to assure maturity of composted animal manures. Considering this, all the composts could be considered mature.

3.3.4. Nitrogen content and mass reduction.

N content of final composts ranged from 1.7 to 2.4% (Table 3.5). Piles A and B overcame the 2% N value. The amendment of MDFS resulted in a 1.7% N in compost of pile C, due to both the lower content in N of MDFS when compared with SRB and the lower L/S ratio.

Table 3.5. Final compost elemental composition and reduction (%) at the end of the composting process (92 days for piles A, B and C, 141 days for pile D).

	Composting pile			
	A	**B**	**C**	**D**
% N	2.37 ± 0.20	2.18 ± 0.00	1.75 ± 0.09	1.97 ± 0.12
% C	45.5 ± 0.8	46.1 ± 1.3	42.2 ± 1.0	41.4 ± 1.5
% TOC	42.9 ± 2.0	43.2 ± 2.7	39.3 ± 1.9	38.4 ± 2.5
C/N	18.1	19.8	22.4	19.5
Cd (mg/kg)	0.073 ± 0.001	0.068 ± 0.001	0.170 ± 0.001	0.091 ± 0.001
Pb (mg/kg)	0.97 ± 0.01	0.91 ± 0.02	1.5 ± 0.01	2.6 ± 0.01
Hg (mg/kg)	<0.050	<0.050	0.066 ± 0.001	0.176 ± 0.003
Cr (mg/kg)	5.0 ± 0.2	4.6 ± 0.0	21.2 ± 0.9	19.3 ± 0.2
Ni (mg/kg)	3.6 ± 0.1	3.4 ± 0.1	11.2 ± 0.4	10.8 ± 0.3
Cu (mg/kg)	13.4 ± 0.3	13.4 ± 0.1	9.9 ± 0.4	17.6 ± 0.1
Zn (mg/kg)	58.3 ± 0.9	57.8 ± 1.2	70.0 ± 1.8	69.4 ± 1.1
Reduction				
Volume (%)	66.8	46.9	39.7	58.6
Mass (%)	78.1	74.3	54.0	54.9
TS (%)	56.5	45.3	26.6	36.2
TOC (%)	54.0	41.2	24.8	32.9
N (%)	39.3	33.6	17.0	8.9

Reduction of TS and TOC appeared highly correlated (R^2=0.994) as well as TS and total mass (R^2=0.862). A positive correlation also exists for N losses, although pile D showed a distinctly lower percentage of N loss. TOC losses were higher than N losses, leading to the reduction of the C/N ratio, in accordance with the general evolution of composting systems [18].

N losses can be attributed mainly to NH_3-volatilisation as the high O_2 content during composting (Figure 3.2 and Figure 3.3) ensured the absence of anaerobic conditions which could lead to denitrification processes. Net leachates were not produced as the small amount produced in pile C were returned to pile.

Highest N losses occurred in piles A and B. The higher N loss in pile A with respect to pile B was in contradiction with the findings of El Kader et al. [11], who reported that compaction apparently reduced ammonia losses. Besides, water condensation in the upper layer could favour ammonia accumulation and retention then lowering N losses [22]. However, our findings revealed both larger N losses and higher MC stratification and accumulation at the upper layer corresponded to pile A. The slightly higher N losses in pile A could be the reason for the higher temperature in this pile and ammonia volatilisation. Pile A also presented the highest losses in volume, TS and TOC. However, when comparing all piles, lower N losses occurred in piles C and D, which in turn showed higher mean temperatures and a large number of days at thermophilic temperature. This behaviour may be related to other characteristics of piles such as the self-insulating properties in pile D and the lower N content in pile C. The lower biodegradability of materials in piles C and D, as indicated by lower reductions of TS and TOC (Table 3.4), probably played a role in N conservation.

Chemical composition of raw materials could also influence N losses. Santos et al. [23] found that composting chestnut wastes (peels and rejected fruits) produced lower NH_3 and NO emissions comparatively with other agro-food wastes. These authors supported that materials rich in lignocellulose and phenolic compounds could highly influence emissions during composting. Whilst MDFS stands out for its high lignin content (48%, data not shown), CST presents high content in phenols [24]. Thus, this kind of chemical compounds in piles C and D might have helped in reducing N losses.

The concentration of HM of in the final samples (Table 3.5) appeared under the legal thresholds [25] of Class A composts in Spain and therefore compatible with the limits for organic farming of the European Commission [5].

3.4. DISCUSSION.

3.4.1. Nitrogen content of forest green waste and composting.

Chemical composition of forest green waste and scrubland species depends on many factors, such as the season of harvesting, the vegetative cycle stage or soil conditions. Ventorino et al. [10] composted CST and SRB with two to three times lower N content than that of CST and SRB of the present study. Composting of CST with up to 6 times lower N content was reported by [9].

However, these authors could not reach thermophilic temperatures because of the too high C/N ratios of 58 [10] or 251 [9]. On the contrary, due to a lower C/N in raw solids materials and aided by PM additions, all the initial mixtures in the present study reached C/N ratios in the range of 23 to 27 (Table 3.3), similar to those recommended for composting [18].

Arias et al. [4] reported that the adittion of PM did not guarantee thermophilic profiles in the composting of forest green wastes containing 1.6% of N. However, these authors used a much-diluted PM and pointed out that high loaded PM could favour the composting temperature. This is the case of the present study as the used PM was twice near concentrated than that of Arias et al. [4]. Addition of poultry manure also favoured higher temperatures during gorse composting [7].

3.4.2. Pre-drying raw materials and PM watering rate.

Reduction of MC is a common operation during forest biomass collection to rise energy efficiency and low transport costs. Núñez-Regueira et al. [26] recommended drying sheds, stating that the simple storage in adequate premises reduces and maintains moisture at 30%. Under the experiences here reported, MC of CST and SRB was effectively reduced to less than 20%, and to 35% for MDFS. Preliminary shredding of green forest wastes would be preferable in order to accelerate drying and facilitate spreading, rotation and ventilation.

Achieving this MC reduction enhanced the amount of PM treated (higher L/S ratio). L/S ratio used in the present study ranged from 1.8 to 2.5 L PM/kg TS (Table 3.3). Approximately 40% of the PM was added initially, and the rest during watering operations over the first 2 or 3 weeks of composting. Thus, pre-drying the solid raw materials is considered necessary to reach such high total L/S ratios. In any case, the use of PM to maintain the pile moisture was also a large contribution to the total L/S ratio. Total L/S ratios are in the same range of that reported by Arias et al. [4], that varied from 1.1 to 4.3 L PM/kg TS. However, these authors prolonged composting and PM watering for up to 150 days. In our study, watering (PM addition) only took place during the first 3 weeks, and the piles material was stable after approximately one month (Table 3.4), whilst most of the volume and temperature reduction was obtained after 2 months (piles A, B and C) or 3 months (pile D). Thus, considering a minimum period of composting of 2 months (piles A, B and C) and 3 months (pile D), the obtained PM watering rates were 40.3 (A, B), 29.8 (C) and 27.3 (D) L/t TS·d. These figures are in the range of evaporation rates reported by [5] for co-composting of pig manure and highly biodegradable biowastes, which ranged from 14 to 76 L/t TS·d.

3.4.3. Compost hygienization.

Salmonella and *E. coli* are ubiquitous microorganisms in manure and represent the most common criteria to asses pathogen presence in compost. Regulations in many European countries provide indirect methods to prevent pathogens through the requirement of specific temperature profiles. Galician regulations for sewage sludge composting of turning piles require a minimum 55 ºC during a period exceeding 4 hours between turning episodes combined with at least three turning episodes meeting this criterium [2]. In the present study neither of the met these criteria. However, *Salmonella spp*, and *E. coli* populations in piles C and D were below the Spanish regulation threshold (Table 3.4).

Bernal et al. [18] referenced 55 ºC limit to kill pathogenic microorganisms in composts. However, working with winery and distillery wastes, Bustamante et al. [27] highlighted that reaching relatively high temperatures (50–60 ºC) does not necessarily imply a complete sanitisation of the end-product and that some factors such as humidity, nutrient availability, or competitive microbiota can determine the ability to grow of *E. coli* or *Salmonella*. In addition, several authors [27,28,29] reported regrowth ability of *E. coli* during the cooling and maturation phases of composting.

Our results show advanced hygienization in piles C and D, whilst large amounts of *E. coli* remained in piles A and B. Maximum peak temperatures were reached in piles A and C (61.4 and 64.6 ºC, respectively, both piles A and C underwent 2 days at temperature above 55 ºC), whilst maximum peak temperatures registered in piles B and D were 49.1 and 51.6 ºC, respectively. Thus, maximum peak temperature was not related with *E. coli* removal in the conditions of this work. In fact, a significant correlation ($R2=0.904$, $p=0.049$) between *E. coli* and the number of days at thermophilic temperatures (higher than 40ºC) for the four piles was found.

During the composting of solid and liquid fractions of pig manure with wood shavings, Ros et al. [30] reported thermophilic temperatures of 40-50 ºC, which were similar to those of the present study. After a 13 week composting process, these authors evidenced a strong reduction of *E. coli* populations (under 43 CFU/g fresh weight). According to Ros et al. [30], our results indicate that *E. coli* reduction occurs at temperatures higher than 40ºC and may be effective in the range of 40-50ºC, depending on the duration of the thermophilic period. Optimal temperature for *E. coli* growth is 37 ºC, as outlined by Hijikata et al. [31], but *E. coli* removal at temperatures slightly above 40ºC during compost has been found by other authors. When composting pig slurry solid phase with cereal straw acting as a bulking agent, García-González et al. [32] reported a complete hygienization of pig slurry (no detectable *Salmonella* in 25 g and *E. coli* <1 CFU/mL) reaching lower thermophilic temperatures (above 40ºC) than those here reported.

Additional hygienization mechanisms could be related to the chemical and biological properties of raw materials, such as the content in bioactive polyphenolic compounds [24,33]. Braga et al. [24] outlined that sweet chestnut (Castanea sativa Mill.) by-products (shells and leaves) contained important and abundant bioactive polyphenolic compounds. The content of polyphenols in the MDFS used in the present study was found to be about 0.45 g/kg MDFS on a wet basis (data not shown). Thus, some compounds as tannins might have influenced the hygienization process in piles C and D because of their antimicrobial effect. Recently, chestnut shell has been reported as an important antibacterial activity agent [34,35], with sanitizer effect on the inactivation of foodborne pathogens [33], and *E. coli* in particular [36]. Ventorino et al. [37] outlined that most of the microbiota of chestnut green waste persisted during composting and final compost possessed high suppressive activity against fungal pathogens. In the same line, Bustamante et al. [27] stated that competitive microbiota can influence the ability for growing of some pathogens, such as *E.*

coli. Thus, bacterial and fungal species present on CST might have had a suppressive or antagonistic effect over *E. coli* populations.

3.5. CONCLUSIONS.

Co-composting of forest and farm wastes produces organic amendments suitable to be recycled to agriculture and forest crops in a sustainable way. Stable compost with 1.7 to 2.4% N content was obtained after about two month of composting. Heavy metal content remained under the limits for the best quality Class A composts in Spain, in spite of large concentrations of Cu and Zn of the used PM.

A significant correlation between *E. coli* and the number of days at temperatures higher than 40ºC was found. This way, satisfactory reduction of pathogen indicators was obtained for piles C and D, whilst piles A and B presented *E. coli* populations above the current legal limits for commercial organic fertilizers in Spain. On the other hand, lower N losses (17.0% and 8.9% in piles C and D versus 39.3% and 33.6% in piles A and B, respectively) were attributed to the chemical characteristics of MDFS and CST substrates, which could also contribute to complete hygienization of composts.

Compaction increased the bulk density of SRB initial composting matrix from 0.11 to 0.18 kg/L leading to higher composting temperatures. Pre-drying of solid raw substrates led to high PM watering rates, which ranged from 1.8 to 2.5 L/kg d.m.

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CAPÍTULO IV

AVALIACIÓN DO ENSAIO DE DBO_5 COMO MÉTODO PARA A DETERMINACIÓN DA BIODEGRADABILIDADE E ESTABILIDADE DE RESIDUOS ORGÁNICOS E COMPOST

4. AVALIACIÓN DO ENSAIO DE DBO5 COMO MÉTODO PARA A DETERMINACIÓN DA BIODEGRADABILIDADE E ESTABILIDADE DE RESIDUOS ORGÁNICOS E COMPOST.

RESUMO

A compostaxe estendeuse nos últimos anos a pequenos municipios e incluso a composteiros a escala doméstica ou comunitaria. Isto provocou que un gran número de persoas estean involucradas na xestión de residuos orgánicos, no proceso de compostaxe e no uso de compost. Sen embargo, estas persoas e en xeral non teñen acceso a laboratorios especializados. Xorde así a necesidade de métodos simples e económicos para determinar a estabilidade do compost. No presente traballo, avaliouse a utilización dos equipos empregados de xeito habitual nos ensaios DBO_5 para a obtención de índices respirométricos. Os resultados comparáronse cos obtidos mediante dous métodos de referencia: un respirométrico (velocidade máxima de consumo de oxíxeno e taxa de consumo acumulado de oxíxeno ao cabo de 20 h) e o autoquecemento estándar (incremento de temperatura). Os índices obtidos mediante o ensaios de DBO_5 correlacionáronse axeitadamente cos resultados dos anteditos métodos de referencia. O emprego da DBO_5 caracterizase pola súa sinxeleza e por ofrecer un parámetro único, correspondente ao consumo de oxíxeno acumulado ao cabo de 5 días de ensaio. Por comparación cos métodos de referencia, o limiar de estabilidade pode establecerse en 25 mg O_2 g SV^{-1} de DBO_5.

Palabras clave: Residuos orgánicos, compost, estabilidade, respirometría, ensaio DBO_5.

4.1. INTRODUCIÓN.

Os residuos orgánicos constitúen a maior parte dos sólidos urbanos e existe unha necesidade da súa reutilización e reciclaxe baixo criterios ambientalmente sustentables. A compostaxe constitúe unha das alternativas máis atractivas nunha rexión como Galicia onde os límites entre as interfaces urbanas e agroforestais son a miúdo difusas.

A compostaxe pode valorizar ámbolos dous fluxos de residuos, de orixe urbana e agroforestal, en fertilizantes ou emendas para incorporar ao solo. Os beneficios da compostaxe como unha técnica de xestión de residuos son ben coñecidas mais a aplicación de composts ao solo debe realizarse en condicións de suficiente bioestabilidade (Barrena *et al.*, 2006; Bernal *et al.*, 1998; Vázquez *et al.*, 2015). De xeito contrario produciríanse efectos agronómicos indesexables: inhibición biolóxica da asimilación de N que pode causar serias deficiencias deste elemento nas plantas, rápido descenso da concentración de O_2 e do potencial redox do solo ou emisións de gases de efecto invernadoiro durante o seu almacenamento e uso (Iqbal *et al.*, 2010; EC, 2014).

Para evitar estes efectos negativos e para empregar compost de xeito eficiente, resulta esencial a avaliación da súa bioestabilidade, así como a das materias orgánicas de partida.

Ademais das plantas industriais de compostaxe para áreas máis densamente poboadas, a compostaxe a pequena escala é especialmente útil e complementaria en Galicia, con abundantes áreas rurais de baixa e dispersa poboación, e incluso ultimamente en áreas urbanas a través do que se coñece como compostaxe comunitaria (Comesaña *et al.*, 2017). Con crecente interese pola Administración autonómica, e sobre todo polos concellos, nos últimos anos miles de composteiros foron instalados en Galicia, España e outros países europeos. Está demostrado que a compostaxe caseira é ecolóxica e economicamente viable (Adhikari *et al.*, 2012, 2010; Andersen *et al.*, 2012; Lleó *et al.*, 2013) e diferentes iniciativas conduciron á implicación dunha parte importante da sociedade na xestión dos residuos orgánicos, na compostaxe e no uso do compost. Xeralmente, os usuarios son aconsellados por equipos de persoal experimentado pero sen acceso a laboratorios especializados, sendo a calidade física e química da compostaxe caseira garantida pola correcta selección das materias primas que se van compostar. Sen embargo, a determinación das estabilidade do compost require o emprego de ferramentas analíticas máis sofisticadas. Un amplo e variado abano de técnicas avanzadas son exploradas constantemente para a avaliación da bioestabilidade pero a súa viabilidade depende en último termo no establecemento de relacións cos métodos convencionais, especialmente naqueles baseados nunha resposta biótica (Lü *et al.*, 2017).

Os procedementos baseados no consumo de oxíxeno ou na xeración de dióxido de carbono por unha mostra de compost, solo ou residuo orgánico, son coñecidos como técnicas respirométricas (Barrena *et al.*, 2006; Lasaridi and Stentiford, 1998). Os métodos baseados na taxa de consumo de O_2 divídense en dúas clases: estáticos e dinámicos. Nos dinámicos, o ensaio é levado a cabo mediante un aporte continuo de oxíxeno á biomasa namentres nos métodos estáticos non existe ese aporte continuo de aire. O material organicamente biodegradable ou o substrato non estabilizado será degradado polos microorganismos. A maior actividade, maior será a taxa de consumo de oxíxeno.

Lasaridi e Stentiford (1998) propuxeron un procedemento para un método respirométrico en fase líquida (test VECO, Specific Oxigen Uptake Rate) que, entre outros equipos, require o emprego dunha sonda que mida o oxíxeno disolto que debe ser periodicamente calibrada e mantida baixo estritas condicións, así como a realización de cálculos e interpretación posterior de resultados complexos. Estas circunstancias convirten este método en pouco asequible en termos monetarios e demandante de persoal moi especializado. O test VECO permite establecer unha escala de estabilidade do compost baseado na velocidade específica de consumo de oxíxeno (por exemplo VECO, mg O_2 g $SV^{-1} \cdot h^{-1}$) ou na demanda específica de consumo de oxíxeno satisfeita nun intervalo de tempo determinado (por exemplo, $DEAO_{20h}$, mg O_2 g SV^{-1}). Este test, xunto co de autoquecemento en vasos Dewar ou test Rottegrade (Brinton *et al.*, 1995), está recoñecido como unha das dúas probas propostas polo Grupo de Traballo do Joint Research

Centre, para a súa inclusión nos criterios de decisión da condición de fin de residuo pola Comisión Europea (CE) para residuos biodegradables (Aspray *et al.*, 2015).

Recentemente, foron desenvolvidas diferentes achegas baseadas na determinación no oxíxeno consumido pola medición da presión da fase gasosa sobre unha suspensión líquida contida en recipientes herméticos. O comercialmente dispoñible sistema de medición OxiTop® proporciona índices de respiración estáticos e resultou un método menos complicado que outras técnicas estáticas (métodos de xeración de oxíxeno) e métodos dinámicos. Binner *et al.* (2012) atoparon unha forte correlación entre o índice de respiración obtido polos métodos Sapromat® e OxiTop®, aínda que o OxiTop® proporcionou valores claramente inferiores (88% de media) con respecto ao Sapromat®. Sen embargo, o método OxiTop® segue a ser un método caro e sofisticado que non é accesible para a maioría de aplicacións en países en desenvolvemento (Bożym, 2012) así como en instalacións de compostaxe de pequenos municipios (Oviedo-Ocaña *et al.*, 2015).

Daquela resulta de moito interese o emprego de técnicas máis sinxelas para determinar a estabilidade de composts e residuos orgánicos. No campo do tratamento de augas, a demanda biolóxica de oxíxeno (DBO_5) é universalmente usada e aceptada como un método estándar para a determinación da materia orgánica facilmente biodegradable. De feito e como foi indicado con anterioridade (Grigatti *et al.*, 2007; Aspray *et al.*, 2015), o método OxiTop® cunha mostra en suspensión está baseado nos mesmos principios que a DBO_5,. A determinación directa da DBO_5 en eluatos obtidos pola extracción mediante auga do residuo ou mostras de compost ten obtido resultados contraditorios, sendo descartada como un índice de estabilidade para mostras sólidas de residuo frescas (Barrena *et al.*, 2009), mentres que foi atopada unha correlación entre o consumo acumulado de oxíxeno durante 4 días e a DBO_5 do eluato. Resultados similares foron obtidos por Cossu e Raga (2008), atopando unha correlación entre o cociente da demanda biolóxica e química de oxíxeno (DBO e DQO, respectivamente) en eluatos e os índices de respiración estáticos de mostras sólidas de compost. Estes intentos previos de empregar a DBO_5 como un indicador da estabilidade foron prometedores. Así, a nosa hipótese é que a determinación da DBO_5 nunha dispersión de compost, tal como as empregadas por Lasaridi e Stentiford (1998) para o método respirométrico estándar, en lugar do eluato do compost podería ofrecer mellores resultados.

Neste sentido, Vázquez (2015) suxeriu un valor de 23 mg O_2 g SV^{-1} de DBO_5 en equivalencia co límite establecido polo test VECO de 1 mg O_2 g $SV^{-1}\cdot h^{-1}$ para compost estable. Ademais, a relación da DBO_5 coa demanda acumulada de oxíxeno ás 20 horas obtida polo test VECO resultou en 1.55±0.15 independentemente do grao de estabilización do compost. Sen embargo, os resultados foron obtidos unicamente a partires de dúas mostras de compost procedentes das áreas de compostaxe do campus da UDC.

O obxecto da presente investigación foi ampliar as experiencias iniciais levadas a cabo por Vázquez (2015) na procura do desenvolvemento dun método respirométrico baseado no ensaio de DBO_5 aplicado a mostras de compost e residuos orgánicos. Búscase ampliar a aplicación dunha técnica económica, simple e robusta que xa está habitualmente presente como equipamento ordinario na maioría de laboratorios de análise de augas en todo o mundo. Para este propósito ensaiáronse varias mostras representativas do proceso de tratamento da fracción orgánica de residuos urbanos dunha Planta de Tratamento de residuos urbanos de Galicia: orgánico bruto, dixestato e o compost final. A aplicación do método ampliouse a mostras doutra planta similar, desde o residuo inicial ao compost estabilizado. Finalmente, comprobouse se os resultados eran extrapolables a outros residuos do ámbito agroforestal galego, como son os xurros de granxas de porcino, biomasa residual procedentes dos soutos e matogueiras, e lodos dunha industria forestal.

O método estándar para a determinación da DBO_5 en augas residuais (APHA, 2005) foi adaptado para obter a demanda acumulada de oxíxeno en mostras de compost e residuos orgánicos, así como foron determinadas as condicións da súa aplicación. Os resultados foron comparados con aqueloutros obtidos por un método de referencia respirométrico (test VECO) e polo test de autoquecemento, ambos universalmente empregados en estudios de estabilidade de compost.

4.2. MATERIAIS E MÉTODOS.

4.2.1. Recollida de mostras e características.

Os materiais ensaiados foron de dous tipos: a) mostras de plantas de compostaxe da fracción orgánica de residuos urbanos (FORU), incluíndo pequenos composteiros de residuos orgánicos de comedor; b) diferentes residuos orgánicos non asociados a plantas de compostaxe, tanto de biomasa forestal como lodos de procesos industriais (Táboa 4.1).

Un primeiro grupo de mostras (N1 a N3) orixináronse nunha planta de tratamento na que a FORU era xestionada por un proceso combinado de dixestión anaerobia e post-tratamento aerobio. Durante este último, unha fracción do dixestato é compostado con outra parte de FORU non sometida á dixestión anaerobia. Un segundo grupo de mostras (L1 a L4) procedeu dunha planta de tratamento na que a FORU era tratada mediante un proceso de compostaxe clásico. Finalmente, un terceiro grupo de mostras (C1 a C4) recolléronse das áreas de compostaxe da Universidade de A Coruña na que foron tratados residuos orgánicos de cafetería.

Procurouse a obtención de mostras con distinto grao de proceso e estabilidade, dende a materia prima ou FORU sen tratar ata o compost rematado, co fin de testar os resultados fronte a variados graos de madurez (Táboa 4.1).

Táboa 4.1. Contido de humidade, sólidos volátiles e orixe das mostras ensaiadas.

Mostra		Humidade (%)	Sólidos volátiles (%)	Orixe da mostra
Planta de tratamento anaerobio-aerobio de FORU (N)	N1	71,9	75.2	FORU antes da dixestión anaerobia
	N2	81.0	47.7	Dixestato (despois da dixestión anaerobia)
	N3	34.0	54.8	Final do proceso aerobio de compostaxe
Planta de tratamento aerobio de FORU (L)	L1	60,0	54,5	FORU antes da compostaxe
	L2	45,4	39,6	Final da primeira etapa en compotúneles
	L3	16,8	35,0	Final proceso compostaxe
	L4	32,0	41,0	Compost comercial
Composteiros de residuos de comedor do Campus universitario (C)	C1	67,2	77,6	Composteiros estáticos de 340 L, etapa final
	C2	65,5	70,1	Composteiros estáticos de 900 L, etapa final
	C3	71,2	80,7	Dixestor aerobio (1500 L) con mestura mecánica (zona de alimentación)
	C4	68,8	60,5	Dixestor aerobio (1500 L) con mestura mecánica (zona de saída)
Outros residuos orgánicos agroforestais (AG)	AG1-pur	97.2	60.7	Granxa de porcino intensiva
	AG2-mat	66.6	94.4	Matogueira
	AG3-cst	22.8	95.5	Plantación de castiñeiros
	AG4-lod	79.7	69.7	Fábrica de taboleiros de fibras de densidade media
	AG5-lod	80.7	89.5	

Na Planta de Tratamento anaerobio-aerobio de FORU (N) seleccionouse unha mostra inicial (N1) de residuo orgánico da que se desbotaron como impropios os voluminosos de maior tamaño, correspondentes á fracción inorgánica dos residuos urbanos (plásticos, cristal, metais, axentes estruturantes e outros de difícil clasificación). Esta fracción de impropios atinxía preto do 50% da mostra inicial. Unha segunda mostra (N2) tomouse á saída do dixestor anaerobio que operaba a unha temperatura de proceso aproximada de 35 ºC. Por último, obtívose outra mostra (N3) de compost peneirado, correspondente ao produto da compostaxe aerobia das fraccións de FORU e dixestato anteriores (a compostaxe en planta ten unha duración aproximada de 20-25 días). En tódolos casos o volume da mostra foi aproximadamente de 20 L.

Da planta de tratamento por compostaxe aerobia de FORU (L) obtivéronse mostras de material peneirado e correspondentes a diferentes graos de proceso (L1 a L4), segundo se indica na Táboa 4.1. Tratábanse de mostras integradas de 10 L que foron transportadas directamente ao laboratorio onde, logo dunha retirada manual das fraccións inorgánicas e non biodegradables, e da súa coidadosa mestura, almacenáronse a temperatura ambiente previo ao seu posterior procesado nos días seguintes.

As mostras recollidas nas áreas de compostaxe da UDC e en comparación coas obtidas nas plantas de tratamento N e L, especialmente na Planta de Tratamento (N), presentan un contido en impurezas moito menor, resultado dun maior control sobre a selección da materia prima a compostar. Neste sentido, poderían ser asimiladas a aquelas derivadas da compostaxe caseira.

Os outros materiais e residuos orgánicos están relacionados co sector agroforestal de Galicia. Unha mostra de xurro líquido de porcino (XLP) foi recollida dunha granxa intensiva. AG2-mat estivo composta das partes vivas non lignificadas das especies de mato máis representadas nos sistemas forestais de Galicia (toxos, fentos, silvas e xestas). A mostra AG3-cst, constituída por follas principalmente, foi recollido dunha plantación de castiñeiros sen moita demora logo da abscisión foliar. Ao tratarse de necromasa, o seu contido en auga é moito menor que a do AG2-mat (Táboa 4.1). Unha fábrica de taboleiros de fibras de media densidade proporcionou o lodo, residuo resultante logo do tratamento físico-químico das augas industrias procedentes do desfibrado de astillas de madeira, sometidas previamente a a un proceso de vaporización. Este lodo é transportado por tongadas de 2 m3 dende a instalación de tratamento de augas ata o parque de madeira, onde logo é retirado en camións de 20 t. AG4-lod e AG5-lod son mostras integradas do lodo recollido, respectivamente, no parque de madeira da fábrica e na instalación de tratamento das augas industriais.

O inóculo empregado para os ensaios de biodegradabilidade foi compost maduro recollido dende unidades de compostaxe da Universidade de A Coruña.

4.2.2. Métodos analíticos.

4.2.2.1. Medición da estabilidade.

Taxa de consumo específico de oxíxeno (VECO).

Como referencia, empregouse unha adaptación do método respirométrico de Lasaridi e Stentiford (1998) (Figura 4.1.A) para a avaliación da estabilidade dos residuos orgánicos dispersados en auga destilada tal e como se sinala na Sección 4.2.3.

Este método permitiu a obtención de valores de referencia para a demanda especifica de oxíxeno (VECO) e a demanda específica acumulada de oxíxeno ($DEAO_{20h}$) para as dispersións de residuos orgánicos de cada mostra estudada. Durante un mínimo de 20 horas as solucións foron axitadas, e aireadas durante 45 minutos ininterrompidos cada hora co auxilio dun temporizador e unha bomba de acuario TETRA APS50 que dispuña dunha válvula para a regulación do caudal de aire. Empregouse un difusor de pedra porosa para unha distribución homoxénea do aire, periodicamente axitado, ou reemplazado (no caso de AG4-lod, AG5-lodou AG1-pur) para evitar obstrucións.

Os primeiros ensaios foron realizados en matraces Erlenmeyer con dispersións de substratos en 500 mL tal e como indicaron Lasaridi and Stentiford (1998). Nestes matraces detectáronse dous problemas, non corrixidos con distintas velocidades de aireación e axitación: a formación de espuma así como a proxección de sólidos e posterior pegado sobre o vidro do matraz, quedando desa forma excluídos dos resultados do ensaio. Velocidades de axitación baixas non ocasionaban turbulencias pero os respirogramas resultantes eran borrosos e as pendentes provocadas polos descensos de consumo de O_2 non eran detectables. En canto á aireación, taxas demasiado elevadas e demasiado baixas, xeraban, respectivamente, salpicaduras (e/ou espuma) e unha insuficiente recuperación de O_2, especialmente naquelas mostras cunha alta actividade biolóxica nas que as taxas de consumo de O_2 eran moito máis elevadas que o oxíxeno externo subministrado. O emprego de vasos de precipitado e dispersións de 1 L evitaron estes inconvenientes. Os mellores resultados conseguíronse con velocidades de axitación de 250-350 r.p.m. e un caudal medio de aire (metade do percorrido total da válvula de regulación).Todas estas circunstancias son expositivas da complexidade e dificultade para a operación do método VECO seguindo os procedementos de Lasaridi e Stentiford (1998).

Un exemplo do respirograma obtido para compost inestable, e das típicas curvas VECO no tempo son amosadas, tanto para compost estable como inestable, na Figura 4.2A e Figura 4.2B. Tomáronse medidas do oxíxeno disolto cada dous minutos dende a posta en marcha da proba, usando o YSI Pro ODO Optical Dissolved Oxygen Instrument (sonda portátil de oxíxeno disolto). A análise do respirograma realizouse cunha folla de cálculo e consistiu na obtención das pendentes do respirograma (a taxa da concentración de oxíxeno) durante os períodos de non aireación. A curva VECO obtívose dividindo a pendente pola concentración de sólidos volátiles (SV) e representándoa graficamente no tempo. Segundo isto, obtivéronse dous parámetros:

$\underline{VECO_m}$: A máxima demanda específica de oxíxeno (en mg O_2 g $SV^{-1} \cdot h^{-1}$).

$\underline{DEAO_{20h}}$: A demanda específica de oxíxeno (en mg O_2 g SV^{-1}) acumulada ao longo de 20 horas, que representa a área baixo a curva VECO entre o período de tempo comprendido entre t=0 e t=20 h.

Test de autoquecemento (Dewar test).

O test de autoquecemento é empregado habitualmente coa fracción orgánica do residuo municipal e mostras de compost. Establece cinco escalas de estabilidade, dende I (material fresco) ata V (compost maduro ou finalizado). Os ensaios foron realizados en duplicado con vasos Dewar isotérmicos de 1.5 L. (Figura 4.1C), tal e como se indicou por Brinton *et al.* (1995) a unha temperatura de 25 ± 2 ºC. A humidade das diferentes mostras orgánicas foi regulada a un valor de entre o 60% e o 70%. A temperatura foi rexistrada mediante termómetros de agulla inoxidable ata que o seu equilibrio co ambiente foi inequivocamente confirmado.

Con respecto ao residuo municipal, a fracción orgánica foi picada manualmente con tesoiras de poda ata un tamaño inferior aos 15 mm mentres que para as mostras de compost, os inertes e os materiais de baixa biodegradabilidade foron previamente eliminados nos casos necesarios.

Os materiais foron convintemente mesturados e cuarteados antes de introducilos nos vasos Dewar. Non se engadiu estruturante adicional en ningún dos ensaios coas mostras N3, L1 a L4 e C1 a C4.

No caso de AG4-lod, AG5-lod e N2, o procedemento foi adaptado pola posible conveniencia de material estruturante. Os ensaios de biodegradabilidade deste material na bibliografía son escasos mais a previa caracterización química suxeriu o potencial autoquecemento por si mesmo debido a aparentemente axeitados ratios de C/N (28 en Arias *et al.* (2017) e 34 en Arias *et al.* (2019)). Para a confirmación, realizáronse ensaios con (AG4-lod) e sen (AG5-lod) estruturante. O dixestato, como se exporá máis adiante, presentaba un alto contido en humidade. En ambos casos, utilizouse como estruturante astillas de madeira peneiradas a un tamaño menor dos 2 mm, nas seguintes proporcións volumétricas de axente estruturante:substrato: 1:0.67 (AG4-lod) e 1:3.15 (dixestato).

Para outros substratos, os intentos de aplicar o método de autoquecemento non acadou resultados satisfactorios. AG3-cst presentou unha proporción C/N demasiado baixa (Arias *et al.*, 2017). O tamaño de partícula acadado para a mostra AG2-mat non foi o suficientemente baixo para inducir o autoquecemento debido a un exceso de aireación entre as súas partículas. No caso da mostra AG1-pur, as astillas de madeira dispoñibles non resultaron útiles xa que flotaban pola súa menor densidade. Por este motivo, nestes casos só se pudo tomar como referencia o test VECO, xa que mediante esta técnica o proceso ten lugar en fase líquida.

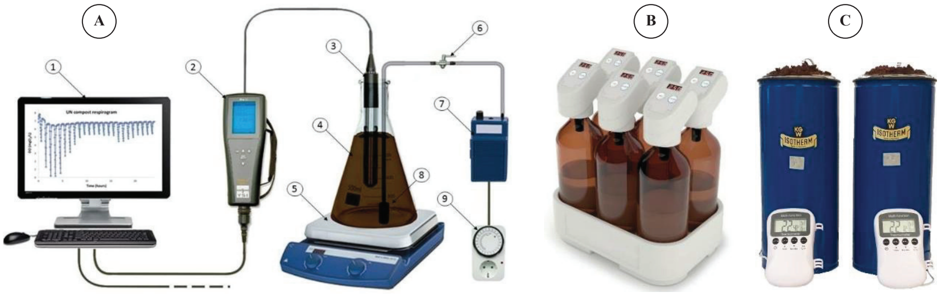

Figura 4.1. A: Esquema do ensaio da respirometría mediante a sonda de osíxeno disolto (VECO test), na que: 1) Ordenador, 2) Rexistro do osíxeno disolto, 3) Sonda do osíxeno disolto, 4) Suspensión de compost, 5) Axitador magnético, 6) Válvula, 7) Bomba de aire, 8) Difusor, 9) Programador. B: Sistema de monitorización DBO (VELP Scientifica). Nótese que o sistema A só permite a determinación dunha mostra cada vez (debe haber varias réplicas), namentres o compacto sistema B permite ata a análise de 6 mostras dunha vez simultaneamente. C: Vasos Dewar para o test de autoquecemento. Fonte: Adaptado de Vázquez (2015).

Demanda biolóxica de oxíxeno (DBO).

Para a determinación deste parámetro, a mostra de compost foi previamente dispersada en auga. As medidas foron realizadas baixo condicións definidas de dispoñibilidade de nutrientes e inhibición da nitrificación.

Os ensaios foron realizados por duplicado en laboratorio nunha habitación a 20ºC±2ºC e consistiron na medición da baixada de presión no espazo libre superior sobre a botella pechada. Empregouse o equipo "BOD Sensor VELP Scientifica" (Figura 4.1B), consistente en botellas DBO de 525 mL de volume total, lentellas de hidróxido de sodio (NaOH) para a absorción do CO_2 producido e un transdutor da redución de presión para a medición do oxíxeno consumido. O sistema rexistrou o valor da DBO cada 24 horas durante 5 días consecutivos. Nesta investigación usáronse dúas escalas simultaneamente para previr que os valores rexistrados sobrepasasen o rango da escala e daquela asegurar ao menos unha serie de valores válida. Na comparación dos resultados fíxose uso unicamente dos datos dunha das escalas.

Obtívose unha alícuota, de volume variable entre 100 mL e 400 mL, representativa da dispersión de compost preparada e suplementada como se indica na Sección 4.2.3Preparación de mostras.. Sobre esta alícuota realizáronse as medicións da DBO seguindo as instrucións dos fabricantes do equipo da DBO. O ensaio proporciona a curva DBO (mg O_2 L^{-1}) representada graficamente en días (Figura 4.2C e Figura 4.2D). Esta curva asumirase como a taxa específica de consumo biolóxico de oxíxeno (DBO_r) en cada momento t, mediante a seguinte ecuación (para cada medida t de tempo):

$$DBO_r\ (\text{mg } O_2 \text{ g } SV^{-1} \cdot d^{-1}) = DBO / (t * SV)$$

onde t é o tempo de medida (d) e SV a concentración de sólidos volátiles na mostra (mg SV L^{-1}).

Adicionalmente, apréciase que a demanda específica acumulada de oxíxeno despois dos 5 días do ensaio é igual que o valor da DBO_{5d} da proba estándar da DBO. A DBO_{5d} (mg O_2 g SV^{-1}) obtívose dividindo a lectura de 5 días (mg O_2 L^{-1}) pola concentración de compost (g SV L^{-1}).

Como o equipo da DBO só rexistrou o consumo acumulado de oxíxeno ao final de cada día, parece claro que a máxima $LDBO_r$ (Figura 4.2D) non pode ter valores equivalentes nin o mesmo significado que o valor da $VECO_m$ obtida polo método da proba do oxíxeno disolto (Figura 4.2B). Por outro lado, a Figura 4.2D indica que, cando as condicións do ensaio son variables (por exemplo, concentracións de SV, volume de mostra ou escala escollida para o método da DBO), valores comparables da taxa de consumo específico de oxíxeno foron obtidos só despois de 4 a 5 días de experimento. Tendo en conta este comportamento, só os valores da DBO ou da DBO_r aos 5 días poden ser usados como índices respirométricos (Vázquez, 2015). De feito, estes dous índices teñen o mesmo significado, xa que $DBO_{r5d} = DBO_{5d}/5$. Sen embargo, e de igual xeito que nos ensaios con augas residuais, a observación da evolución da curva DBO ofrece valiosa información ao operador especializado para interpretar a calidade da proba. O criterio útil é que a curva DBO ao final de 4-5 días debe aproximarse á asíntota.

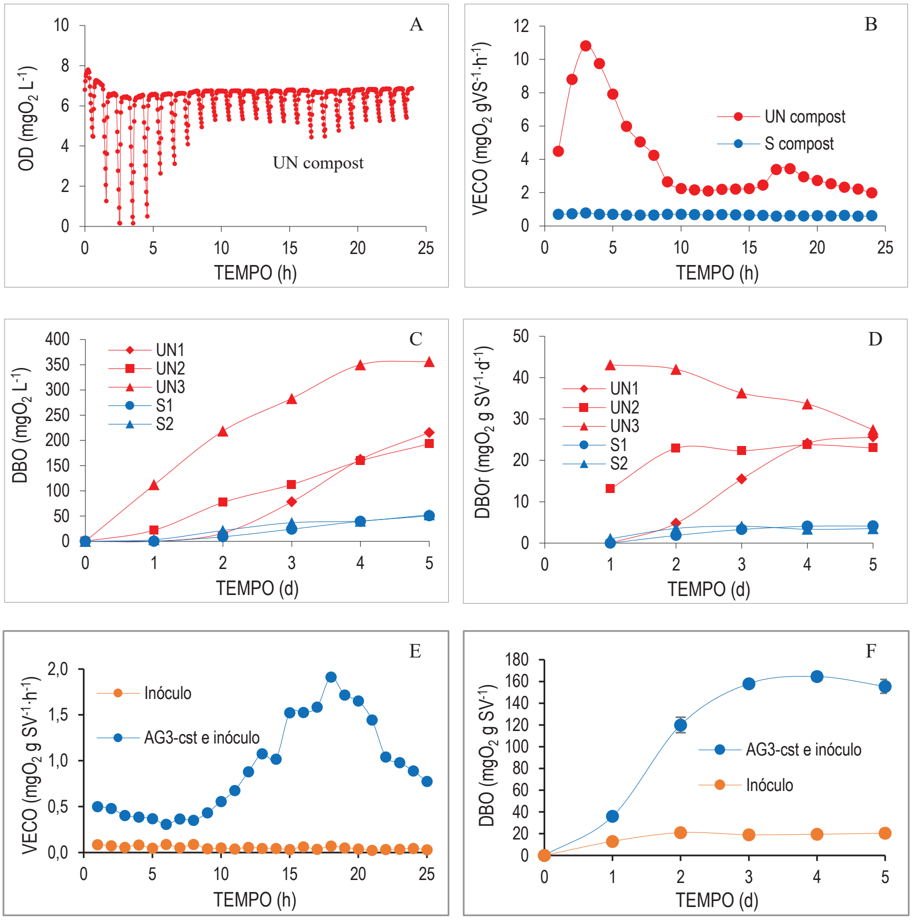

Figura 4.2. A) Respirogramas obtidos para compost inestable (UN) (VECO test). B) Típica curva VECO para compost estable (S) e inestable (UN). C), D) Evolución das curvas DBO (c) e curvas DBOr (d) para dous tipos de compost (UN: inestable, S: estable). E), F) Exemplos de respirometría (E) e BDO5 (F) para materiais sen actividade utilizando inóculo.

4.2.3. Preparación de mostras.

Na determinación da VECO e do método da DBO en fase líquida, unha mesma mostra de compost ou residuo orgánico foi dispersada en 800 mL de auga destilada mediante unha batidora de cociña, e logo filtrada por unha malla de 3 mm de luz para eliminar as partículas grosas que non lograron ser trituradas. Isto significa que case todas as partículas de materia orgánica foron trituradas a un tamaño inferior aos 3 mm e todo o substrato biodegradable foi transferido á suspensión líquida. O volume total foi completado con auga destilada ata os 4.000 mL.

O tamaño da mostra a dispersar variou entre 2 g e 5 g de materia fresca para composts e a fracción orgánica do residuo sólido municipal, dependendo na actividade agardada. No caso de materiais de baixa biodegradabilidade, AG4-lod, AG5-lod , AG3-cst e AG2-mat aproximáronse respectivamente aos 3, 9 e 18 g SV L^{-1}. O AG1-pur foi dispersado a unha concentración do 2.5%. En tódolos casos, a humidade e os SV determináronse de acordo con Standard Methods (APHA, 2005).

Para previr as limitacións causadas polas flutuacións de pH ou dispoñibilidade de nutrientes, 30 mL de tampón fosfato, 10 mL de cada unha das solucións de nutrientes de $CaCl_2$ (27.5 g L^{-1}), $FeCl_3$*$6H_2O$ (0.25 g L^{-1}) e $MgSO_4$*$7H_2O$ (22.5 g L-1) foron engadidas a esta dispersión. Esas solucións foron preparadas segundo os métodos estandarizados para a determinación da DBO (APHA, 2005). Ademais, 2 mL da solución de atiltiourea (ATU, 1 g L^{-1}) foron tamén engadidos como inhibidores da nitrificación de nitróxeno. O pH foi regulado a 7.0-7.1 mediante solucións diluídas de NaOH ou HCl.

O inóculo non foi engadido no caso de FORU, AG1-pur e mostras de compost xa que considerouse que esas mostras contiñan en si mesmas unha carga suficientemente alta de microorganismos activos. Naquelas mostras ensaiadas que a priori non contarían con suficiente flora microbiana (AG3-cst, AG2-mat, AG4-lod e AG5-lod), empregouse compost maduro como inóculo. En canto á concentración de inóculo, estimouse como suficiente 3-4 g SV L^{-1}. Neste caso, os ensaios de VECO e DBO realizáronse en paralelo para a mestura de substrato e inóculo, e para a dispersión con só inoculo a modo de branco (Figura 2E, 2F). Como criterio debe observarse que o consumo de oxíxeno do ensaio branco (só con inóculo) sexa moi baixo. No caso de emprego de inóculo, os valores para cada substrato correspondéronse coa diferenza entre ambos:

$$VECO_{susbtrato} = VECO_{(susbtrato+inóculo)} - VECO_{inóculo}$$

$$DBO_{susbtrato} = DBO_{(susbtrato+inóculo)} - DBO_{inóculo}$$

4.2.4. Análises numéricas.

Os cálculos dos valores das medias e desviacións típicas, análises de regresión e integración numérica foron realizadas mediante Microsoft Excel, así como a análise de varianza para comparar os conxuntos de datos mediante o valor da probabilidade (p).

4.3. RESULTADOS E DISCUSIÓN.

4.3.1. Mostras de plantas de compostaxe de fracción orgánica de residuos urbanos.

Na Figura 4.3 amósanse de forma comparativa os resultados dos ensaios cos tres métodos (respirometría, DBO_5 e auto-quecemento) aplicados ás mostras procedentes da planta de tratamento de FORU por dixestión anaerobia e compostaxe aerobio (mostras N1, N2 e N3). A reproducibilidade dos ensaios resultou moi aceptable, como reflicten5 as curvas duplicadas de respirometría, ou as barras de desviación estándar nos ensaios de DBO e auto-quecemento.

A mostra N1 (FORU sen tratar) acadou os valores máis altos de biodegradabilidade cunha VECO máxima de aproximadamente 13 mg O_2 g SV^{-1} h^{-1} ás 13 horas de ensaio (Figura 4.3a). En consonancia, a $DEAO_{20h}$ acadou os 121 mg O_2 g SV-1 e a DBO_5 superou os 300 mg O_2 g SV^{-1} (Figura 4.3b). O test de autoquecemento revelou unha Clase I, correspondente a material fresco, cun gradiente de temperatura sobre o ambiente maior de 40ºC durante 13 días (Figura 4.3c).

En canto ao dixestato (N2), a respirometría amosou de novo un pico máximo de consumo ás 13 horas, mais neste caso o valor máximo da VECO acadou só os 3 mg O_2 g SV^{-1} h^{-1}, un 70% inferior ao da mostra N1, pero claramente indicativo dun material non estabilizado. A súa vez a DBO_5 superou os 140 mg O_2 g SV^{-1} e o valor máximo do gradiente no test de autoquecemento acadou os 20 ºC (Figura 4.3e e Figura 4.3f), polo que estaríamos fronte a un material, compost de ser o caso, moderadamente estable (Clase IV). Estes resultados indican que a dixestión anaerobia produciu unha redución importante da materia orgánica facilmente biodegradable. De todas formas, e como se verá máis adiante, a necesidade de utilizar estruturante no ensaio de auto-quecemento do dixestato podería condicionar a validez deste índice á hora de comparalo cos respirométricos.

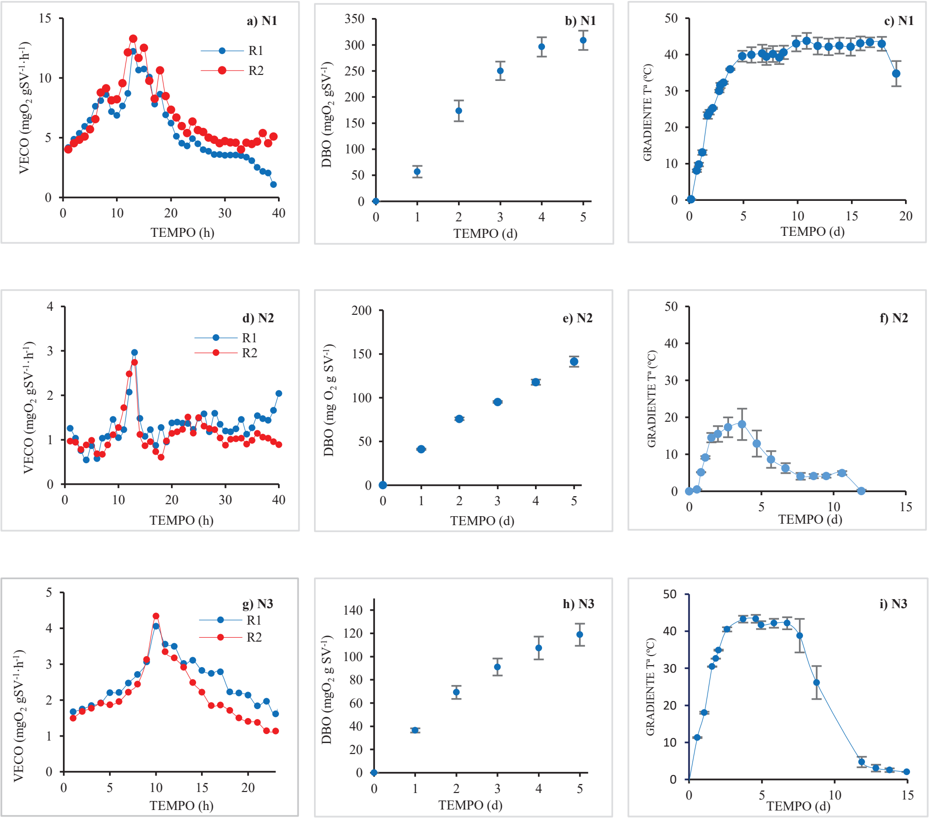

Figura 4.3. Curvas VECO, DBO e gradientes do test de autoquecemento das mostras N1, N2 e N3 da Planta de Tratamento FORU (N)e FORU en diferentes estados de transformación(inicial-fresco, intermedio-dixestato e final-compost).

Finalmente, o compost rematado (N3), amosa variacións dos valores de VECO e $DEAO_{20h}$ intermedios entre o dixestato (N2) e a FORU (N1). O test de autoquecemento volve dar como resultado unha clasificación do material compostado como Clase I, material fresco ou inestable, pero mantendo un gradiente de temperatura > 40ºC durante un período moito menor (4 días) que a FORU. Isto explícase polo feito de que no proceso de compostaxe na Planta de Tratamento (N) engádese o dixestato sobre unha fracción de FORU non sometida a dixestión, xunto cun proceso de estabilización aerobia claramente insuficiente.

De forma similar realizáronse ensaios cos tres métodos aplicados ás mostras procedentes dunha segunda planta de tratamento de FORU (mostras L1 a L4) e de compostaxe de residuos de comedor no campus da Universidade de A Coruña (mostras C1 a C4). Os valores para os indicadores $VECO_m$, $DEAO_{20h}$, DBO e incremento de temperatura (test de autoquecemento) mostraron pouca variación entre réplicas, reflectindo a homoxeneidade da mostra e a reproducibilidade do ensaio (Figura 4.2).

Táboa 4.2. Resultados de estabilidade, madurez e DBO_5 das mostras estudadas.

ORIXE	MOSTRA	$VECO_m$ (mg O_2 g SV^{-1} h^{-1})	$DEAO_{20h}$ (mg O_2 gSV^{-1})	Media DBO (mg O_2 gSV^{-1})	Estabilidade		Ratio DBO/DEAO
					Dewar[a] (ºC)	Clase[b]	
Unidade tratamento 2 de FORU	N1	12,7 ± 0.7	124,6 ± 15.5	308,8 ± 18.5	43,9 ± 2.1	I	2,48
	N2	2,9 ± 0.2	21,5 ± 0.9	141,2 ± 5.9	18,3 ± 4.0	IV	6,57
	N3	4,2 ± 0.2	46,5 ± 4.2	118,8 ± 9.5	43,3 ± 0.9	I	2,55
Unidade tratamento 1 de FORU	L1	16,08 ± 5.3	64,0 ± 2.4	141,6 ± 8.1	54,55 ± 0.85	I	2,21
	L2	13,38	108	225,4 ± 5.4	46,60	I	2,07
	L3	0,66	7,115 ±	15,1 ±	4,70	V	2,12
	L4	1,29	14,155 ±	36,0 ±	15,40	IV	2,54
Campus universitario	C1	0,35 ± 0.01	4,7 ± 0.7	18,3 ± 2.0	3,13	V	3,89
	C2	0,65 ± 0.11	9.0 ± 1.3	19,8 ± 1.7	14,50	IV	2,21
	C3	4,15 ± 0.05	54,7 ± 5.2	130,1 ± 23.7	41,20	I	2,38
	C4	4,15	50,1*	109,3 ± 1.7	46,15.	I	2,18

[a] Gradiente de temperatura sobre o ambiente (20 ºC ± 2). [b] Grao de madurez segundo a escala de Brinton *et al.* (1995).

Os compost máis evolucionados presentaron as menores taxas de consumo de oxíxeno ao quedaren esgotada a súa fracción facilmente biodegradable (C1, L3) e obteron unha Clase V de madurez (Brinton *et al.*, 1995), ou parcialmente esgotada (C2, L4), con Clase IV. Outras 6 mostras corresponderon a material non estabilizado (C3, C4, L1, L2, N1, N3) e Clase I, mentres a mostra N2 situouse entre clase III e IV.

4.3.2. Correlación entre os diferentes índices de estabilidade para mostras e compost de fracción orgánica de residuos urbanos.

Os resultados dos indicadores de estabilidade das diferentes mostras empregáronse para estudar a correlación entre os diferentes índices (Táboa 4.3). Estes axustes requiriron excluír da análise ben a mostra do dixestato (N2) ou a mostra de compost de FORU L1 (Táboa 4.3) ao presentaren diferentes particularidades. A mostra N2 ofreceu valores comparativamente elevados de DBO, fóra da correlación cos outros indicadores, que correlacionaron entre si. No caso de L1 foi a $VECO_m$ o indicador que presentou valores relativamente máis elevados que non correlacionaron coa DEAO nin coa DBO.

O dixestato é o residuo resultante da dixestión anaerobia do FORU polo que non pode entenderse como unha mostra de compost ao estaren composto nun 81% por auga (Táboa 4.1). Este feito pode ter influído na distinta composición das poboacións microbianas con respecto ás restantes mostras sólidas. O ensaio de DBO amosou valores elevados, propios de compost fresco, pero esta correspondencia non se viu reflectida na $DEAO_{20h}$, onde o consumo acumulado de O_2 estivo máis próximo aos valores dos composts maduros (Táboa 4.2). A explicación podería vir dada polo feito de que o ensaio de DBO, con 5 días de duración, permitiría o desenvolvemento de microorganismos aerobios suficientes, o que non tería ocorrido no caso do ensaio de VECO, con só 20 h de duración. No caso de tratarse dun problema de aclimatación e crecemento de microorganismos aerobios, este podería ser resolto cunha segunda alimentación de substrato sobre o medio da primeira alimentación. Por outro lado, o test de autoquecemento foi inicialmente concibido para mostras sólidas de compost, polo que a necesaria adición de estruturante en altas proporcións (3,15 veces máis en volume de estruturante que de dixestato) cuestiona en certo modo a validez da análise comparativa da correlación.

A mostra L1 presentou un período de latencia que retrasou os consumos de O_2 tanto nas probas de estabilidade (10 horas nos test VECO e Rottegrade, e 24 horas na DBO) podendo ser debido a unha poboación inicial de microorganismos moi baixa ou a un período de adaptación ás novas condicións do medio máis longo con respecto a outras mostras estables. O test VECO para L1 amosou a $VECO_m$ máis alta para o conxunto das mostras de compost (16,08 mg O_2 g SV^{-1} h^{-1}) mais este consumo estivo inhibido nas primeiras horas do ensaio. Os baixos valores de DEAO e DBO poderían corrixirse, posiblemente, realizando unha segunda alimentación na que o contido da primeira actuaría como inóculo. A observación das curvas de respirometría no tempo permite detectar a posible fase de latencia, e no seu caso corrixila mediante unha segunda alimentación. Porén, esta proposta non foi comprobada no presente estudo.

Táboa 4.3. Correlacións entre os distintos indicadores considerados. DEAO: Demanda específica de oxíxeno acumulada; VECO: A demanda específica de oxíxeno; IncT: Gradiente máximo de temperatura.

Correlacións entre parámetros	Ecuación	R²	N	Excluído
DBO vs DEAO	$y = 2,2847x + 1,8256$	0,984	10	N2
DEAO vs $VECO_m$	$y = 8,7411x + 5,2611$	0,961	10	L1
DBO vs $VECO_m$	$y = 19,063x + 27,553$	0,878	10	L1
IncT vs DEAO	$y = -0,0076x^2 + 1,2949x - 1,8912$	0,967	11	
IncT vs DBO	$y = -0,0013x^2 + 0,5258x - 1,1012$	0,941	10	N2
IncT vs $VECO_m$	$y = -0,4351x^2 + 9,5063x + 4,0429$	0,832	11	

Todas as correlacións corresponden a un nivel de probabilidade $p<0,001$.

Os resultados de correlación amosados na Táboa 4.3 indican que, con independencia do seu contido en materia orgánica e grao de humidade, as mostras de FORU e compost procedentes de FORU presentaron unha forte correlación entre o consumo de oxíxeno determinado pola DBO e a DEAO ($R^2=0.984$, n=10, $p<0.001$). Para a correlación entre outros pares de indicadores, o valor de R^2 variou entre 0,83 e 0,96, sempre cun nivel de probabilidade estatística $p<0,01$ (Táboa 4.3). A mellor correlación entre DBO_5 e $DEAO_{20h}$, como índices integrados no tempo, fronte ás correlacións que inclúen o índice puntual $VECO_m$, suxiren que os indicadores integrados poden caracterizar mellor os substratos estudados. Isto está de acordo con resultados previos publicados para métodos respirométricos (Scaglia *et al.*, 2007; Wagland *et al.*, 2009).

4.3.3. Valores límites indicadores de estabilidade para mostras de compost de fracción orgánica de residuos urbanos.

A $VECO_m$ constitúe o índice máis empregado como indicador de estabilidade nos ensaios con respirometría en fase líquida (EC, 2014). Por isto, será empregado como referencia para a obtención dos valores límites dos outros índices para compost estable. O valor de referencia para compost estable tense situado nunha $VECO_m$ de 1 mg O_2 g $SV^{-1}\cdot h^{-1}$, ou incluso no rango de 0,4-1,0 mg O_2 g SV^{-1} h^{-1} (Lasaridi and Stentiford, 1998; EC, 2014). A partir dos datos obtidos para as mostras estudadas (Táboa 4.2) podemos obter os valores de DBO_5 e $DEAO_{20h}$ que se corresponden cunha $VECO_m$ de 1 mg O_2 g SV^{-1} h^{-1}, que consideraremos indicadores do limiar de estabilidade. Para isto, analizaremos primeiro a variación dos cocientes DBO_5 / $VECO_m$ e $DEAO_{20h}$ / $VECO_m$ fronte á $VECO_m$ (Figura 4.4).

Como xa vimos, as mostras analizadas ofreceron resultados moi parellos e correlacionados entre todos os índices (Táboa 4.3). A Figura 4.4 amosa que os valores dos cocientes $DEAO_{20h}$ / $VECO_m$ e DBO / $VECO_m$ vense reducidos para residuos moi biodegradables ou compost moi pouco estables, pero mantense en valores moi similares a valores de $VECO_m$ inferiores a 5 mg O_2 g SV^{-1} h^{-1}. Son excepción a isto o cociente DBO_5 / $VECO_m$ para C1 e N2, e o cociente DEAO / $VECO_m$ para N2. O comportamento dispar de N2 en relación aos diversos índices xa se analizou na Sección 4.3.2. En canto a C1, a desviación do cociente DBO_5 / VECOm pode ser debida á moi baixa biodegradabilidade desta mostra, que presenta unha $VECO_m$ de tan só 0,36 mg O_2 g SV^{-1} h^{-1} (Táboa 4.2), o que pode causar un agrandamento dos erros relativos.

Na Figura 4.4B tamén se amosa a variación da relación $DBO_5/DEAO_{20h}$, que é moito menos acusada que a dos outros cocientes que implican o parámetro $VECO_m$. Isto pode considerarse relacionado co feito de que ambos parámetros DBO_5 e $DEAO_{20h}$ son parámetros integrados no tempo, abarcando por iso un abano máis amplos de propiedades do substrato que o parámetro VECOm. Este aspecto, xunto coa mellor correlación obtida para DBO fronte a DEAO (Táboa 4.3) suxiren a maior idoneidade destes parámetros para o estudo da estabilidade de mostras de compost e de residuos orgánicos, e particularmente do ensaio DBO_5 pola amplitude do tempo considerado.

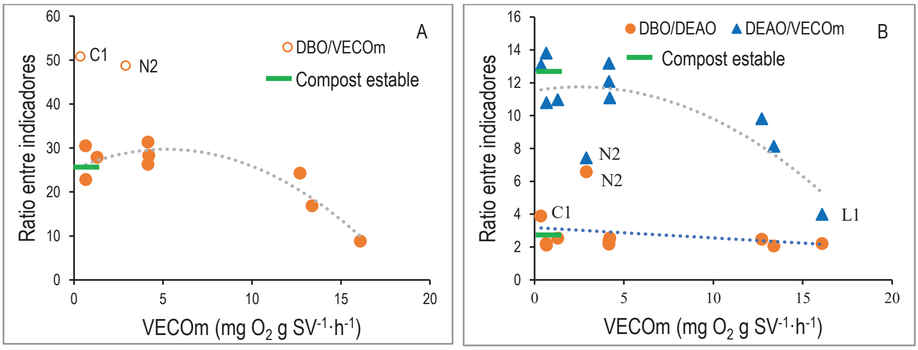

Figura 4.4. Correlación entre os cocientes de diversos índices e o índice de referencia VECOm e valores de referencia propostos para compost estable.

Excluídos estes puntos (C1 e N2 para DBO$_5$ e N2 para DEAO$_{20h}$), e en consideración do valor constante destes cocientes no rango de VECO$_m$ de 0 a 5 mg O$_2$ g SV^{-1} h^{-1}, procedemos a obter os valores dos respectivos cocientes DBO$_5$/ VECO$_m$, DEAO$_{20h}$ / VECO$_m$ e DBO$_5$ / DEAO$_{20h}$ para VECO$_m$ < 5 mg O$_2$ g SV^{-1} h^{-1}. Os valores que se obtiveron son os seguintes:

DBO / VECO$_m$ = 27,9 ± 3,1 (n=6)

DEAO$_{20h}$ / VECO$_m$ =12,1 ± 1,2 (n=7)

DBO / DEAO = 2.3 ± 0.2 (n=6)

Así, os limiares para compost estable equivalentes a VECO$_m$ de 1 mg O$_2$ g SV^{-1} h^{-1} veñen dados por valores de DBO$_5$ de 27,9 mg O$_2$ g SV^{-1} ou de DEAO$_{20h}$ de 12,1 mg O$_2$ g SV^{-1}. Por aproximación, propomos adoptar como limiares os valores de 25 mg DBO$_5$ g SV^{-1} e de 12 mg DEAO$_{20h}$ g SV^{-1}. Con todo, a Figura 4.4 suxire que estes limiares poderían situarse no rango de 20 a 30 mg DBO$_5$ g SV^{-1} e 10 a 15 mg DEAO$_{20h}$ g SV^{-1}. Isto é razoable considerando a variabilidade innata dos ensaios biolóxicos.

4.3.4. Aplicación a residuos agroforestais.

4.3.4.1. Efecto do inóculo nas respirometrías con lodo da industria forestal.

Os ensaios de biodegradabilidade estendéronse a outro tipo de residuos que previamente foron obxecto de estudo en procesos de compostaxe (Arias *et al.*, 2019, 2017). No caso das mostras de biomasa de orixe forestal (AG4-lod, AG5-lod, AG3-cst e AG2-mat) pensouse que podían carecer dunha poboación de flora microbiana suficiente para un correcto desenvolvemento do proceso de degradación. Por este motivo, decidiuse comprobar o efecto do emprego de compost maduro de FORU como inóculo para a degradación de AG4-lod e AG5-lod, co obxectivo de achegar aqueles microorganismos que posteriormente producirían a degradación dos distintos substratos a estudar e a menor cantidade de substrato biodegradable. Como xa se indicou na Sección 4.2.3, o consumo de oxíxeno medido no ensaio con inóculo foi descontado do ensaio con substrato.

A Figura 4.5 reflicte a evolución das curvas de consumo de oxíxeno nos ensaios de VECO e de DBO_5 para as mostras AG4-lod e AG5-lod. A ausencia de inóculo condiciona os ensaios de biodegradabilidade e determina patróns de consumo de O_2 diferentes, e polo tanto diferentes valores dos respectivos índices obxecto de estudo. No ensaio sen inóculo, as velocidades de consumo de O_2 son menores ao inicio en relación ao ensaio con inóculo. No caso da mostra sen inóculo do test VECO (Figura 4.5C), o consumo foi lento ao principio e avanzou gradualmente ata acadar un valor máximo ás 20 horas, momento no que se avalía o valor da $DEAO_{20h}$. No ensaio para o mesmo substrato con inóculo (Figura 4.5A), o crecemento da velocidade de consumo de oxíxeno foi moito máis rápido e o máximo acadouse xa ás 6 h. Desta forma, aínda que os valores de $VECO_m$ resultaron similares, os valores de $DEAO_{20h}$ foi menor no ensaio sen inóculo pola limitación deste. A falta de suficiente inóculo pode verse igualmente ao comparar as curvas de DBO_5 dos ensaios con e sen inóculo (Figura 4.5B e Figura 4.5C).

Desta maneira, consideramos probada a nosa hipótese e concluímos que nos ensaios de respirometría con materiais non activados bioloxicamente ou cunha carga inherente de microorganismos moi inferior á que presenta outros materiais como é o compost (ou no seu caso os lodos de depuración ou os xurros) é necesaria a adición dun inóculo que active os consumos de O_2 dende o inicio do test. Cabe considerar incluso máis necesario o uso de inóculo no caso dos materiais AG3-cst e AG2-mat, xa que as mostras AG4-lod, AG5-lod contiñan unha pequena proporción de lodo biolóxico procedente do tratamento aerobio dos efluentes da industria de taboleiros de fibra de media densidade. Posiblemente a alta temperatura ou o baixo pH das mostras de AG4-lod, AG5-lod provocaran a inactivación dese lodo biolóxico e a clara necesidade de inóculo. Pola contra, o inóculo non se engadiu no caso da mostra de xurro e os perfís das respirometrías realizadas (datos non amosados) confirmaron que non era necesario.

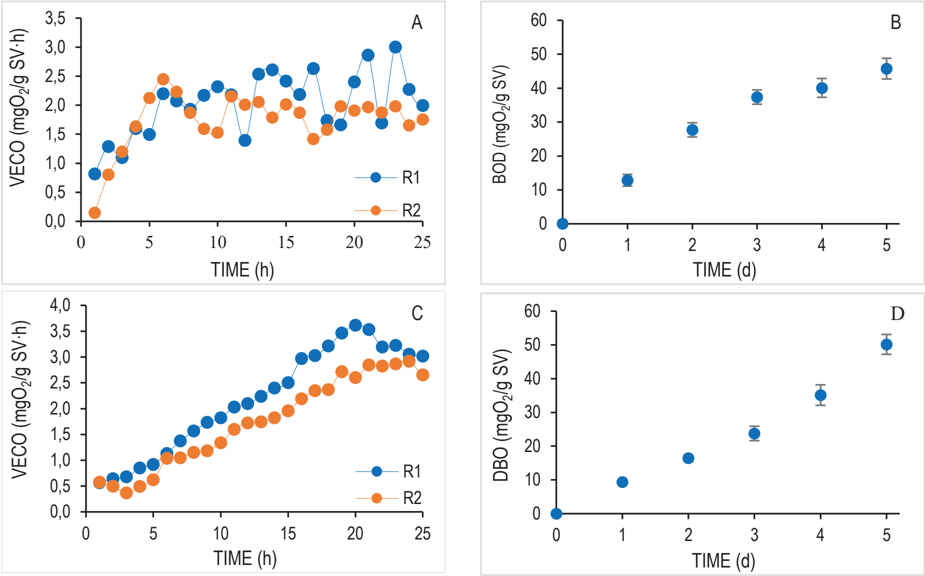

Figura 4.5. Efecto do inóculo nas probas respirométricas efectuadas con AG4-lod (A e B, con inóculo) e AG5-lod (C e D, sen inóculo). As barras de erro representan o valor da desviación estándar nas DBO.

4.3.4.2. Índices de biodegradabilidade para AG3-cst, AG2-mat, AG4-lod, AG5-lod e AG1-pur.

Os resultados obtidos dos diversos índices para estes residuos e materiais son recollidos na Táboa 4. Atendendo aos valores da VECO$_m$ e a categorización proposta por Barrena *et al.* (2011), AG3-cst e AG2-mat serían substratos de baixa degradabilidade con índices respirométricos propios de axentes estruturantes, AG4-lod E AG5-lod poderían considerarse como de moderada biodegradabilidade (VECO$_m$ de 2-5 mg O_2 g SV^{-1} h^{-1}) e o AG1-pur como material altamente biodegradable, obtendo nos nosos ensaios valores moi superiores aos destes autores.

Por un lado, o AG1-pur rexistrou os maiores valores de biodegradabilidade e é un material amplamente tratado en procesos de transformación biolóxica. Baixo as condicións nas que se realizaron os ensaios, non son recomendables concentracións con AG1-pur superiores ao 2.5% dada a súa elevada biodegradabilidade. Nun extremo oposto, os residuos lignocelulósicos forestais obtiveron as menores taxas de biodegradación, con valores próximos aos 1.5 mg O_2 g SV^{-1} h^{-1}, superiores en calquera caso ao limiar de estabilidade comunmente aceptado de 1 mg O_2 g SV^{-1} h^{-1}. No caso do AG3-cst, porén, esta relación non se reflectiu no ensaio da DBO, sendo o consumo tres veces inferior ao rexistrado polo AG2-mat (7.3 fronte a 21.8 mg O_2 g SV^{-1}). En ambos casos, a pesares do elevado contido en materia orgánica de AG3-cst e AG2-mat (aproximadamente 95%), esta é maiormente de carácter recalcitrante e dificilmente biodegradable polos microorganismos.

Táboa 4.4. Indicadores de biodegradabilidade para residuos agroforestais amplamente representados en Galicia.

	VECO$_m$ (mg O_2 $SV^{1}\cdot h^{-1}$)	**DEAO$_{20h}$** (mg O_2 g SV^{1})	**Media DBO** (mg O_2 g SV^{1})	**Inc. T ºC***	**ratio DBO/DEAO**
AG2-mat	1,6	17,1	21,8	nd	1,27
AG4-lod 1	2,5 ± 0.1	34,4 ± 2.6	48,6 ± 4.0	36.1^{a} ± 0.3	1,41
AG5-lod	3,2 ± 0.6	31,3 ± 6.1	50,2 ± 2.9	27.5^{b} ± 1.3	1,60
AG3-cst	1,5 ± 1.0	12,9 ± 8.2	7,3 ± 0.3	nd	0,57
AG1-pur	38,3 ± 14.3	346,8 ± 56.2	1327.0 ± 7.5	nd	3,83

a: con estruturante. b: sen estruturante. nd: Non dispoñible.

Do mesmo xeito, no caso de AG4-lod e AG5-lod, a pesares do seu elevado contido en materia orgánica (cerca do 90%) os ensaios respirométricos amosan unha baixa taxa de degradabilidade (VECO$_m$ aproximada de 3 mg O_2 g SV^{-1}). O alto contido en lignina (48%, datos non amosados), celulosa e hemicelulosa de AG4-lod e AG5-lod poderían explicar este resultado. Porén, no test Dewar este material acada unha clasificación de inestabilidade (36.1 ºC, Clase II, empregando estruturante) ou moderadamente inestable (27.5 ºC, clase III, sen o emprego de estruturante). No primeiro caso, a función da evolución do gradiente de temperatura contra o tempo adopta a clásica forma cóncava cun único e máximo punto de inflexión que acada o valor de 36ºC aos 6 días. En ausencia de estruturante a forma da función é oscilante, acadando un primeiro máximo de 23ºC aos 3 días, e un segundo máximo de 27.2 ºC aos 15 días. Esta variabilidade de resultados en materiais diferentes ao compost, material para o que foi inicialmente testado o método de Brinton *et al.* (1995), pon de manifesto a necesidade de definición das condicións de operación para outro tipo de materiais distintos ao compost, como pode ser o caso da propia FORU, e en xeral daqueles materiais que poidan precisar ben estruturante ou inóculo.

A Táboa 4.5 contén as correlacións entre parámetros para estas mostras, excluída a mostra AG1-pur pola elevada diferenza en biodegradabilidade ás outras catro. Os valores de DEAO$_{20h}$ e DBO aumentan a maiores valores da VECO$_m$, se ben as correlacións obtidas non son estatisticamente significativas (p>0,05), probablemente debido ao reducido número de mostras. A correlación entre DBO$_5$ e DEAO$_{20h}$ si resultou significativa (p=0,02), e presenta unha pendente moi similar á que se obtivo para as mostras de FORU e compost (Táboa 2). A diferenza principal amósase na ordenada na orixe, que indicaría unha DBO$_5$ sistematicamente máis reducida, de tal forma que a DBO$_5$ sería nula para valores de DEAO inferiores a 8 mg O_2 g SV^{-1}.

Táboa 4.5. Correlacións entre parámetros para as mostras AG3-cst, AG2-mat, AG4-lod e AG5-lod.

Correlacións	**Ecuación**	**R²**	**Nº**	**p**
DBO vs DEAO	y = 1,96x - 14,83	R^2 = 0,963	4	0,02
DEAO vs VECO$_m$	y = 11,51x - 1,40	R^2 = 0,774	4	0,08
DBO vs VECO$_m$	y = 24,02x - 20,86	R^2 = 0,847	4	0,12

Aínda que, polas razóns indicadas, non se incluíron os valores de AG1-pur nas correlacións da Táboa 4.5, os parámetros obtidos correlacionan ben entre si. A DEAO e a DBO_5 resultan próximos aos que se poden predicir por extrapolación das ecuacións das Táboas 4.2 e 4.5.

Tomando como referencia os materiais procedentes da compostaxe de FORU (DBO / DEAO = 2,3 ± 0,2 para $VECO_m < 5$ mg O_2 g SV^{-1} h^{-1}), neste outro tipo de residuos as relacións DBO/DEAO non parecen gardar un valor central tan marcado, tendo resultado claramente menor (Táboa 4.4). Isto non pode ser atribuído á ausencia de microorganismos debido ao seu aporte externo (inóculo) nas probas aquí practicadas. Para materiais de difícil ou máis lenta degradación, os valores desta ratio oscilaron entre os 0.57 para o AG3-cst e 1.60 para o LIF. Deste rango, disociase o AG1-pur de natureza oposta en canto a biodegradación no que se acada un valor de 3.8.

4.3.5. Valoración global e discusión.

A Figura 4.6 contén a correlación global para todas as mostras, excluídas N2 e AG1-pur. Cun valor elevado do coeficiente de correlación (R^2 = 0,971), a correlación entre ambos métodos é estatisticamente significativa a un nivel p=0,001. Nesta perspectiva, o menor valor do cociente DBO_5 / $DEAO_{20h}$ para as mostras AG apréciase menos significativo, e podería deberse simplemente á variabilidade intrínseca dos ensaios biolóxicos como os empregados neste estudo. De feito, Vázquez (2015) tamén obtivo valores de 1,6 para o cociente DBO_5/ $DEAO_{20h}$ con mostras de compost, aínda que o número de ensaios era moi limitado.

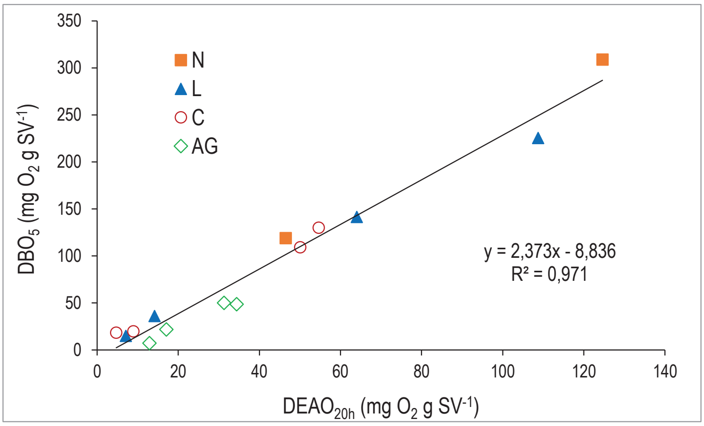

Figura 4.6. Relación entre a DBO5 e a DEAO20h para as mostras de diferente orixe (excluídas N2 e AG1-pur).

Veeken *et al.* (2007) e Aspray *et al.* (2015) empregaron o OxiTop® con mostras de compost en suspensión incubadas durante 7 días. Veeken *et al.* (2007) propuxeron unha escala de estabilidade en función dos valores da DBO7 (mg O_2 g SV^{-1}): <28 (moi estable), 28-77 (estable), 77-161 (inestable) e > 161 (moi inestable). Os nosos resultados coinciden parcialmente con esta clasificación, xa que se obtivo o índice de respiración para compost estable (mostras con $VECO_m$ por baixo de 1 mg O_2 g SV^{-1} d^{-1}) de 25 mg O_2 g SV^{-1} (como DBO_5) como se indicou anteriormente. Aínda que nos nosos ensaios o tempo de medición estendeuse a 7 días, a evolución das curvas DBO (ver por exemplo a Figura 4.2 e Figura 4.3) suxire que o correspondente DBO7 non debe ser moi diferente ao DBO_5 obtido. Ademais, Veeken *et al.* (2007) obtiveron valores ao redor de 140 mg O_2 g SV^{-1} para biorresiduos compostados durante 1-2 semanas, similares ás nosas mostras de compostos inestables, mentres que os valores máis altos, que oscilan entre os 280-1610 mg O_2 g SV^{-1} foron obtidos para biorresiduos frescos. No noso estudo, todos os valores de DBO_5 superiores a 100 mg O_2 g SV^{-1} correspondían a biorresiduos frescos ou compostos moi inestables (Táboas 4.2 e 4.4).

Aspray *et al.* (2015) subliñou unha forte correlación entre o índice de respiración obtido mediante o OxiTop® cunha mostra en suspensión e dous respirómetros dinámicos. O OxiTop® ofreceu valores similares de taxas de respiración de ata 50 mg O_2 g SV^{-1} d^{-1} pero valores aproximadamente 2,5 veces maiores para as taxas de respiración comprendidas entre 70 e 212 mg O_2 g SV^{-1} d^{-1}. Esta sobreestimación de altas taxas de biodegradabilidade explicouse porque as mostras altamente activas saíron do rango do test requirindo estimacións de resultados mediante extrapolación a partires dunha cantidade de datos limitados. Os resultados de Aspray *et al.* (2015) suxiren que non se debe obter un índice de respiración extrapolando a partir de períodos limitados de datos, preferíndose a unha nova aireación abrindo as botellas e reiniciando as lecturas.

Os ensaios respirométricos en fase líquida requiren a dispersión dunha mostra de compost na auga. Lasaridi e Stentiford (1998) propuxeron o uso dunha cantidade dentro do rango de 3-8 g de mostra húmida. Na práctica, o establecemento dunha mostra mínima de compost de 5 g (en base húmida) a dispersar en 500 ml de auga, e considerando un rango de 0,1-0,4 g SV por g de materia fresca para a maioría dos composts de orixes diferentes, o valor máximo da DBO_5 para este equipo de DBO (escala A, de ata 1000 mg de DBO L^{-1} con 100 ml de mostra líquida) estará no rango de 250-1000 mg O_2 g SV^{-1}.

Aínda que este rango é representativo da taxa de respiración de varios residuos orgánicos frescos, tamén significa que as lecturas poden quedar fóra do rango e nalgúns casos pode ser necesaria a apertura, o restablecemento e reinicio da lectura. Con esta operación, o método da DBO proposto pode aplicarse a calquera residuo orgánico independentemente da súa taxa de biodegradabilidade. Non obstante, en vez de preparar só 500 ml de dispersión, recomendamos o uso dunha mostra maior nun grande volume, como por exemplo 50 g de materia fresca en 5 L de auga, o que permite o uso dunha mostra moito máis representativa.

Os nosos resultados, así como os de Veeken *et al.* (2007) e Aspray *et al.* (2015) indican claramente que a determinación da DBO dunha dispersión de compost en auga é un método fiable para obter o seu índice de respiración. Non obstante, mentres que Veeken *et al.* (2007) e Aspray *et al.* (2015) usaron equipos sofisticados especificamente designados para a análise de mostras de compost e residuos orgánicos, os nosos resultados confirman que se poden obter resultados similares con aparellos manométricos ordinarios empregados para a análise da DBO de augas residuais. A principal vantaxe deste método alternativo é a sinxeleza de operación, o baixo custo dos equipos e a súa frecuente dispoñibilidade na marioría de laboratorios, conservando as vantaxes dos métodos de suspensión acuosa en comparación cos métodos nos que se emprega unha mostra sólida (Lasaridi e Stentiford, 1998 ; Grigatti *et al.*, 2007; Wagland *et al.*, 2009).

A pesar da boa correlación entre indicadores obtida (Figura 4.6), a validación do método da DBO como unha técnica aplicable a residuos distintos do FORU e compost de FORU, precisaría do estudo dun maior número de mostras e tipos de residuos. Tamén sería necesario estudar e definir axeitadamente as condicións de realización dos ensaios de respirometría no que se refire ao uso de inóculo e concentración de substrato. A relación entre biomasa activa e substrato non está definida en xeral nestes métodos biolóxicos, nin sequera no método estándar de DBO_5 para augas residuais, pero esa relación pode afectar significativamente os valores dos índices obtidos, dado o carácter limitado no tempo dos ensaios e a degradación parcial acadada nos mesmos. De feito, a presenza de inóculo en suficiente cantidade podería explicar un valor relativamente máis elevado dos índices obtidos cos ensaios máis curtos como a DEAO, fronte aos máis longos como a DBO5, e desta forma a menor relación DBO5/ $DEAO_{20h}$ que se mostra na Táboa 4.4.

4.4. CONCLUSIÓNS.

Para o presente estudo utilizáronse 7 mostras representativas do proceso de tratamento da FORU, procedentes de dúas plantas a escala industrial, 4 mostras procedentes de pequenos composteiros domésticos ou de compostaxe local, e 5 mostras de residuos agroforestais. Os índices respirométricos obtidos mediante o ensaios de DBO_5 correlacionáronse a un nivel estatisticamente significativo ($p<0.001$) cos obtidos no método respirométrico de referencia ($VECO_m$ e $DEAO_{20h}$) e no método de autoquecemento estándar (incremento de temperatura).

O limiar de estabilidade para mostras de FORU e compost procedentes de FORU estableceuse en 25 mg O_2 /g SV^{-1} de DBO_5. Tamén se obtivo un valor de limiar para $DEAO_{20h}$ de 12 mg O_2 g SV^{-1}. Para este tipo de mostras obtivéronse as seguintes relacións: DBO_5/ $VECO_m$ = 27,9 ± 3,1 (n=6), $DEAO_{20h}$ / $VECO_m$ =12,1 ± 1,2 (n=7) e DBO_5/ $DEAO_{20h}$= 2.3 ± 0.2 (n=6). A aplicación a residuos agroforestais ofreceu resultados similares, se ben a relación DBO_5/ $DEAO_{20h}$ foi inferior, situándose arredor de 1,5.

Como conclusión xeral, a aplicación do ensaio da DBO_5 á determinación da estabilidade de compost e residuos orgánicos caracterizase pola súa sinxeleza e por ofrecer un parámetro único, correspondente ao consumo de oxíxeno acumulado ao cabo de 5 días de ensaio. A súa aplicación a residuos ou materiais orgánicos con reducido contido en microorganismos activos require a adición dun inóculo, do mesmo modo que para os métodos de referencia. Este aspecto e a aplicación dos diferentes métodos ao este tipo de residuos precisa de maior investigación.

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CAPÍTULO V

METHANE PRODUCTION POTENTIAL AND ANAEROBIC TREATABILITY OF WASTEWATER AND SLUDGE FROM MEDIUM DENSITY FIBREBOARD MANUFACTURING

Unha versión adaptada deste capítulo foi publicada como:

Arias, O., Ligero, P., Soto, M., 2020. Methane production potential and anaerobic treatability of wastewater and sludge from medium density fibre board manufacturing. Journal of Cleaner Production 123283. https://doi.org/10.1016/j.jclepro.2020.123283

5. METHANE PRODUCTION POTENTIAL AND ANAEROBIC TREATABILITY OF WASTEWATER AND SLUDGE FROM MEDIUM DENSITY FIBREBOARD MANUFACTURING.

ABSTRACT

This research evaluates the suitability of anaerobic digestion of different waste streams derived from Medium Density Fibreboard (MDF) manufacturing. Methane production potential and anaerobic treatability were firstly assessed in batch assays from raw wastewater, physical-chemical pre-treated wastewater, as well as from sludge generated by current wastewater treatment at an industrial facility. Single-feeding and multi-feeding (semi-continuous feeding) experiments were conducted to quantify methane production and methanogenic toxicity. Digestion of the raw wastewater produced 4.0 L CH_4/L, which required dilution of the wastewater to 30-40% because severe toxicity was observed at 40% raw wastewater. Digestion of current process sludge produced 21.4 mL CH_4/g raw sludge, but it also required dilution to avoid toxicity. Working with these substrates, the necessary dilution led to a maximum concentration of soluble chemical oxygen demand (COD) of 4.2-4.6 g/L in the digestion medium, while the conversion of total COD to methane remained below 22%. Pre-treated wastewater in the current industrial process did not show inhibition, but gave a low methane production of only 0.8 L CH_4/L. An alternative treatment scheme consisting of simple sedimentation of raw wastewater followed by pre-aeration showed enhanced methane production of 4-4.8 L CH_4/L at higher concentrations of up to 80% wastewater in the assay medium. Sedimentation allows increasing the SCOD in the digestion medium up to 6.9 g/L, while the additional pre-aeration further increased the SCOD to 12.9 g/L without inhibition of methane production. Conversion of total COD to methane during the exponential phase increased to 64%. Simple sedimentation also removed 82% of suspended solids, which would help prevent clogging and improve anaerobic treatability in continuous digesters.

Keywords: MDF industry; wastewater; sludge; methane; bioenergy.

Abbreviations list

COD	Chemical Oxygen Demand
SCOD	Soluble Chemical Oxygen Demand
TSS	Total Suspended Solids
VSS	Volatile Suspended Solids
VFA	Volatile Fatty Acids
RW	Raw wastewater
TW	Treated raw wastewater
MDF	Medium Density Fibreboard
MDFS	Medium Density Fibreboard Sludge
PTW	Pre-treated wastewater
DW	Decanted wastewater
ADW	Pre-aerated decanted wastewater
SS	Sedimentation sludge
MPP	Methane Production Potential
MMPR	Maximum Methane Production Rate
MPPe	Cumulative methane produced during the high rate exponential phase
ACT	Percentage of methanogenic activity

5.1. INTRODUCTION.

Medium Density Fibreboard (MDF) production grew worldwide over the last decade. The capacity of the largest global MDF producers constantly increased during the 2005-2015 decade. Records of 2016 indicate a global production of 123.569.000 m^3/year. About one quarter of that total production was located in Europe (Tarling, L. *et al.*, 2016). MDF factories are energy-consuming facilities. Electricity and thermal energy are produced from wood-based fuels and natural gas. When there is no ready access to natural gas, liquid fuels are used as an alternative (Raunkjær *et al.*, 2016). 280.5 kWh of electricity, 167.6 kg of wood fuel and 17.4 m^3 of natural gas are needed to produce 1.0 m^3 of MDF panel (Piekarski *et al.*, 2017). This production requires more electricity (almost twice) and natural gas than other wood particleboards. Thus, the main proposed ways to improve the environmental life cycle of MDF panels involve the elimination or reduction of natural gas and electricity consumption (Piekarski *et al.*, 2017). On-site production of biogas from MDF waste and wastewater could be an interesting option to consider.

Water requirements for MDF manufacturing are usually higher than for other wood-based panels (Raunkjær *et al.*, 2016). Van Asch *et al.* (2016) and Fernández *et al.* (2001). Quantified significant consumption ratios of 1.5 and 3 m^3, respectively, for the production of 1 m^3 of MDF panel. Raunkjær *et al.* (2016) reported wastewater discharge figures between 0.07 and 3.1 m^3/t of dry pulp, while Fernández *et al.* (2001) reported the correlation between flow and organic content in wastewater. From these data, an average wastewater generation of approximately 0.32 m^3/m^3 of MDF panel can be estimated as a reference value. The type of wood used in the fibreboard production process affects the composition of the final effluent (Ben *et al.*, 2011).

MDF raw wastewater is poor in nutrients, rich in carbohydrates and wood extractives (polyphenols and organic acids), presents low pH (ranging from 4 to 5 pH units), high content of total and volatile suspended solids (TSS, VSS) and high chemical oxygen demand (COD) (Lindemann *et al.*, 2019; Balcik-Canbolat *et al.*, 2016; Ben *et al.*, 2011; Galehdar *et al.*, 2009). Particulate matter ranges from 10 to 35 g TSS/L and total organic matter from 30 to 55 g COD/L. Data about the soluble fraction and the biodegradability is scarce but Ben *et al.* (2011) reported 35% of COD as soluble (14767 mg soluble COD/L) whilst a similar percentage was biodegradable in aerobic conditions. MDF wastewater is very different from wastewater of the wet process of fibreboard production because of the higher content of suspended solids of the former. Typical fibreboard wastewater contains less than 2 g TSS/L and a TSS/COD ratio lower than 0.06 (Soto *et al.*, 1991a; Eroglu *et al.*, 1994; Fernández *et al.*, 2001). This difference could be the reason why fibreboard wastewater is being anaerobically treated whilst MDF wastewater is not.

Treatment of MDF wastewater is required prior its free discharge over aquatic or terrestrial ecosystems. In MDF facilities, wastewater treatment consists of physicochemical techniques to remove wood fines and solids prior to the secondary aerobic biological process (Raunkjær *et al.*, 2016). As for physicochemical primary treatment, flocculation and sedimentation or coagulation-assisted flotation are the most common (Raunkjær *et al.*, 2016). Using these processes, data from four MDF production plants indicate that removal rates range from 50 to 95% for TSS and from 30 to 60% for COD. Laboratory optimized experiments using the response surface methodology increased the efficiency of the coagulation-flocculation process to 91.1, 85.5, and 93.4 percentage elimination of COD, TSS, and turbidity, respectively (Ghorbannezhad *et al.*, 2016). Among other proposed methods, evaporation presents serious disadvantages (too expensive in terms of energy and maintenance besides inadequacy of capacity) (Galehdar *et al.*, 2009). Reverse osmosis required strict pre-cleaning operations of the effluent (Portenkirchner *et al.*, 2003). Other physicochemical treatments were proposed to reduce COD, colour and suspended solids of pre-treated MDF wastewater: Photo-assisted Fenton Oxidation process reached COD removal of up to 96% (Galehdar *et al.*, 2009); Fenton enhanced hydrodynamic cavitation process reached 70% COD, 80% formaldehyde and 89% colour removal (Balcik-Canbolat *et al.*, 2016).

A literature review reported that biological treatments resulted ineffective due the presence of non-biodegradable and refractory compounds (Balcik-Canbolat *et al.*, 2016; Galehdar *et al.*, 2009). At this respect, Lindermann *et al.* (2019) proposed the selective recovery of polyphenols from MDF process wastewater as polyphenols constitute a potential valuable resource and its removal would reduce toxicity for possible subsequent biological treatments. Nevertheless no references were found in relation to biological treatments in the absence of oxygen despite anaerobic digestion largely being used to treat a wide range of wastewaters (Poh *et al.*, 2015; Prakash *et al.*, 2018).

Biogas is a renewable fuel whose production is increasing worldwide, accounting for 1.2% of total electricity production and almost 10% of renewable energy (Kamusoko *et al.*, 2019; Ali *et al.*, 2020). More than half of biogas production takes place in Europe from organic waste such as the organic fraction of municipal solid waste, sewage sludge, food waste and industrial effluents, as well as energy crops and livestock waste (Xu *et al.*, 2018; Esteves *et al.*, 2019; Kamusoko *et al.*, 2019; Ali *et al.*, 2020). The same substrates are used worldwide, although the potential of livestock and crop residues for biogas generation may be higher in other regions (Esteves *et al.*, 2019; Ali *et al.*, 2020). The type of substrate, the transport needs of raw materials or biogasification products and the efficiency of the anaerobic reactor and biogas use (transformation to electricity, residual heat, etc.) are the main factors that determine the sustainability of biogas production (Aghbashlo *et al.*, 2019; Esteves *et al.*, 2019 ; Tabatabaei *et al.*, 2020). The use of organic waste is generally advisable over the use of agricultural substrates such as energy crops, but the efficiency of digestion of various waste streams is reduced and the application of pre-treatments may be necessary to increase biogas production (Esteves *et al.*, 2019; Tabatabaei *et al.*, 2020).

Differently to aerobic processes that demand high energy for constant aeration, anaerobic digestion is an energy-generating process. This technology might suppose an alternative waste management strategy and use MDF wastewaters as a source of no-cost substrate to obtain bioenergy. This complies with Directive 2009/28 (EC, 2009) which promotes the use of energy from renewable sources. The production of this “green fuel” would imply a reduction of primary energy consumption for MDF companies, often fossil fuel based.

References to methane production from MDF wastewater were not found in the literature. However, Ben *et al.* (2011) reported anaerobic acidification of the soluble fraction in a process aiming at the production of bioplastics. These authors obtained about 40% acidification of MDF wastewater, giving 16.9 g COD/L that could be easily transformed by acidogenic fermentation. The entire acidified substrate is potentially convertible to methane. Considering the production of MDF worldwide, the estimated production of raw wastewater of 0.32 m^3/m^3 of MDF and that 40% of the total COD would be converted to methane (as derived from the direct acidification potential reported by Ben *et al.*, 2011), the total methane potential would reach 235 M m^3 CH_4/year. This amount would equate to approximately 0.7% of the reported global biogas production for 2016 (Kamusoko *et al.*, 2019). In other words, the methane potential could reach approximately the amount of 1.9 m^3 CH_4/m^3 of MDF panel, which could satisfy nearly 12% of the natural gas consumption indicated by Piekarski *et al.* (2017) for these facilities. However, these figures could even increase in the future, if biodegradability is increased by pre-treatment or co-digestion of the substrate.

After acidification, the methanogenic step is crucial in the overall process of methane production from wastewater. Methanogenesis is a low rate process sensitive to the environmental conditions, such as pH, temperature and the presence of inhibitors or toxicants. Common toxic substances in wood-processing wastewater include resin compounds, phenolic compounds and tannins (Field, 1989; Sierra-Alvarez *et al.*, 1994). Fibreboard manufacturing wastewater with mostly soluble COD was effectively treated by anaerobic digestion, reaching 70-78% of COD conversion to methane (Soto *et al.*, 1991a; Fernández *et al.*, 2001, 1995). Fibreboard raw wastewater was partially detoxified by previous autoxidation by pre-aeration (Field, 1989; Soto *et al.*, 1991a) and the negative effect of particulate matter minimized through physical-chemical pre-treatment (Eroglu *et al.*, 1994; Fernández *et al.*, 2001).

The objective of the present research is to assess the potential of methane production from residuals of a MDF factory that currently applies physical-chemical pre-treatment of raw wastewater generating large amounts of MDF sludge and biological (aerobic) post-treatment to reach discharge standards. In addition, an alternative wastewater treatment layout was also evaluated. Aiming to optimize of methane production and overall wastewater treatment, the conditions that allow to overcome the phenomena of methanogenic toxicity and the restrictions derived from the TSS content have been assessed.

5.2. MATERIAL AND METHODS.

5.2.1. MDF process and wastewater sampling.

Raw materials came from the facilities of a MDF factory located in Galicia (North Western Spain). At the time of sampling input wood feeding was composed of pine (40%), eucalyptus (40%) and other broadleaf species (20%), as indicated by company officials. Wastewater resulted from the steaming of wood chips. Current wastewater treatment consisted of a first physical-chemical treatment where TSS and COD values were highly reduced, by more than 96% and 99%, respectively (Figure 5.1A). At this stage, sludge was generated by coagulation-flocculation and centrifugation, and the volume of wastewater was reduced by approximately 10%. Concerning to wastewater, after the primary treatment, a second biological (aerobic) process ensured that properties reached the standards limits fixed by Spanish legislation prior to free disposal to a nearby river. This step was not of analysis in the present work.

Integrated water samples were collected before and after the physical-chemical treatment. Sludge samples were taken from different points of a heap as it was forming. All samples were transported immediately to the laboratory and stored at 4 ºC until processing.

5.2.2. Processing of raw materials.

Raw wastewater (RW), pre-treated wastewater (PTW) and MDF sludge (MDFS) were used as direct substrates for anaerobic assays. In addition, RW was subjected to sedimentation and aeration pre-treatment as follows (Figure 5.1B). For simple sedimentation, an aliquot of RW was introduced into a graduated cylinder and left to sediment for 43 hours. After this period, two phases were differentiated in terms of colour and TSS content. The upper fraction (75% in volume) was separated by decanting and named as decanted wastewater (DW). The remaining bottom fraction (25% vol.) generated the sedimentation sludge (SS). Both DW and SS fractions were subjected to later analysis and anaerobic batch assays. An aliquot of the DW was subjected to a thermal-alkaline pre-treatment combined with micro-aeration in glass flasks. Initially, the pH was raised to 11.5 by the addition of NaOH. Flask were then placed in a heater where inner thermocouples kept temperature within 60–70 ºC for three hours. During this time, aeration was supplied by a fish tank pump through a hose that had a passage valve to regulate the air flow at a rate of 1.4 volume of air per reactor volume per minute. This pre-aerated decanted wastewater (ADW) was also subjected to characterization and anaerobic batch assays.

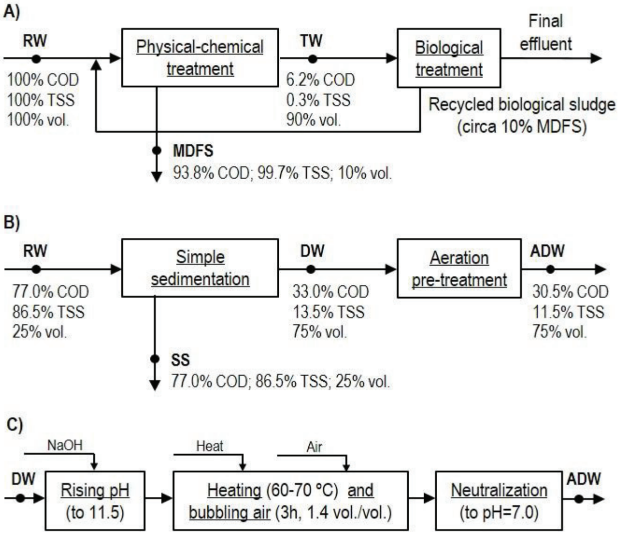

Figure 5.1. Current wastewater treatment (A), alternative treatment checked to methane production potential determination (B), and detail of aeration pre-treatment (C). Sampling points: RW: raw wastewater, TW: currently treated wastewater (1st step), MDFS: current MDF sludge; DW: decanted wastewater, ADW: (pre-) aerated decanted wastewater, SS: sedimentation sludge.

5.2.3. Anaerobic batch assays.

Anaerobic batch assays were carried out in duplicates in glass lab bottles of 350 mL of capacity and 100 mL of working volume. Methane production was monitored by means of the head-space gas analysis method (Soto *et al.*, 1993). An anaerobic sludge was used as inoculum at the concentration of 5.5 g VSS/L for all assays. A volatile fatty acid (VFA) mixture (acetic acid, 2 g/L; propionic, 0.5 g/L and n-butyric, 0.5 g/L) was used as substrate for the control assays, while blank assays contained inoculum but no substrate. 100 mg/L of $Na_2S·9H_2O$ and Na_2CO_3 at a ratio of 1 g/g dry matter of MDFS (or 1 g/g COD in the case of wastewater) were added to each assay at the beginning, in order to obtain an anoxic medium and sufficient buffer capacity, respectively. The pH during the first run with RW was found to be above 7.0, indicating the buffer capacity was sufficiently high. Macro and micronutrients were added only at the beginning of the assays (first feeding) in the amounts previously indicated (i.e. 1 mL of each macro and micronutrient stock solutions per L of assay medium. The composition detailed by Ferreiro and Soto (2003)).

Substrates were initially raised to pH values of 6.5 using NaOH. Once all assay ingredients were added, the pH was adjusted to 7.0 with dilute HCl or NaOH solutions. After purging air in the headspace with pure N_2 for three minutes, each bottle was sealed using a rubber septum and placed at 30ºC in a temperature-controlled chamber under a continuous stirring speed of 130 rpm. Gas samples (0.5 mL) were extracted with syringes at different time intervals, which were estimated for each assay or lot of assays depending on the methane production rate.

Methane production potential (MPP) and maximum methane production rates (MMPR) were obtained from the same anaerobic batch assays. MPP of each substrate sample was obtained from the final cumulative methane production after subtracting the blank value, and dividing it by the amount of substrate fed. The theoretical potential of methane production was calculated by multiplying the substrate COD by the factor 350 ml CH_4/g COD, corresponding to methane at 0°C and 1 atm. The percentage of substrate converted to methane (M (%)) represents the MPP obtained with respect to the theoretical.

MMPR was determined from the slope of cumulative methane production curves during the exponential phase of methane production after each feed (Soto *et al.*, 2015). The percentage of methanogenic activity (ACT%) of a substrate-added assay was obtained as the ratio between the MMPR of that assay and the MMPR of the VFA control assay in the same feeding multiplied by 100. The methanogenic toxicity expressed in percentage corresponded to 100-ACT%. The cumulative methane produced during the high rate exponential phase (MPPe) was obtained and expressed as percentage of the final MPP.

Various substrate concentrations were tested for methanogenic toxicity. Assays at different substrate concentrations were also needed to obtain the MPP under non-toxic conditions. In addition, the level of dilution must be adapted to the toxicity intensity of each substrate. The concentration values used are indicated in the Results Section.

In the case of some assays, successive feedings were carried out once the substrate was depleted. The use of successive feedings is a strategy to check the inhibitory effect of the non-biodegradable components of the substrate, as well as to confirm the possible adaptation to toxic compounds. The interest of a second or third feeding depends on the results of the previous one, so its use is indicated in the results section. Assay bottles were placed at room temperature to decant for 24 hours. A supernatant portion was extracted and replaced with the same volume of fresh substrate. After that, the pH in the media was regulated to the range of 7.0–7.1 by adding diluted HCl solution and the headspace purged with pure N_2.

5.2.4. Analytical methods.

Analysis were carried out in duplicate. The pH, COD (total), SCOD (soluble COD), TSS and VSS were measured following Standard Methods (APHA, 2005).

The composition of gas samples from anaerobic assays was determined by chromatography with a Hewlett Packard Series II 5890 instrument equipped with a thermal conductivity detector. Helium (200 kPa with a 15 mL/min flowing rate) was used as the carrier gas. The injection, oven, and detection temperatures were maintained at 90, 30, and 100 ºC, respectively.

The total phenolic content was determined by spectrophotometry at 765 nm according to the Folin-Ciocalteu method (Singleton and Rossi, 1965). Sugars (cellobiose, glucose, xylose, mannose and galactose) were determined using high performance liquid chromatography (HPLC) with Refractive Index Detectors (Bio-Rad aminex-HPX87-H column and acidulated water as mobile phase). The pH values were measured using a HANNA HI 208 electrode. Nitrate, nitrite, ammonium, phosphate, sodium, chloride and sulphate determination was carried out by Ionic Chromatography (Metrohm, model 850 Professional IC) using a Metrosep A Supp 7 - 250/4.0 column for anions and a Metrosep C6 - 100/4.0 column for cations.

VFA were determined by HPLC using a Hewlett Packard chromatograph equipped with supelcogel C-610, a column and two detectors connected in line, an ultraviolet detector and a refractive index detector. Phosphoric acid 0.1% was used as mobile phase with a flow rate of 0.5 ml/min. The column was kept at 30 ºC. The wavelength for detection was set at 210 nm.

The suitability of the least-squares fitting was evaluated by the square of the coefficient of determination (R2), the statistical F-value and probability (p). Data were processed with Microsoft Excel 2016.

The MPP of the duplicate assays was very similar. Statistical data indicated that the coefficients of variation for MPP were in the range of 0.1–10.9%, with a mean value of 4.3 ± 3.7%, n = 33, for all assays excluding blanks. The coefficients of variation of the blank assays were higher (26.4 ± 20.0, n = 4) because of the very low methane production recorded in these assays (1.0 ± 1.4 mL CH_4). Thus, accurate measurements of MPP were obtained. In the results section, only the average accumulated methane production curves and the mean MPP values are shown because of greater graphical and reading clarity.

5.3. RESULTS.

5.3.1. Characteristics of different waste streams.

RW is acidic, showing a pH around 4.5 (Table 1), which is due to the extraction of organic acids from the wood (Portenkirchner *et al.*, 2003). PTW and MDFS presented a higher pH value as lime and soda were added during the treatment process in order to enhance posterior performance of microorganisms in the secondary treatment. The organic matter content of RW was very high, reaching 44 g of COD / L of which 73% was particulate matter (14 g TSS / L). Physical-chemical treatment highly reduced the organic matter content of RW (Table 1), reaching 99.6, 99.7 and 88.6% removal of TSS, VSS and COD, respectively. These removal efficiency values are in accordance with the best results for optimized coagulation–flocculation treatment of MDF wastewater indicated by Ghorbannezhad *et al.* (2016).

At the same time, simple sedimentation at lab scale reduced TSS by 82% and COD by 56% of the decanted fraction (DW) whilst soluble COD was only reduced by 5% (Table 5.1). Sedimentation also generated a sludge stream containing about 43 g TSS/L and 128 g COD/L. The pre-aeration of DW showed little effect on the organic matter content, but it reduced the content of polyphenols by 41%, completely removing the ammonia present and slightly increasing the content in sulphate. This reduction is in accordance with the results of Soto *et al.* (1991a), who reported 17% and 52% removal of phenolic and tannin content after aeration treatment of fibreboard wastewater. Other constituents of the wastewater streams showed little variations (Table 5.1). However, MDFS and SS showed very different properties, the former being a solid material and the second a liquid stream. In addition to the moisture content, MDFS contained most of the soluble organic matter present in the RW (approximately 76% of the SCOD), while the SS contained a smaller portion.

Probably an additional thickening or centrifugation operations of SS would lead to its concentration and volume reduction, but this has not been tested in the present study. In any case, the different streams included in Table 5.1 offer several possibilities to apply anaerobic digestion to MDF waste streams to obtain biogas while also recovering energy and treating waste. All of them have undergone anaerobic tests to determine the potential for methane production and analyse anaerobic treatability.

Applying COD and mass balances to the data in Table 5.1, the following equivalences (given in the form of RW-based ratios in Figure 5.1) were obtained:

- Current wastewater treatment produced 117 g of MDFS/L RW and reduced the volume of RW by 9.7%. Consequently, 0.903 L PTW/L RW were produced in the current wastewater treatment.

- The alternative treatment produced 0.75 L DW/L RW and 0.25 L SS/L RW, while pre-aeration did not change the volume, so 0.75 L ADW/L RW were obtained.

Table 5.1. Characterization of the MDF waste streams used in this study.

Waste stream	pH	TSS	VSS	COD	SCOD	Cl-	NO_2-N	NO_3-N	PO_4-P	SO_4	Na	NH_4-N	Poly-phenols	Cello-biose	Glu-cose	Xil+man +gal
Current wastewater treatment																
RW	4.47 ± 0.04	13733 ± 231	13467 ± 306	44183 ± 900	12024 ± 224	62.05	udl	udl	19.66	97.87	udl	7.99	739 ± 23	306	996	728
PTW	5.24 ± 0.01	47 ± 12	40 ± 0	3021 ± 112	2860 ± 100	na	na	na	na	na	na	na	na	na	na	na
MDFS	5.52 ± 0.04 [a]	17.0 ± 0.1 [b]	90.0 ± 0.2 [b]	377 ± 4 [c]	na	2.69 [c]	udl	udl	udl	3.60 [c]	udl	udl	0.45±0.01 [c]	udl	udl	udl
Alternative wastewater treatment																
DW	4.08 ± 0.03	2467 ± 115	2400 ± 200	19544 ± 238	11424 ± 240	65.76	udl	udl	17.78	99.90	udl	11.23	710 ± 14	128	1045	197
ADW	7.11 ± 0.02	2103 ± 142	1900 ± 140	18030 ± 1039	16089 ± 429	68.85	udl	udl	16.28	120.36	896.1	udl	417 ± 5	udl	1185	228
SS	4.11 ± 0.01	43400 ± 200	42200 ± 200	128000 ± 2060	11974 ± 290	59.70	udl	udl	14.34	88.15	udl	4.24	675 ± 19	170	1065	207

Concentration in mg/L (mean ± standard deviation). RW: MDF raw wastewater, PTW: pre-treated wastewater (physical-chemical treatment), MDFS: Sludge from physical-chemical treatment of MDF raw wastewater, DW: decanted wastewater, ADW: aerated decanted wastewater, SS: Sludge from sedimentation of MDF raw wastewater. na: not available. udl: under the detection limit.

[a] pH corresponding to a dispersion of 1 g MDFS/L. [b] For MDFS, these amounts correspond to total solids (% wet basis) and volatile solids (% dry basis). [c] Amounts expresses as mg/g of MDS on a wet basis.

5.3.2. Methane potential of pre-treated wastewater.

Assays were performed for two different concentrations of pre-treated wastewater, corresponding to 30% and 77% of PTW in the assay. In addition, a parallel assay was conducted with 77% PTW and VFA as well as VFA control and blank assays. The results are shown in Figure 5.2 and Table 5.2. No second feeding was performed, considering the results of the first feeding conclusive.

The assays lasted approximately 30 days. The methane production of the blank was practically zero, indicating that the sludge used as inoculum was well stabilized. The control assay showed an adaptation phase of about 4 days and from that point on, it began to produce methane at a constant rate until the substrate was depleted after approximately 12 days of digestion.

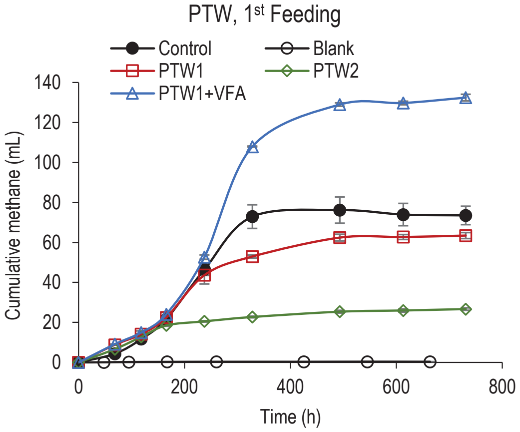

Figure 5.2. Cumulative methane production from anaerobic assays with PTW (concentration in PTW assays is given in Table 5.2; for acronyms, see section 2.3).

The methane production in PTW assays increased with PTW concentration, being almost proportional to this one. The %M was 83.1% and 77.5% for the lowest and highest concentration, respectively. In the assays with PTW and VFA as substrate, methane production was almost equivalent (96.7%) to the sum of the production of the two assays with PTW and VFA separately.

The rate of methane production during the exponential phase was similar in the assay with higher PTW concentration and in the VFA control (Table 5.2), indicating the absence of inhibition of methanogenesis. This was even clearer when comparing the VFA control and PTW+VFA assay, as the latter achieved a higher methane production rate.

About 69% of the methane obtained from the wastewater occurred during the exponential phase, while the remaining 31% was obtained at the lower rate retard phase. The latter part could be due to the slow hydrolysis and acidification of part of the biodegradable substrate. This is in accordance with the results of analytical determinations that discarded the accumulation of any of the three most common components of VFA in the digestion medium after the exponential phase.

Table 5.2. Methanogenic potential of pre-treated MDF wastewater (PTW).

Assay	PTW1	PTW2	PTW1+VFA
PTW conc. (% in assay medium)	77	30	77
MPP (L CH_4/L PTW)	0.820	0.878	-
M (%)	77.5	83.1	96.7 [a]
MPPe (%)	68.7	69.3	-
MMPR (mL/h) [b]	0.294	0.121	0.52
ACT (%)	93.6	38.5	165.6

[a] Percentage with respect to the sum of the methane production of assays with the same individual substrates. [b] The MMPR for the VFA control assay was 0.344 mL CH_4/h. For acronyms, see the text (section 2.3).

5.3.3. Anaerobic digestion of raw wastewater.

5.3.3.1. First feeding assays with RW.

Initially, assays were conducted with four different concentrations of RW, in the range of 5% to 40% RW in the assay medium, as well as an assay in parallel with 10% RW and VFA. After the first few days of these assays, lower concentrations of 1% and 2% RW were also checked. The results are shown in Table 5.3 and Figure 5.3. Cumulative methane production in methanogenic assays with raw wastewater. The RW concentrations are given in Table 5.3.Figure 5.3..

Table 5.3. Methanogenic potential of MDF raw wastewater (RW).

	1st feeding							**2nd feeding**			**3rd feeding**		
Assay	**RW1**	**RW2**	**RW3**	**RW4**	**RW2+VFA**	**RW5**	**RW6**	**RW2**	**RW3**	**RW2+VFA**	**RW2**	**RW3**	**RW2+VFA**
RW conc. (% in assay medium)	5	10	20	40	10	2	1	10	20	10	10	20	10
MPP (L CH_4/L RW)	4.07	3.96	3.60	0.21	-	5.62	6.34	4.93	4.25	-	7.84	5.18	-
M (%)	26.3	25.6	23.3	1.4	102.2 [a]	36.3	41.0	31.9	27.5	95.6 [a]	50.7	33.5	83.4 [a]
MPPe (%)	84.8	89.3	94.5	100.0		69.2	60.0	80.5	96.3	-	58.2	71.4	-
MMPR (mL/h) [b]	0.074	0.147	0.209	0.009	0.365	0.051	0.044	0.216	0.398	0.484	0.296	0.384	0.308
ACT (%)	21.5	42.6	60.7	2.7	106.2	14.9	12.6	29.4	54.2	65.9	33.7	43.8	35.1

[a] Percentage with respect to the sum of the methane production of assays with the same individual substrates. [b] The MMPR for the VFA control assay was 0.344 (1st feeding), 0.735 (2nd feeding) and 0.878 mL CH_4/h (3rd feeding). For acronyms, see the text (section 2.3).

The assays lasted approximately 30 days, but all assays with raw wastewater started methane production later than the control assay. Thus, RW caused a clear increase in the latency phase. Methane production increased with increasing RW concentration up to 20% but was almost zero at 40% RW. Specific methane production, and therefore M (%), decreased as RW concentration increased. In the range of 5 to 20% RW, 3.6-4.1 L CH_4/L RW was obtained, equivalent to 23-26% conversion of the theoretical methane production potential. M (%) was higher for very low concentrations (up to 41% M at 1% RW), but these values are considered of little interest as the additional yields were obtained from very slowly biodegradable fractions, as shown by the drop of MPPe to values around the 60%.

In the RW+VFA assay, methane production was almost equivalent (102.2%) to the sum of the production of the RW and VFA assays separately, indicating that there was no inhibition at that RW concentration (10%) or that it would be very limited.

The evolution of methane production curves show that the rate during the exponential phase at low concentrations (up to 10% RW, Figure 5.3B) was lower than that of the control, indicating either substrate limitation (low concentration of easily biodegradable substrate in assays with lower RW concentration, <5% RW) or presence of inhibition of the methanogenic process. This inhibition was clear for the 10% RW assay, which showed a delay in methane production relative to the 5% RW assay. However, after a certain acclimation time, the assays in the 5%-20% RW range achieved higher maximum production rates for higher RW concentration (Table 5.3), indicating adaptation and overcoming of the inhibitory effect. The same conclusion is reached by comparing assays with VFA (control) and with 10% RW and VFA (RW2+VFA), since the RW2+VFA assay delayed the phase of maximum methane production rate with respect to the control (Figure 3A), but once the exponential phase was reached, the rates were virtually similar (Table 5.3). This behaviour indicates that up to 20% RW concentration, the inhibitory effect was low and was overcome by adaptation. In contrast, the assay with 40% RW maintained very low or virtually zero methane production for 28 days (Figure 5.3A), showing an inhibition of methanogenesis greater than 97% (Table 5.3).

For RW concentrations of 5% or more, approximately 80-90% methane obtained during the high-rate exponential phase (MPPe), while the remaining fraction was obtained in a second, slower phase (Figure 5.3A, Table 5.3).

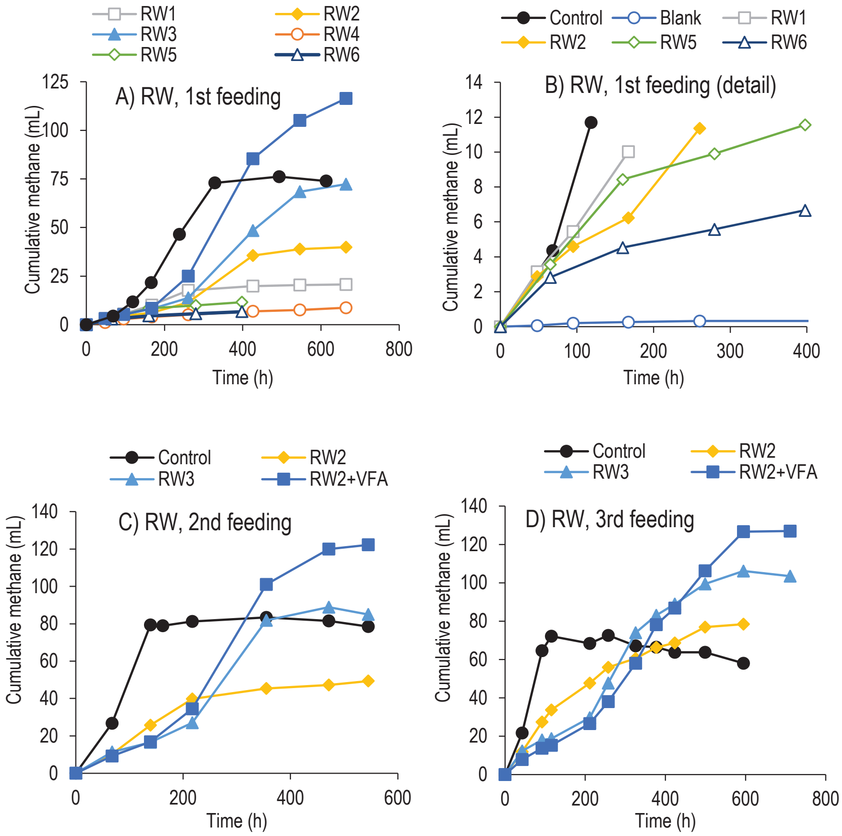

Figure 5.3. Cumulative methane production in methanogenic assays with raw wastewater. The RW concentrations are given in Table 5.3.

5.3.3.2. Second and third feeding with RW.

A second and third feeding were performed for assays with 10% (RW2) and 20% (RW3) as well as for 10% RW2+VFA. The results (Figure 5.3C and Figure 5.3D, Table 5.3) show that, despite the adaptation observed in the first feeding, there is still a delay in the beginning of the exponential phase in RW assays relative to VFA (control), as well as in the VFA assay containing RW. The M (%) rose slightly, reaching the range of 28-32% in the 2nd feeding and up to 56% for the RW2 assay in the 3rd feeding. This increase in M (%) is probably due to the accumulation of slowly biodegradable fractions from the preceding feedings, which prolongs the time of methane production and the total amount obtained, especially when the inhibition is not very strong.

At the end of the 3rd feeding, assays RW2 and RW3 accumulate a raw wastewater concentration of 30% and 60%, respectively. As it can be obtained from data in Table 5.3, overall M (%) across the three feedings was 40% for RW2 but only 26% for RW3. This difference was mainly due to the difference recorded in the 3rd feeding, because with the higher concentration of RW3 a longer time would be required to achieve a similar degradation of the slowly biodegradable fractions. By contrast, the MMPR remained higher in RW3 than in RW2, demonstrating the effect of substrate limitation on kinetics in assays with 10% wastewater.

However, the RW2+VFA assay should be considered free of substrate limitation. This assay showed higher MMPR in the 1st and 2nd feedings, but not so in the 3rd feeding. Thus, a clear inhibition of methane production by the presence of slowly biodegradable or non-biodegradable substrate occurred during RW2+VFA assay, when a cumulative concentration of 30% RW was reached.

Both the 10% RW2 assay and the control showed a continuous increase in MMPR from 1st to 3rd feeding (Table 5.3). In contrast, the assay at 20% RW3 increased its MMPR from 1st to 2nd feeding, but not at the 3rd feeding. Compared with the 40% assay performed on the 1st feeding (RW4), which had a very low methane production and recorded almost complete inhibition (Table 5.3), the distribution of the same amount of substrate in two feedings (RW3, 1st and 2nd feedings) indicates that much of the substrate components that are potentially inhibitors of methanogenesis were biodegraded and eliminated during the process. However, in the 3rd feeding, the MMPR in RW3 assay no longer increased (Table 5.3), indicating a clear accumulation of inhibitory substances at 60% accumulated RW concentration.

The above comparison between MMPR in RW2 and RW3 assays reflects the behaviour in the presence of substrate limitation. The evolution of RW2+VFA allows for the analysis of the possible inhibition of methanogenesis by eliminating the effect of substrate limitation. As indicated previously, the MMPR of the RW2+VFA assay slightly increased from 1st to 2nd feeding but dropped at 3rd feeding (Table 5.3). Compared with the VFA control, ACT (%) reached 100% in the first feeding but dropped to 66% in the second feeding and 35% in the third feeding. Therefore, although the RW2 assay has been progressively increasing its activity from first to third feeding, indicating growth of the methanogenic flora under these conditions, there is also an increasing inhibition process caused by the accumulation of non-biodegradable inhibitory components. In the 3rd feeding, with 30% RW accumulated, the activities of RW2 and RW2+VFA were equated, suggesting that this might be the optimal concentration to feed a continuous digester, as a compromise between the effects on kinetic of substrate limitation and inhibition by substrate (Figure 5.4). The evolution of the RW3 assay suggests that even an optimal concentration of 40% could be achieved, while 60% leads to a sharp drop in the percentage of substrate converted to methane (from 40% at 30% RW to only 26% at 60% RW as indicated above).

In this way, Figure 5.4 shows the effect of substrate limitation on low concentration assays, which causes MMPR to increase with concentration up to 40% of accumulated RW, while MMPR in the absence of substrate limitation (RW2+VFA assays) begins to decrease from 20% of accumulated

RW. In conclusion, optimal operating conditions for a continuous digester will be between 30% and 40% RW concentration.

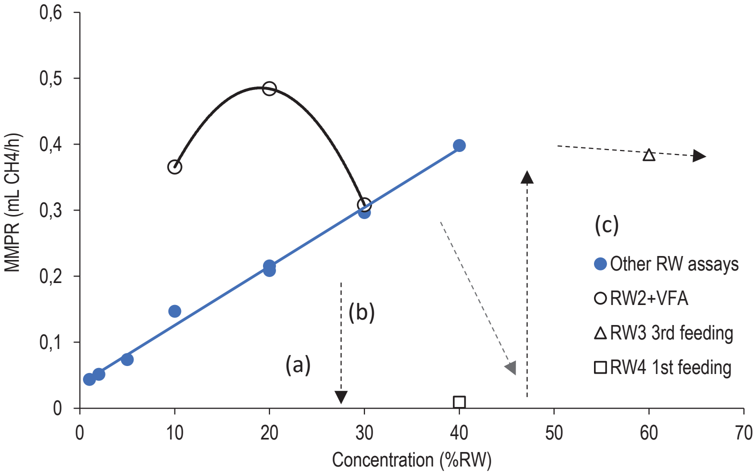

Figure 5.4. Maximum methane production rate as a function of accumulated raw wastewater concentration. "Other assays" include accumulated RW concentrations ranging from 1% to 20% (1st feeding), 20% and 40% (2nd feeding), and 30% (3rd feeding). Zones (a), (b) and (c) indicate zones with no inhibition, total adaptation to inhibition, and partial adaptation to inhibition, respectively.

5.3.4. Anaerobic digestion of MDF sludge.

The results of the anaerobic assays with MDF sludge are shown in Table 5.4 and Figure 5.5. The first feeding was performed with different concentrations of MDFS ranging from 3.3 to 60 g/L. The second feeding was performed only for the 30 g MDFS/L assay. The results show that methane production is proportional to the amount of sludge fed (Table 5.4), decreasing slightly MPP as the concentration increased. Regarding substrate inhibition, no effect on MMPR was observed, probably because the biodegradable substrate concentration was low, so all assays took place under substrate limiting conditions. However, the highest concentration assay (60 g MDFS / L) delayed reaching the exponential phase (Figure 5.5A). The second feeding in the 30 g MDFS/L assay also showed a delay in reaching the exponential phase (Figure 5.5B) and, despite a slight increase in MMPR, also showed a sharp drop in methanogenic activity relative to the control (Table 5.4). An average MPP of 21.4 mL CH_4/g MDFS was obtained for the assays at 30 and 60 g/L.

These results indicate that the substrate withdrawn as MDFS from RW continues to show methanogenic toxicity, although it was less marked in the first feeding than for RW. Thus, while with 40% RW the inhibition was almost complete, with MDFS equivalent to 51% RW the inhibition was greatly reduced (89% ACT). However, during the second feeding, the same cumulative concentration caused a clear delay in achieving the exponential phase (Figure 5.5B) as well as a marked reduction in methanogenic activity (33% ACT, Table 5.4).

Since no toxicity was observed in the treated water and approximately 94% of the COD of the RW passes to the MDFS, all toxicity of the RW should be in the MDFS. Thus, the lower toxicity observed in MDFS relative to RW could be due to the detoxification effects caused during the MDFS handling process. In this regard, it should be noted that MDFS is a solid material exposed to the oxidizing action of atmospheric oxygen. Despite its high water content (83%, Table 5.1), this material does not leach and may hold some interstitial air content that would facilitate micro-aeration of the material and a degree of pre-composting.

Table 5.4. Methanogenic potential of MDF sludge (MDFS).

	1st feeding				2nd feeding
Assay	MDFS1	MDFS2	MDFS3	MDFS4	MDFS3
MDFS Conc. (g/L in assay medium) wet basis	3.3	13.3	30.0	60.0	30.0 [b]
MPP (mL CH_4/g MDFS wet basis)	29.7	25.7	17.45 [a]	22.3	20.5
M (%)	22.5	19.5	13.2 [a]	16.9	15.5
MPPe (%)	66.3	72.0	84	100	74.7
MMPR (mL CH_4/h)	0.025	0.123	0.189	0.281	0.241
ACT (%)	8.0	39.2	59.6	89.4	32.8
Equiv. RW conc. (%RW in assay medium)	2.8	11.4	25.5	51.0	25.5 [b]

[a] The lower values of the MDFS3 assay were due to the earlier discontinuation in the measurement. [b] Cumulative concentration of 60% MDFS and equivalent concentration of 51% RW.

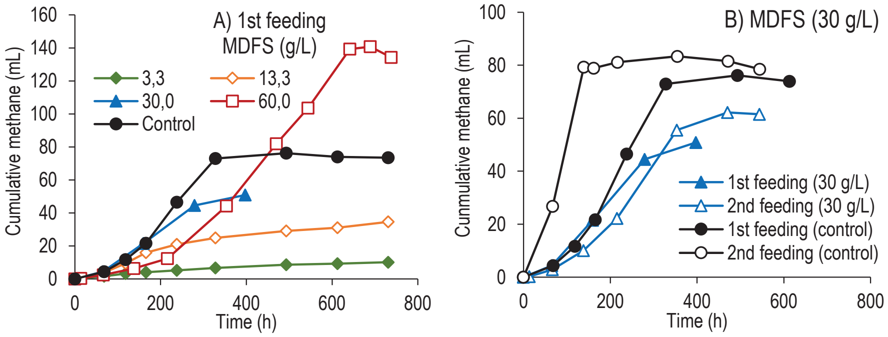

Figure 5.5. Cumulative methane production in methanogenic assays with MDF sludge: A) First feeding, B) Comparison between first and second feeding for 30 g MDFS/L assay and control.

5.3.5. Anaerobic digestion of decanted wastewater and aerated decanted wastewater.

Assays with DW and ADW were performed according to the substrate concentrations indicated in Table 5.5. Some delay in reaching the exponential phase was observed in the treatments with respect to control (Figure 5.6A and Figure 5.6B), being larger as the concentration of DW and ADW increased. However, the delay in the first feeding was lower than that observed with raw wastewater (Figure 5.3). On the other hand, the amount of methane obtained per mL of DW and ADW was similar to that obtained with RW and viable in a wider range of concentration (i.e. a concentration of 5-40% DW or ADW versus a concentration of 5-20% RW). Thus, the percentage of methanization increased considerably (Table 5.5), to 57-60% for DW (conc. 5-30%) and 66-84% for ADW (conc. 5-40%). MMPR increased with wastewater concentration, exceeding control MMPR in assays with a concentration of more than 20% of DW and ADW. This indicates the absence of methanogenic toxicity in the first feeding. Comparison of the 20% DW assay with and without VFA also indicates that there was no inhibition. Instead, DW stimulated methane production by increasing MMPR by more than 70%. Likewise, the MMPRs obtained with ADW were higher than those obtained with DW, particularly at wastewater concentrations of 30% and 40%.

Table 5.5. Methanogenic potential of decanted wastewater (DW) and aerated decanted wastewater (ADW).

Assay	**DW1**	**DW2**	**DW3**	**DW4**	**DW5**	**DW6**	**DW5+VFA**	**ADW1**	**ADW2**	**ADW3**
DW or ADW conc. [a]	**2**	**5**	**10**	**20**	**30**	**40**	**30**	**10**	**30**	**40**
1st feeding										
MPP (L CH_4/L DW, ADW)	5.52	3.97	4.09	3.95	3.93	3.33	na	4.16	5.29	4.80
M (%)	80.7	58.1	59.8	57.8	57.4	48.8	89.4 [b]	66.0	83.8	76.0
MPPe (%)	55.5	77.2	92.8	96.6	76.6	77.5	na	97.4	83.3	76.7
MMPR (mL CH_4/h) [c]	0.09	0.21	0.30	0.43	0.71	0.95	1.10	0.28	1.07	1.41
ACT (%)	14.1	33.0	47.7	68.1	111.0	149.0	172.7	43.6	167.2	221.4
2nd feeding										
MMPR (mL CH_4/h) [c]					0.44	0.32	0.40		0.59	0.51
ACT (%)					61.3	44.1	55.9		81.1	70.0

[a] Concentration: % in assay medium. [b] Percentage with respect to the sum of the methane production of assays with the same individual substrates. [c] The MMPR for the VFA control assay was 0.64 (1st feeding) and 0.72 mL CH_4/h (2nd feeding). For acronyms, see text (section 2.3).

The second feeding was performed only for the 30 and 40% wastewater assays and was maintained only until the exponential phase was reached (Figure 5.6C), with the aim of determining the MMPR. During this second feeding, the latency phase increased, and the maximum rates and methanogenic activities decreased. Even though, ACT (%) in the second feeding with 30-40% DW or ADW (Table 5.5) was higher than that obtained with 10-20% RW (Table 5.3). Nevertheless, some inhibition continues to occur for DW and ADW, as indicated by the latency phase and the lower activity at the second feeding with respect to the first feeding. In any case, the inhibition caused under these conditions (60-80% of non-biodegradable substrate concentration in the test medium) would no longer prevent continuous treatment of the decanted wastewater, and in particular when subjected to pre-aeration. In this case, the activity in the second feeding was greater than 70% of that corresponding to the control.

Finally, SS (concentrate containing the suspended solids removed to produce DW), at 20% concentration, showed very low methane production during the first 500 hours of incubation (Figure 5.6D), indicating high methanogenic toxicity (6% ACT, 2.4% M). This corroborated that a large part of the substrate causing the inhibition was removed from the wastewater by simple sedimentation, being in the sludge produced, which agrees with the lower toxicity shown by DW.

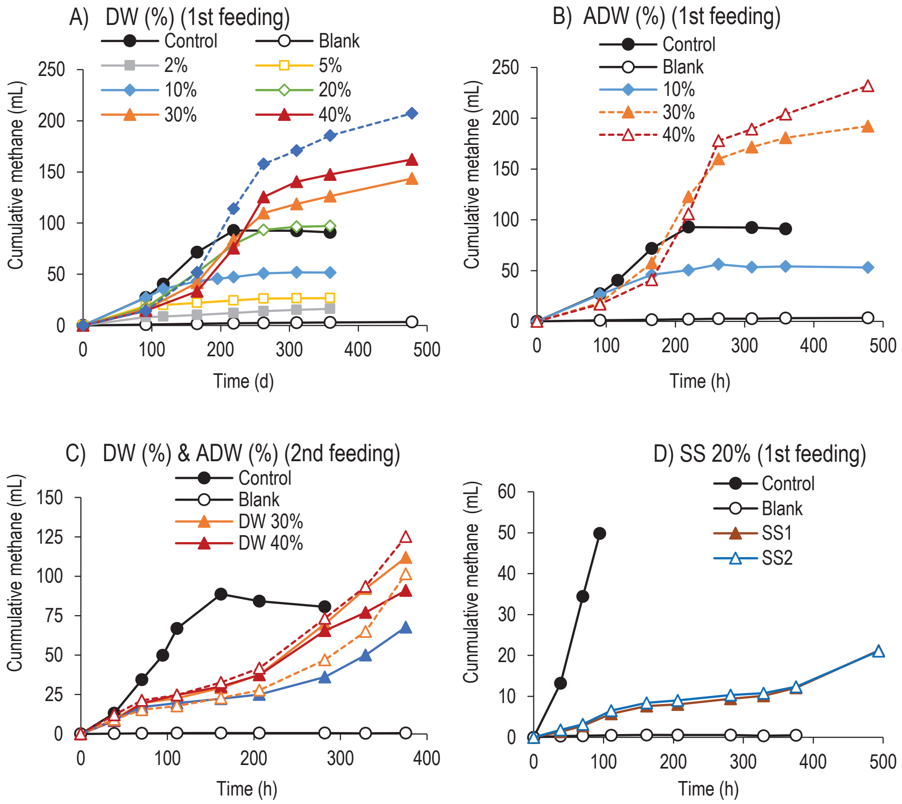

Figure 5.6. Cumulative methane production in methanogenic assays with decanted wastewater, aerated decanted wastewater and sedimentation sludge. Substrate concentrations are given in Table 5.5.

5.3.6. COD and polyphenols removal.

Various chemical parameters were determined at the end of some of the anaerobic assays as indicated in Table 5.6. For 10% and 20% RW assays, SCOD removal was 81.2 and 84.9% at the end of the 3rd feeding, respectively. Similar or somewhat higher values were obtained for 30% and 40% DW and ADW. However, when the removed SCOD is referred to total COD, the removal percentage varied widely from 22% to 78%, because the insoluble fraction varied widely among substrates. For these assays, a linear relationship was found between the soluble COD removed (expressed as a percentage of total COD) and the percentage of methanization (R2 = 0.993). In addition, % M was on average 5% higher than the percentage of COD removed, which may be due to biodegradation and conversion to methane of a small fraction of the suspended solids. These results indicate that biodegradation of suspended solids was very limited under the conditions of assays listed in Table 5.6. The case was probably different for RW assays at very low concentration (1 and 2%, Table 5.3), which reached a much higher % M. This means that the highest MPP of 6.3 L CH_4/L RW does incorporate significant solubilisation of suspended solids.

Polyphenol removal was even greater than SCOD for RW and DW (88-91%), but lower for ADW (62-68%). Sugar removal reached 100% in all cases, whereas at the end of the assays no VFA were detected. On the one hand, sulphate removal was in the range of 30-50%, while the content of nutrient-related compounds increased in the final assay medium relative to the content supplied by the wastewater, due to the initial addition of nutrients to avoid their limitation in the process. N and P concentrations indicate sufficient nutrient availability for the growth of anaerobic microorganisms. On the other hand, methanogenic toxicity due to compounds such as sodium or ammonium must be discarded.

Table 5.6. Concentration of different chemical components at the end of some anaerobic assays ([a]).

Assay	Feeding, time	Cl mg/L	PO$_4$ mg P/L	SO$_4$ mg/L	Na mg/L	NH$_4$ mg N/L	Polyphenols mg/L	SCOD mg/L	Removal (%) Polyphenols	Removal (%) SCOD	Removal (%) COD [b]
RW (10%)	3rd, 499h	253.77	21.8	40.5	603.0	53.1	23.0 ± 0.4	778	89.7	81.2	22.1
RW (20%)	3rd, 499h	199.83	30.6	39.1	1004.3	35.4	41.8 ± 0.6	1090	90.6	86.4	23.5
DW (30%)	2nd. 283h	482.32	28.2	36.1	1338.6	92.7	44.2 ± 0.4	675	89.6	91.8	53.6
DW (40%)	2nd, 283h	558.96	32.5	39.8	1759.3	81.9	65.6 ± 0.6	1557	88.4	84.1	49.1
ADW (30%)	2nd, 283h	591.96	32.6	37.6	1507.5	94.0	95.3 ± 0.8	1297	61.9	87.7	78.2
ADW (40%)	2nd, 283h	586.56	29.1	57.8	1307.8	55.3	108.2 ± 2.2	2335	67.6	82.6	73.8

[a] Other components (NO_2, NO_3, VFA, Cellobiose, Glucose, Xylose, Mannose, Galactose) were below the detection limit. [b] SCOD removal referred to total COD feed.

5.4. OVERALL ASSESSMENT AND DISCUSSION.

As expected, the organic matter content was higher than that of Kraft pulping effluents (Vidal *et al.*, 1997) or paper mill effluents (Ferreira *et al.*, 2019). These authors reported that COD concentrations ranged from 0.6 to 1.9 g/L. Differently, the TSS content was higher than typical of board effluents. Fernández *et al.* (2001) achieved efficient anaerobic treatment of fibreboard mill effluent with 98.8% SCOD, while the percentage of SCOD for RW in this study is only 27.2% (Table 5.1). Despite this, the SCOD concentration is almost 7 times higher in the RW of this MDF facility (as well as in DW and ADW streams from the alternative pre-treatment process, Table 5.1) than that of the paper mill effluent treated in the UASB (up flow anaerobic sludge bed) reactor-based biorefinery, as reported by Ferreira *et al.* (2019). Thus, the substrate is available in the facilities of the MDF industry, its efficient conversion to biogas will depend on the anaerobic treatability factors such as methanogenic toxicity and biodegradability.

Almost complete inhibition of methane production was observed at 40% RW and 20% SS but was clearly lower for DW and ADW. The results indicate that the inhibition of methane production was mainly due to suspended solids but also to soluble compounds. Forest industry wastewater typically contains toxic substances such as wood extractives (mainly solubilized during pulping under alkaline conditions), lignin derivatives, tannins generated in the debarking, and chlorophenols from bleaching processes (Sierra *et al.*, 1994). Inhibitory concentrations for the methanogenic process can range from less than 1 mg COD/L for some halomethanes and chlorophenols. While many wood-derived substances can exert inhibition at concentrations ranging from a few tens to several hundred mg COD/L. This includes lignin monomers and low molecular weight tannins, while high molecular weight compounds are less toxic or non-toxic. Thermomechanical pulping wastewater has been considered one of the least toxic effluents in the forest industry. Concentrations causing 50% toxicity ranged from 11 to 20 g COD/L (Soto *et al.*, 1991; Sierra *et al.*, 1994). However, the high content of suspended solids also caused the deterioration of the methanogenic process. Meyer and Edwards (2014) established that TSS concentrations should not exceed 10–20% of the COD concentration in the influent of the UASB and EGSB (expanded granular sludge bed) reactors, with a limit of approximately 500 mg/L for the more concentrated substrates.

The MDF wastewater used in the present study comes from the pulping of debarked wood under acidic conditions and therefore a low toxicity can be expected compared to other forest effluents. However, the reduction of the use of process water has led to high COD concentrations (Fernández *et al.*, 1995), which may increase the inhibitory effect. The data in Table 5.3 indicates that the 50% inhibition of methane production by RW was reached at the concentration of approximately 25%, which corresponds to 11.0 g COD/L, the lowest value of the range indicated by Sierra *et al.* (1994). The threshold toxicity concentration was even lower in terms of SCOD, because the 50% inhibition corresponded to only 3.0 g/L. Despite that, the methanogenic process appeared viable at higher concentrations of up to 40% (Figure 5.4) because of partial detoxification during digestion. In fact, almost 90% of the polyphenols were eliminated during RW digestion (Table 5.6). However, other toxic compounds such as terpenes are not biodegradable in anaerobic environments. The polymerization of toxic tannins and lignin monomers by micro-aeration under alkaline conditions provided a partial detoxification of forest wastewater, which is in agreement with previous reports (Sierra *et al.*, 1994; Soto *et al.*, 1991). The effect of aeration pre-treatment was reflected in the reduction of polyphenols from approximately 710–740 mg/L in RW and DW to 417 mg/L in ADW (Table 5.6). In addition, polymerized tannins and phenols were non-toxic, although they were no longer biodegraded under anaerobic conditions (Sierra *et al.*, 1994).

Regarding biodegradability, the maximum methane production potential obtained from raw wastewater was 6.3 L CH_4/L RW (low concentration assays, Table 5.3). Obtaining this maximum MPP from RW requires a high dilution that allows it to operate in the absence of substrate toxicity. It also requires a low methanogenic substrate/biomass ratio, along with very high digestion times that allow methane conversion of the slowly biodegradable fractions. The MPPe data for RW (Table 5.3) shows how the percentage of methane obtained in the high rate phase drops as the MPP increases because of increased substrate dilution. Thus, reaching maximum methane potential for RW is considered non-viable. In fact, the methane production rates after the exponential phase were only 20-25% of those of the exponential phase (data from the RW tests the concentration of 1% and 2%), indicating the very low rate of suspended solids biodegradation. However, this value of 6.3 L CH_4/L RW is used as a reference to assess the methanogenic potential of the various options and conditions considered feasible.

This Section summarizes the main results obtained in the present study for the biomethanization of wastewater and sludge from the MDF industry. In order to compare the different options assessed (RW, PTW, DW, ADW, MDFS or SS), the following parameters were selected:

- The volume ratio of the substrate subjected to anaerobic digestion to the RW volume.

- The MPPe expressed in L CH_4/L, which was obtained for each substrate by multiplying the MPP by MPPe(%)/100 (values given in Section 5.3).

- The equivalent MPPe (MPPe.eq) or MPPe referred to the volume unit of RW, which is calculated multiplying MPPe by the volume ratio of each substrate to RW (or the concentration ratio, in the case of MDFS). It is expressed in L CH_4/L RW and as the percentage of maximum MPP obtained for RW (6.3 L CH_4/L RW).

- The percentage of COD converted to methane during the exponential phase (Me), which was obtained by multiplying the M (%) by MPPe(%)/100.

- The viable concentrations of COD and SCOD, corresponding to the tested substrate concentration that allowed the production of methane under batch assay conditions with ACT (%) above 50% of the control.

MPPe represents the methane production potential achieved during the exponential (high rate) phase, which is considered more indicative of practical anaerobic digestion in continuous digesters. For each option, MPPe and Me must be selected from assay results (Section 5.3) considering the conditions necessary for the practical feasibility imposed by factors such as methanogenic toxicity and dilution requirements. The results of this comparison are summarized in Table 5.7. Data in Table 5.7 clearly shows how the viable SCOD increased for the DW (6.9 g/L) and ADW (12.9 g/L) in comparison to the RW (4.2 g/L) or the MDFS (4.6 g/L), indicating the strong positive effect of sedimentation and pre-aeration in reducing the methanogenic toxicity. These results are discussed with respect to the feasibility of continuous treatment in anaerobic digesters. Taking into account factors such as the type of digester, the required dilution, the risk of clogging by suspended solids, or the opportunities for co-digestion.

The percentage of methanisation under non-toxic conditions during the exponential phase varies greatly from 14% for MDFS to 64% for ADW, including 22% for RW, 52% for DW and 53% for PTW. As a general criteria, anaerobic treatability improves as Me(%) increases, as less substrate remains in the digestion medium, including suspended solids or refractory soluble organic compounds.

Table 5.7. Methane production potential for the different approaches.

Waste stream	**Ratio (% vol. RW)**	**MPPe (L CH_4/L)**	**MPPe.eq (L CH_4/L RW) (% maximum)** [a]	**Me (%)**	**Viable COD (SCOD) conc.** [e]	**Observations about anaerobic treatability**
RW	100	3.46	3.46 (54.9)	22	15.5 (4.2)	Estimated maximum concentration: 30% -40% RW. Large risk of digester clogging by suspended solids.
MDFS	(117) [b]	18.8 [c]	2.2 (34.9)	14	22.6 (4.6)	Requires dilution. Possible operation at equivalent RW concentration of 50%. Risk of clogging by suspended solids.
PTW	90.3	0.56	0.5(8.0)	53	3.0 (2.9)	No operation problems but low methane recovery.
DW	75.0	3.54	2.70 (42.1)	52	11.7 (6.9)	Possible operation at DW concentration of 60% (equivalent RW concentration of 80%).
ADW	75.0	4.05	3.04 (48.2)	64	14.4 (12.9)	Possible operation at DW concentration of 80% (equivalent RW concentration of 100%).
SS	25.0	1.0	0.25 (4.0)	2.4 [d]	<25.6 (<2.4)	Severe methanogenic toxicity at 20% SS.

[a] MPPe.eq is MPPe referred to the volume unit of RW, expressed either in L CH_4/L RW or as the percentage of maximum MPP obtained for RW (6.3 L CH_4/L RW). [b] Ratio: g MDFS/L RW. [c] MPPe: mL CH_4/g MDFS. [d] Me (%) was obtained at 20% dilution, showing severe inhibition. [e] The viable concentrations of COD and SCOD correspond to the dilution indicated in the Observations column, which allow the production of methane under batch assay conditions while maintaining an ACT (%) above 50% of the control.

On the one hand, regarding RW, toxicity effects would be compatible with the continuous operation at concentrations of the order of 30-40% RW (Figure 5.4). In these conditions, MPPe.eq reached 3.46 L CH_4/L RW (54.9% of maximum). Dilution of RW with clean water is not considered an appropriate solution. It would only make sense to operate at such a high dilution in case of availability of a residual effluent that provides biodegradable organic load but not methanogenic toxicity. In such a situation, co-digestion could make it possible to obtain methane from the RW of the MDF industry. In this regard, it has been shown that co-digestion of different substrates decreases toxicity and establishes a more robust microbial community (Meyer and Edwards, 2014). Co-digestion of sludge from the paper industry with urban wastewater sludge has favoured the methane production process (Hagelqvist, 2013). In other experiences, co-digestion with microalgae has allowed significant increases in methane production by effectively reducing toxicity (Bohutskyi *et al.*, 2019; Solé-Bundó *et al.*, 2019). Given the pattern of RW toxicity shown in Figure 4, a proper co-digestion process could probably work at an RW concentration above 40%.

On the other hand, co-digestion will help balance nutrient requirements for methane production from MDF waste. The total nitrogen content in the MDF waste streams was not determined in this study, but the ammonia nitrogen was in low concentrations (Table 5.1). The C:N ratio for MDFS flow has been previously reported by Arias *et al.* (2017, 2019), standing in the range of 28-34, which would be considered suitable for anaerobic digestion. These authors also reported high P and Ca content and low K content in MDFS. However, the total nitrogen and the C:N ratio itself does not report on the bioavailability of the nutrients present in the waste. Nutrient content was expected to be low in the studied substrates, as it is the general case in forest biomass, and was therefore supplemented in this study to avoid nutrient limitation and achieve maximum methane production. The addition of macronutrients provided a minimum COD:N ratio in the assay medium that ranged from 20 (PTW) to 100 (RW, considering soluble COD). Anaerobic batch assays can be successfully performed at highly variable COD:N ratios, ranging from 1 to 300 (Soto *et al.*, 1991a, b). This is because methane production potential assays do not seek the growth of anaerobic consortia and digester start-up, but rather the maximum methane production potential under various digestion conditions using a previously developed inoculum. During continuous anaerobic treatment, nutrient availability and, in particular, micronutrient availability may be a factor constraining digester performance (Xu *et al.*, 2018). More research is needed, using continuous digesters, both at laboratory and pilot scale (Tabatabaei *et al.*, 2020).

Another problem with continuous anaerobic treatability of RW is the high load on suspended solids. At 30% dilution, the TSS concentration in the influent under continuous treatment would still be 4.2 g TSS/L, with a TSS/SCOD ratio of 1.14. Under these conditions, a continuous digester would not develop a stable high-quality anaerobic sludge (high methanogenic activity and good sediment ability) that would allow optimal operation at short hydraulic retention times (Fernández *et al.*, 1995; Álvarez *et al.*, 2004). Thus, the UASB digester would not have a promising application. The high content of suspended solids would also affect the proper functioning of other types of digesters, being a common problem with biodegradation of different organic waste (Soto *et al.*, 2015). The completely mixed anaerobic digester, usually applied for concentrated effluents rich in suspended solids, also loses its viability by requiring dilution of the influent to prevent substrate toxicity. An alternative might be anaerobic digestion in two sequential stages, the first being hydrolysis and acidification of the biodegradable substrate. This option will only be of interest if prior acidification facilitates the subsequent separation of the soluble and suspended fractions, an aspect that has not been studied so far.

Anaerobic digestion of MDFS presents problems similar to those of RW digestion in terms of toxicity and suspended solids, as well as a lower volumetric methane production rate and MPPe. Thus, the option of MDFS single digestion would not be preferable over the direct use of RW. However, co-digestion of MDFS would be of interest (Hagelqvist, 2013).

The effluent from the current physical-chemical pre-treatment process contains 90% of the volume of raw wastewater but only 6% of the COD (Figure 5.1). Its treatment by anaerobic digestion does not present problems of toxicity nor of clogging by suspended solids and would not need dilution. However, the yield that would be obtained in methane production with respect to the potential of raw wastewater is very small, being only 0.5 L CH_4/L RW (8% of the maximum possible).

Previous sedimentation of the raw wastewater in order to treat only the supernatant fraction seems to be a very interesting operation from the point of view of optimizing the conversion of the residual substrate into methane. The TSS content is markedly reduced and the TSS/SCOD ratio drops to 0.22. The methanogenic toxicity relative to RW is clearly reduced, allowing operation at higher concentrations, up to 60% DW (Table 5.7). The MPPe.eq from DW reached 2.7 L CH_4/L RW, approximately 42% of the maximum MPP of the RW. Anaerobic digestion of DW is shown to be a viable option in high-rate digesters, although optimization of operating conditions may require further reduction of TSS load.

Aeration pre-treatment under alkaline conditions of decanted wastewater enhances methane production and further reduces toxicity phenomena. Anaerobic treatment of ADW is possible at concentrations up to 80% and MPPe.eq from ADW reaches 3.0 L CH_4/L RW, approximately half of the maximum MPP of RW (Table 5.7). Increasing this value is possible through enhanced sedimentation that increases the recovery of the soluble fraction in the DW and ADW fractions. For example, by thickening or centrifuging the SS fraction. In the present study, the recovery of the soluble fraction was limited to 75%.

The literature is abundant in references to pre-treatments applicable to lignocellulosic waste to improve methane production (Cotana *et al.*, 2015; Zheng *et al.*, 2014; Li *et al.*, 2019; Xu *et al.*, 2020) or to minimize the formation of inhibitory substances (Jönsson and Martín, 2016). Li *et al.* (2019) reported that the methane yield of wood waste digestion was increased by 38.5% after NaOH pre-treatment. Accordingly, our results indicate 29.3% increase in %M for ADW compared to DW. However, no specific previous references were found for the substrates studied here, from the MDF industry. One possibility would be to incorporate other waste streams as substrates to be digested. Li *et al.* (2019) also reported interesting results for wood waste and pig manure co-digestion. Montalvo *et al.* (2018) reported increases in methane production of 201.6% after the addition of fly ash to sewage sludge followed by an aerobic pre-treatment. This would be an interesting alternative to improve biodegradability and increase methane production from the fraction of suspended solids present in MDFS and SS streams. MDF board mills produce high amounts of ash, which is another waste to be reckoned with.

5.5. CONCLUSIONS AND FUTURE PROSPECTS.

The current treatment of MDF wastewater by physicochemical processes and activated sludge generates large amounts of biodegradable sludge that requires further treatment and consumes energy for aeration. At the same time, the potential for energy recovery is lost.

The present research evaluates the potential of methane production from a MDF plant waste. The maximum MPP was 6.3 L CH_4/L RW. However, direct RW digestion would produce only 3.5 L CH_4/L RW and would require dilution of wastewater to 30-40% RW because of severe methanogenic toxicity observed at 40% RW. In addition, stable operation in high-rate anaerobic digesters seems unlikely due to the high amount of suspended solids in RW. Anaerobic treatment of MDF sludge produced only 2.2 L CH_4/L RW and would need dilution to prevent toxicity.

A new treatment scheme consisting of simple sedimentation of raw wastewater and pre-aeration of decanted wastewater has been proposed to improve anaerobic treatability and methane recovery. Methane production reached 3.0 L CH_4/L RW at higher concentrations of up to 80% of the wastewater in the assay medium. This dilution level corresponded to 14.4 g COD/L (and 12.9 g SCOD/L) and the conversion process reached 64% COD converted to methane during the exponential high rate phase. Probably, the use of a continuous high-rate reactor would not require any dilution of the decanted pre-aerated wastewater. Simple sedimentation also eliminated 82% of suspended solids thus preventing digester obstruction and anaerobic sludge deterioration.

Further research is needed to optimize the proposed treatment scheme and particularly to confirm anaerobic treatability in continuous high-rate digesters. DW and ADW still contain a high concentration of TSS of 2400 mg/L (DW) and 1900 mg/L (ADW). Although methanogenic toxicity was largely removed, this TSS content could impair the operation of high-rate anaerobic digesters. Thus, the sedimentation process can be improved, aiming to remove more suspended solids from the decanted stream while maintaining the most soluble fraction. Coagulation-flocculation process could be considered as pre-treatment if its action is limited to the suspended solids fraction.

More research is also needed to address the recovery of methane from the fraction of suspended solids, both in the current form of MDFS and in the SS flow of the proposed new scheme. These streams still concentrate 94% (MDFS) and 77% (SS) of the original COD. In addition to the toxicity limitations, the biodegradation rate was only 20-25% of that of the soluble fraction. Pre-treatment methods aimed at reducing toxicity and increasing biodegradability should be considered. If the biodegradability of suspended solids and the rate of conversion to methane increase, co-digestion may be of interest with the aim of reducing toxicity and balancing nutrient requirements, because these streams are concentrated in organic matter but are poorer in nitrogen and phosphorus content.

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CAPÍTULO VI

APPLICATION OF ORGANIC WASTES TO GALICIAN SOILS AND LEGISLATIVE INTRICACIES IN A CIRCULAR ECONOMY CONTEXT

6. APPLICATION OF ORGANIC WASTES TO GALICIAN SOILS AND LEGISLATIVE INTRICACIES IN A CIRCULAR ECONOMY CONTEXT.

ABSTRACT

In a circular economy, where wastes are promoted to be injected back as secondary raw materials, the Spanish Circular Economy Strategy promotes advances in the recycling of fertilizers. In Galicia (NW Spain), the absence of specific regulations on soil fertilization gives way to tangential and sectorial normative with diverse approaches regarding the conditions of application, properties and other conditions that organic wastes must meet. The screening of regulations and literature led to a discussion where these and other issues are addressed. After the analysis, final considerations were outlined to promote a more effective recycling of organic wastes and the design of a suitable legislation adapted to the natural conditions of the region.

Abbreviations list

CGAP	Code of good agricultural practices
CE	Circular economy
CI	Concentration indicator
HMs	Heavy metals
MPLs	Maximum permissible legal limits
MSW	Municipal solid waste
NVZs	Nitrate vulnerable zones
OM	Organic matter
P-R articles	Peer-reviewed articles
R.D.	Royal Decree
SSTP	Sewage sludge treated products
SOC	Soil organic carbon
SRM	Silvicultural reference models
VS	Volatile solids

6.1. INTRODUCTION.

Since ancient times, anthropic fertilization constituted a soil management technique to improve yield of crops. Ever since, and under an expected demographic scenario of 9.7 billion in 2050 (UN, 2019), human activities, including modern agriculture as one of the major causes, are susceptible to cause unacceptable environmental change with uncertain consequences (Rockström *et al.*, 2009). The human interference with the N cycle is of one of the planetary boundaries that have been understepped (Rockström *et al.*, 2009). Currently interest in biomass production increases, proportionally to the population rates, with the associated risks of potential soil degradation and unnatural N cycles disturbances.

In the last decades a broad range of environmental policies and normative documents were developed in Europe aiming to protect nature and prevent human activities from crossing these biophysical boundaries highlighted by Rockström *et al.* (2009). Within the framework of the 7th EU Environmental Action Programme (EC, 2013) the concept of Circular Economy (CE) has emerged strongly (Geissdoerfer *et al.*, 2017). Although the term remains ambiguous, it could be defined as "a regenerative system in which resource input and waste, emission, and energy leakage are minimised by slowing, closing, and narrowing material and energy loops" (Geissdoerfer *et al.*, 2017). The CE notion can be referred to multiple topics (Araujo Galvão *et al.*, 2018). In what wastes is concerned, they constitute a large source of biomass that can be, if properly managed, turned into valuable resources on which their nutrients can be returned to soils. In this context, recovery of nutrients becomes a priority, and soil a key element of the natural capital as CE is highly dependent on its functionality (Breure *et al.*, 2018). CE has also gained traction with policymakers, influencing governments and intergovernmental agencies at the local, regional, national, and international level (Geissdoerfer *et al.*, 2017). Among these, the regions take on importance as appropriate areas for the implementation, monitoring and evaluation of the different CE action plans.

In Spain there is currently no specific legislation regarding soil protection or fertilization. The topic is tangentially governed through other environmental protection legislation and thus, nutrient management goes hand in hand with control of pollution (or in other words, with offsite nutrient losses reduction). In fact, nutrients overload from agriculture remains the predominant source of N discharged into the environment (EC, 2018) and this occurs despite recovery of nutrients from wastes becomes a priority in the EU CE Strategy (EU, 2015). Regarding to normative connected with soil fertilization, Spanish legislation imposes quantitative limits to nitrates pollution from agrarian sources (BOE, 1996) and commercial fertilizers (BOE, 2013). Another document involved with the application of wastes to soil is related with biostabilized materials (MAGRAMA, 2013).

Due to the model of territorial organization, regions, among them Galicia autonomous region (NW Spain) may develop and execute basic Spanish State legislation. In Galicia main regulation affecting soil fertilization is Decree 125/2012 that regulates the usage of sewage sludge (DOG, 2012). It is noteworthy outstanding that Galician Decree 125/2012 prohibits direct recovery of sludge and any organic raw materials in agricultural soils. This condition was previously considered in Sewage Sludge third draft (EC, 2000). Various treatments were established in this Decree, similar to those contained in Sewage Sludge third draft (EC, 2000). Specifically: composting, anaerobic digestion, aerobic thermophilic stabilization (any other treatments different to composting), thermal drying and stabilization using lime. In practice, enacting this normative implied a sharp decline in the disposal of SS to soil with agricultural purposes. In the 5 years period before and after the appearance of Decree 125/2012, the total amount of sewage sludge used in agricultures roughly varied from 15.000 to 1.000 t (d.m. basis) (Xunta de Galicia, 2018). In addition to Decree 125/2012, voluntary guidelines concerning fertilization affect agrarian and forestry productive models in the region: Galician Code of Good Agricultural Practices (CGAP) (DOG, 1999), and Silvicultural Reference Models (SRM) along with Best Forestry Practices for more abundant species in Galicia (DOG, 2014). The CGAP contains fertilization recommendations in agricultural lands, mostly based on references to adjust doses to main crops requirements. The SRM recommends inorganic fertilization rates for several forest species, mainly in the early years of the plantation. Galicia also developed a Technical Instruction for the elaboration of technosols from wastes not aimed to fertilization purposes.

This legislative framework often results confusing for farmers (Dupuis, 2012; Ortolano *et al.*, 2009) and in the common thought that fertilization strongly correlates with the crop yield, organic and inorganic fertilization is carried out by farmers following their own criteria. Thus in Galicia annual doses of 40 m^3 ha^{-1} of poultry manure were addressed by Conde-Cid *et al.* (2018) in agriculture areas, 100 m^3 ha^{-1} for cattle slurry and 1000 kg ha^{-1} for mineral fertilizer NPK 8:24:16 were reported in pasturelands (Franco-Uría *et al.*, 2009; Seco-Reigosa *et al.*, 2015), and over 200 kg N ha^{-1} and 50 kg P kg ha^{-1} for grasslands (Paz-Ferreiro *et al.*, 2010). On the other hand, the addition of organic materials different from manures on Galician soils was studied by different authors (Santalla *et al.*, 2011; Seco-Reigosa *et al.*, 2014; Paz-Ferreiro *et al.*, 2012; Pousada-Ferradás *et al.*, 2011) before and after the appearance of Decree 125/2012 that regulates the usage of organic wastes in Galicia.

Legal barriers were outlined as one of the most important in the implementation of the CE (Araujo Galvão *et al.*, 2018) and in the recovery of fertilizer nutrients from materials. Chojnacka *et al.* (2019) outlined that regulations should be more compact and connected with each other. Thus different governmental initiatives, from upper to bottom level, plan to improve the coherence or readjust the normative to fit the CE principles (EC, 2013; EU, 2015; MAPAMA, 2019; Xunta de Galicia, 2019).

De Clercq (2001) compared normative for different fertilizers on nutrient management in Europe aiming to come up with proposals for more harmonisation legislation among countries. For specific materials, the suitability of normative was previously studied: manures worldwide (Qian *et al.*, 2018; Ramsey *et al.*, 2013; Schröder *et al.*, 2007; Zavattaro *et al.*, 2016), biostimulants (La Torre *et al.*, 2016), biofertilizers (Malusá and Vassilev, 2014) or biochar (Meyer *et al.*, 2017) in Europe, SS in Portugal (Alvarenga *et al.*, 2016), commercial fertilizers in Spain (Barral and Paradelo, 2011) or agro-industrial sludge in Galicia (López-Mosquera *et al.*, 2005).

In the concrete case of Spain, Barral and Paradelo (2011) detected paradoxical situations when evaluating the content of legislation related to commercial fertilizers. These authors outlined that sometimes, due to heavy metals limitations, SS might be directly spread on soil but not after composting, despite the beneficial effects of composting. Whilst raw sludge met the MPLs for soil application, final HM concentrations in the same material after composting would exceed limits for class C composts (corresponding with commercial composts with the MPLs of HMs). These authors also evaluated the total annual HM loads for SS and its derivative composted according to MPLs defined in legislation: Comparison resulted in a substantial higher amount of HM load for SS than from composted SS, varying by a factor of 2 to 15, depending on the HM considered.

This paper deepens in legislation involved in the application of organic wastes to soils at a regional scale with fertilization or waste recovery purposes, with Galicia as a case study. The context is characterized by the existence of different administrative levels. The analysis seeks to identify controversial situations created by the existing regulations and bring new insights on the limits and conditions imposed on the recycling of organic wastes as fertilizers. The objective of this study is to evaluate and discuss the suitability of concurrent normative involving the recycling of organic waste as fertilizers or soil improvers in Galicia.

6.2. MATERIALS AND METHODS.

6.2.1. CHARACTERISTICS OF THE STUDY SITE.

6.2.1.1. ADMINISTRATIVE CONTEXTUALIZATION.

This case study is circumscribed in Galicia, (southwestern Europe, Figure 1b and 1c) divided into 4 provinces with 313 municipalities spread over them (Figure 1a).

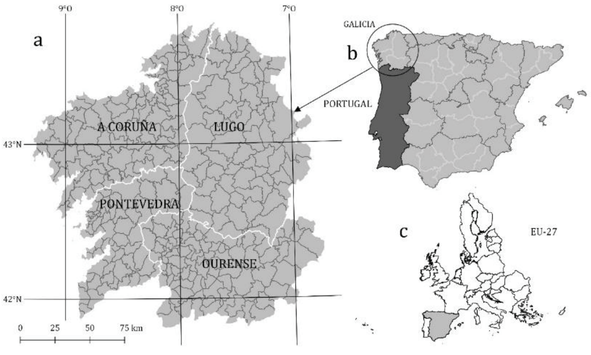

Figure 6.1. Boundaries of Galicia and municipalities within the provinces (the latest separated by white interior lines (a)), location in Spain (b) and position in Europe (c). Source: Own depiction.

Regulations are applied from four hierarchical levels. The European Union is a legislative primary source that frequently binds, through Regulations and Directives, the appearance of environmental normative in EU Member States. Spanish State constitutionally establishes the basic legislation on the protection of the environment and the Autonomous Communities are responsible for its execution and may issue additional or more stringent standards on the environment. The bottom level of government are Municipalities (Figure 6.1a), which might restrict manure application through local by-laws or ordinances. Nevertheless, these were not compiled as the evaluation at the very local scale was not under the scope of this study.

6.2.1.2. SYNOPTIC OVERVIEW ON CLIMATE AND SOILS.

Galicia occupies around 3 million ha. Annual precipitation ranges from 700 to 2000 mm (1400mm as average), whilst annual temperature varies from 8 to 15 ºC with an average value of 12 ºC (Macías and Calvo de Anta, 2002). Soils are characterized by low chemical fertility (Calvo de Anta *et al.*, 2015; Macías and Calvo de Anta, 2002). Aluminium, extended all over the Region in rocks and soils, plays a key role saturating the complex of the exchangeable cations (up to 70-80% over granites) and thus, displacing K, Mg, Ca and Na (mainly), readily leached by rain (Macías and Calvo de Anta, 2002; Seco *et al.*, 2014). Thus, acidity is high with an average pH value of 5 in the Region (Macías and Calvo de Anta, 2002), and 4,5 – 5,0 range on soils settled on so abundant rocks as granites, metamorphic, schists, limestone and filites (Figure 6.2).

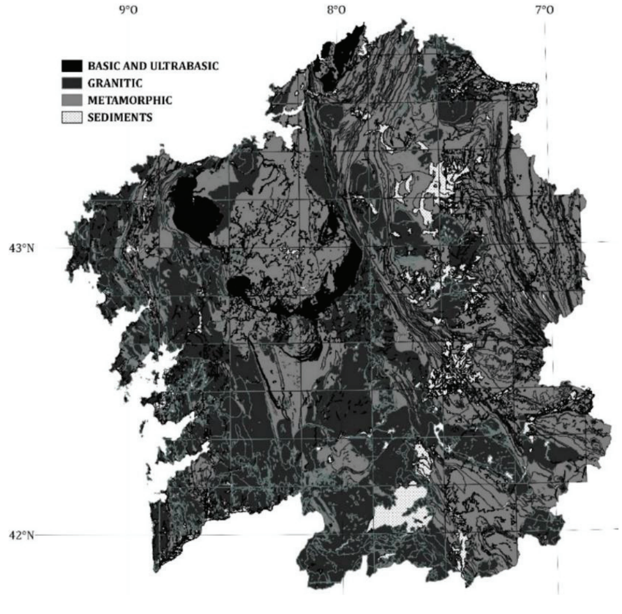

Figure 6.2. Lithological map of Galicia. Source: Own depiction (IGME and IET, 2014). Small surface units omitted for simplification.

It is noteworthy referencing the concentration of HMs in soils as they influence legal fertilization practices. Main lithological formations lay in granitic and metamorphic rocks (slates, schists and phyllites), and to a lower extent, basic (and ultrabasic) rocks, as well as sedimentary deposits (Figure 6.2). Geological parent material influences natural HMs content in soils with large differences depending on the type of substrate (Table 6.1).

Table 6.1. Comparison of soil HMs mean levels in Galicia (Macías and Calvo de Anta, 2009) with European (Tóth *et al.*, 2016) and worldwide references (Kabata-Pendias and Mukherjee, 2007). Italicized numbers indicate situations where natural HM concentrations exceeds the threshold for SS legislation in acidic soils. Values expressed in mg kg^{-1}.

Metal	Geological parent material									Europe	Worldwide
	Granite	Slates	Schists	Basic rocks	Sediments	Ultrabasic rocks	Limestone	Quartzites	Mean values		
Cd	0,08	0,13	0,11	0,16	0,10	0,11	0,50	0,08	0,11	0,11	0,5
Cu	9,8	24,9	23,9	49,9	14,7	***205,1***	36,6	16,8	20,61	9,4	20-30
Ni	23,7	***43,2***	***40,7***	***65,7***	29,2	***2155,9***	***74,4***	***34,9***	55,83	18,15	19-22
Pb	29,8	26,1	31,0	32,0	21,0	18,3	***58,6***	19,2	29,32	8,33	25
Zn	50,9	69,1	65,8	66,3	48,3	81,7	***176,5***	47,0	60,29	n.a.	64
Hg	0,07	0,07	0,08	0,12	0,06	0,08	0,18	0,07	0,07	0,04	< 1
Cr	20,2	43,7	48,8	***128,7***	22,9	***4268,4***	58,2	28,3	80,25	15,7	54

With the exception of Ni and Cr, for which the concentrations are markedly higher in Galicia, particularly in ultrabasic rocks, values could be considered in the range of worldwide values (Kabata-Pendias and Mukherjee, 2007) and in general terms, higher than mean concentrations of European soils.

6.2.2. LITERATURE REVIEW.

Normative.

Legal references were searched to detect those documents directly involved with the application of organic amendments or fertilizers to soils. Search also aimed to identify the MPL that are currently applied and compare the conditions that must be legally met.

Firstly, Programs, Policies and other hierarchical high-ranked documents were overseen but discarded as they established wide regulatory frameworks, distant from the bottom detailed scale under which this paper was focussed. Normative with any reference to soil was selected after a first screening on environmental legislation. In the next step, legislation regarding fertilization and/or waste management practices was revised, either in terms of quantified limits or in conditions that limit their application to soil. Documents imposing quantitative limits, nutrient recovery or soil improvement were positively discriminated from those with vague, tangential, indirect or imprecise references to fertilization. Other references with legal background and special incidence in this paper were also included.

Organic wastes application to soil.

In the region, scientific reports on the application and chemical characterization of materials legally allowed to be applied to soil were reviewed using Scopus® databases. Search words (contained in the article title, abstract or keywords) included “manure”, “slurry”, “waste”, “fertilizer”, “sewage sludge”, “amendment”, “compost”, “Galicia”, “northwest Spain”, “NW Spain” with different combinations of the logical operators “AND” and “OR”. The output results, including abstract, were exported for subsequent external review and organization using Zotero (Corporation for Digital Scholarship, 2009).

Different queries resulted in a total 446 documents and after removing duplicates, 314 remained. From 314 and after reading the article or abstract title, 263 were discarded as they were not aligned with the objectives of the review. Thus, 51 articles were left to which another 18 were added after reading related citing and cited articles.

Among the 69 selected papers, 35% of papers focussed on abundant regional wastes (mussel shells, ash, dairy-industry sludge, seaweed and others). The addition of different materials (technosols, SS, biochar, composts, etc.) for the recovering of degraded mine soils was the scope of another 25% of articles, and 17% of reviewed papers dealt with SS. Inorganic fertilizers, composts, manures and other materials represented the remaining fraction.

The properties of commercial fertilizers produced in Galicia were obtained from the database of the Spanish Agricultural Ministry website (MAPA, 2018). Available data (2018) corresponded to organic fertilizers (classes A and B), mineral organic fertilizers (classes B and C) and organic amendments (classes A, B and C). Legislation defines these products as follows. Organic fertilizers are those products whose main function is to provide nutrients, which are derived from carbonaceous materials of animal or vegetable origin (organic and mineral origin for mineral organic fertilizers). Mineral organic fertilizers are products whose main function is to provide nutrients for plants, which are of organic and mineral origin, and is obtained by mixing or chemical combination of inorganic fertilizers with carbonated materials of animal or vegetable origin or organic fertilizers. Organic amendments are those from carbonaceous materials of vegetable or animal origin, mainly used to maintain or increase the OM content of soil. Categories A, B or C class are in correspondence with their increasing HMs content.

Properties of Galician treated wastes were obtained, after request, from regional agriculture Agency (data corresponded to 2017).

6.3. RESULTS AND DISCUSSION.

6.3.1. REGULATIONS.

From different administrative boundaries, the addition of organic materials to soil affects materials of different nature, for which sectoral regulations have been developed for more than three decades (Figure 6.3).

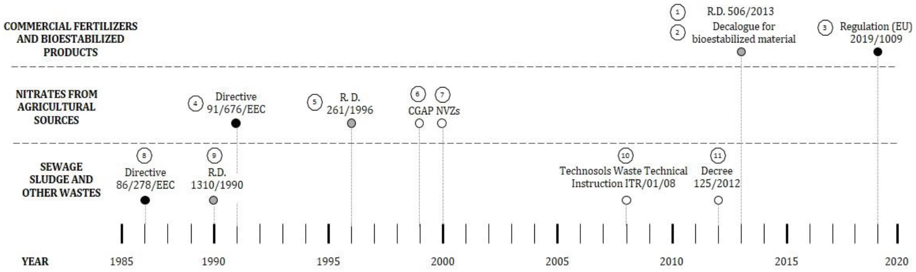

Figure 6.3. Timeline of main sectorial regulations directly involved in fertilization practices in Galicia. Dots filled in black, grey and white respectively indicate European, Spanish State and Galician legislation source. CGAP: Code of Good Agricultural Practices (approval); NVZs: Nitrates Vulnerable Zones (declaration of non existence in Galicia). Sources: 1: (BOE, 2013); 2: (MAGRAMA, 2013); 3: (EC, 2019); 4: (EC, 1991); 5: (BOE, 1996); 6: (Xunta de Galicia, 1999); 7: (DOG, 2000); 8: (EC, 1986); 9: (BOE, 1990); 10: (DOG, 2008); 11: (DOG, 2012).

6.3.1.1. SEWAGE SLUDGE.

Directive 86/278/EEC (SS Directive) regulated the use of SS in agriculture, aiming to protect soil and human health against HMs (Cd, Cr, Cu, Hg, Ni, Pb and Zn) contained in sludge. EU States differently approached the scope of the Directive. Some added limits for new contaminants, established stricter values or even banned its use in agriculture, whereas others used sludge widely (EC, 2014).

In Spain, SS Directive was transposed by R.D. 1310/1990 (BOE, 1990) and Galician Government, by Decree 125/2012 (DOG, 2012), relating organic waste to be applied to soil, adapted the content of both SS Directive and Spanish R.D. 1310/1990 to the particular conditions of Galicia. This Decree comprises SS (from urban wastewater treatment plants, domestic septic tanks and from certain types of agro-industries). It also includes other organic materials expressly included in the Spanish list of biodegradable organic waste (BOE, 2013) under the condition that such waste becomes part of a compost or digestate. Any other waste, will need the authorization from the Galician government. Furthermore, Decree specifies treatments and respective technical requirements for these wastes (Table 6.2) resulting the so-called sewage sludge treatment products (SSTP), global term that includes the also defined treated SS, digestates and composts.

Table 6.2. Treatments required for the processing of organic wastes in Galicia.

TREATMENT	TECHNICAL REQUIREMENTS
Turned aerated piles composting	Temperature ≥ 55 ºC maintained for a time ≥ 4 hours in 3 or more turning episodes. Maturation phase required.
Aerated static piles or tunnel composting	Temperature ≥ 40 ºC maintained for a time ≥ 5 days (more than 55ºC for 4 hours during this period). Maturation phase required.
Different thermophilic aerobic stabilizations	Temperature ≥ 55 ºC in a 20 day batch residence time.
Thermophilic anaerobic digestion	Temperature ≥ 53 ºC in a 20 days residence time (or Temperature ≥ 53 ºC in a 20 hours batch residence time).
Mesophilic anaerobic digestion	Temperature ≥ 35 ºC in a 12 days residence time (previous thermic treatment required for more than 30 minutes and 70ºC).
Lime stabilization	pH ≥ 12 for a time ≥ 24 hours (or pH ≥ 12 for a time ≥ 2 hours plus thermic treatment at 55 ºC).
Thermic drying	Temperature ≥ 80 ºC maintained for a time ≥ 10 minutes.

6.3.1.2. NITRATES FROM AGRICULTURAL SOURCES.

Council Directive 91/676/EEC (Nitrates Directive) aimed to protect waters against pollution caused by nitrates used in agriculture. The Directive instructs the EU Member States to designate the Nitrate Vulnerable Zones (NVZs) and the design of compulsory Action Programmes in these with mandatory measures to reduce the concentration of nitrates. The EU States should establish a voluntary CGAP as a reference for farmers in the country. Nitrates Directive (1990) was transposed by R.D. 261/1996 (BOE, 1996). According to this R.D., in the NVZs the total amount of N contained in manure applied to soils must be lower than 170 Kg ha^{-1} year^{-1}. However, during the first four-year Action Programmes, an amount of manure containing up to 210 kg^{-1} year of N may be allowed.

In Galicia, the implementation concluded with the publication of the Galician CGAP (DOG, 1999) and the declaration of absence of NVZs (DOG, 2000). That implied: a) the no existence of Action Programmes in the whole Autonomous Community and the non-applicability of the aforementioned mandatory N limit of 170 Kg ha^{-1} year^{-1}; b) the optional application of the Galician CGAP, non-binding policy instrument that does not impose compulsory requirements, although episodes of pollution arising from its non-compliance could be the object of a legal complaint (Scholefield, 2001).

6.3.1.3. COMMERCIAL FERTILIZERS.

At the level of Spain, legislation currently in force is Spanish R.D. 506/2013 (BOE, 2013) which regulates fertilizers to be used in agriculture, gardening and degraded soils, updating its content to the Regulation (EC) 2003/2003 on fertilizers (EC, 2003). The Regulation (EC) 2003/2003 has been recently repealed by the Regulation (EU) 2019/1009 (EC, 2019) which intends to create harmonised conditions to promote and make use of recycled or organic materials for fertilising purposes (EU, 2018). The new Regulation established seven Product Function Categories for EU fertilising products (fertilisers, liming materials, soil improvers, growing medium, agronomic additives, plant biostimulants and fertilising product blends). EU fertilising products shall consist solely of component materials listed in an eleven Component Material Categories. For both, Product Function and Component Material Categories, requirements were established regarding quality and safety limits. All producers must respect defined criteria to commercialize their fertilizers in the EU but at the same time they are still allowed to sell their products within the national markets, under the national fertilizer regulations conditions and therefore not obliged within their national boundaries to respect the Regulation (EU) 2019/1009 (Marini *et al.*, 2020).

In the meanwhile, R.D. 506/2013 currently establishes seven groups of fertilizer products, with particular attention to fertilizers that use organic wastes in its formulation. Only materials included in the Spanish list of biodegradable organic waste (BOE, 2013) are allowed. These fertilizers were classified in three classes (A, B and C) according to their HMs content, being required a set of common minimum conditions for all of them. Amount limits for land application were only fixed for Class C fertilizers made from organic wastes or components, 5 t ha^{-1} $year^{-1}$. In any case, fertilizers with organic compounds will be applied following the CGAP. Besides, in those regions with NVZs declared, fertilization should be adjusted to the respective Action Programmes.

6.3.1.4. BIOSTABILIZED MATERIAL.

Spanish waste law (Law 22/2011 on wastes and contaminated soils) differentiates compost (obtained from biodegradable wastes or waste fractions collected separately) and biostabilized material (from mixed wastes treated in mechanical-biological treatment plants). While advancing in separate waste collection, in 2013 Spanish government launched the Decalogue for the use of biostabilized material and composts not included in the Register of Fertilizer Products through the operation R10 (MAGRAMA, 2013).

Under operation R10, the application to soil must produce a benefit to agriculture or an ecological improvement of the soil, aspects that must be justified in the authorization request to the Galician Agency. Possible destinies of biostabilized materials include: agriculture, slope revegetation, coverage of landfills, restoration of quarries and mines and public gardening. In all cases, dosages must be justified case by case. Biostabilized materials must meet specific requirements, in other case options would be restricted to energy recovery or disposal.

In the agricultural application, doses exceeding 5 t d.w. ha^{-1} $year^{-1}$ (and provided that the average annual value in a five years period does not exceed 5 t d.w. ha^{-1} $year^{-1}$) will require a Fertilization Plan which will justify agronomically and environmentally these loads. Same criteria apply for public gardening. Different criteria apply for slope revegetation, coverage of closed landfills and restoration of quarries and mines, in which dosages must be under 50 t d.w. ha^{-1} $year^{-1}$ (unless specific justification).

6.3.1.5. TECHNOSOLS.

The Galician Waste Technical Instruction ITR/01/08 regulates the elaboration of technosols derived from non-hazardous waste, including SS, aiming to fulfil the natural soils functionality, likely to evolve through soil formation processes and achieve efficient carbon stabilization. These technosols should be used in soil and water recovery processes, rock outcrops, landfill cover, areas affected by urban and infrastructures works, industrialized areas, mines and quarries, degraded silvicultural soils from erosion, fire or loss of production capacity, intensive forestry soils and non-food biomass crops (DOG, 2008).

Under the ITR/01/08 a technosol, which can be formulated from different wastes, free of ecotoxicity and some of them with specific limitations, must have structural and nutritional properties that guarantee their quality. A procedure is established for the admission of wastes as well as the characteristics of the technosols created. The application of technosols will require a case by case study and an administrative authorization of the Galician government. Additionally, specific cases involving applications of up to 2.500 t will be subjected to the environmental assessment procedures.

6.3.2. VALORIZATION OF WASTES IN SOILS.

The legal valorisation of organic wastes in soils can be possible following different routes in Galicia (Section 6.3.1). Available information at regional level about quantities of wastes often presents difficulties (Virtanen *et al.*, 2019). Nevertheless Figure 6.4 summarizes the estimated main streams of organic wastes valorised according the beforementioned routes.

Broadly speaking, major quantities come from agrarian activities, mainly manures, with nearly 15,24 Mt year-1, recycled almost entirely as fertilizers in soils by direct application. The remaining fraction, alongside with industrial biowastes, municipal solid (bio)wastes and sewage sludge are transformed in waste treatment facilities. In these facilities, about 52 % of non-recoverable wastes are removed by landfilling or incineration in SOGAMA (Sociedade Galega de Medio Ambiente, S.A.), society to which the majority of the municipalities are attached (295 out of 313) and where nearly 82 % of urban wastes of Galicia are managed (Comesaña *et al.*, 2017).

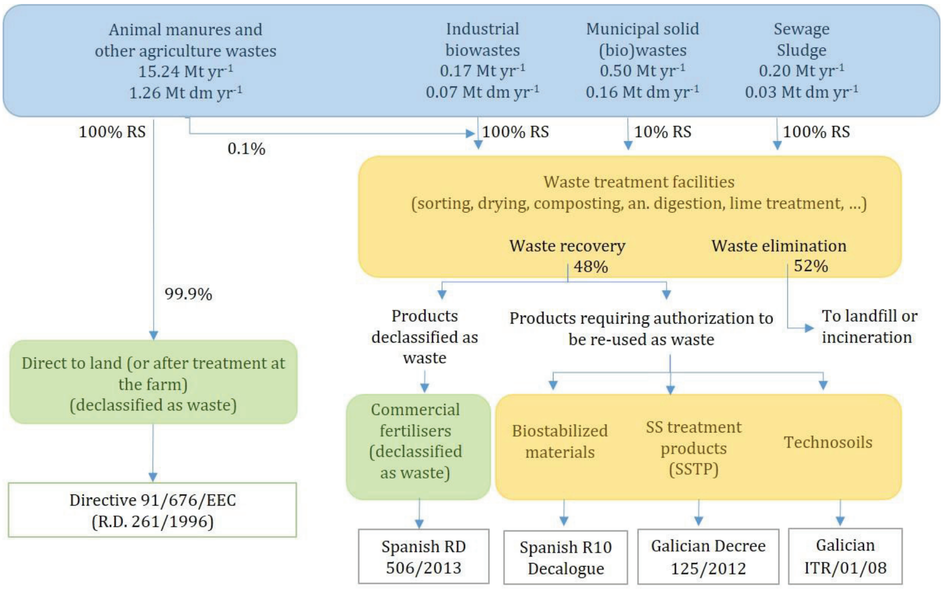

Figure 6.4. Flowchart of the main streams of wastes in Galicia. R.S.: Recovery separately. Source: Own elaboration from several sources (Xunta de Galicia, 2017, 2011).

The recovery rate of organic matter is estimated to be close to 48% in the waste treatment facilities, being produced commercial fertilizers, biostabilized material, SSTP or technosols (Figure 6.4). Commercial fertilizers have the highest added value and can largely relieve the pressure on the extraction of non-renewable resources from nature.

For the elaboration of fertilizers with an organic base, in Galicia a total of 50 types of waste are used, being the most frequently used those indicated in Table 3, present in some proportion, in more than 59% of commercial fertilizers. The most used, in correspondence with the quantities generated, are manure, as well as others from agriculture and forestry, sludges from treatment of urban waste water and waste from the agri-food industry.

Table 6.3. Organic wastes used for the preparation of commercial fertilizers in Galicia. Source: MAPA (2018).

WASTE CODE	 SINOPTIC DESCRIPTION	PRESENCE n	 %
020106	Manures	24	40,7
190805	Sludges from treatment of urban waste water	22	37,3
020204	Sludges from processing of meat, fish and other foods of animal origin	17	28,8
020103	Plant-tissue waste	16	27,1
020107	Wastes from forestry	12	20,3
020502	Sludges from on-site effluent treatment (dairy products industry)	9	15,3
020305	Sludges from on-site effluent treatment (wastes from fruit, vegetables and similar)	8	13,6
020203	Materials unsuitable for consumption or processing (foods of animal origin)	7	11,9
020702	Wastes from spirits distillation (alcoholic and non-alcoholic beverage industry)	6	10,2
200201	Biodegradable waste (garden and park wastes -including cemetery waste-)	5	8,5
020202	Animal-tissue waste (processing of meat, fish and other foods of animal origin)	5	8,5
020304	Unsuitable for consumption or processing (wastes from fruit, vegetables, etc.)	5	8,5
Others	Various	1-4	2-7

In the mixture of wastes for the elaboration of commercial fertilizers, the question to solve is if these treated wastes reach the minimum standards required in the Spanish R.D. 506/2013. If positive response, these fertilizers are excluded from the scope of the Galician Decree 125/2012, aside with composts achieving requirements contained in R.D. 865/2010, relative to growing substrates (not primarily intended for fertilization purposes and thus not studied in this paper) and technosols. If negative response, composts should follow the routes defined in the Decree 125/2012, the Spanish R10 Decalogue for the use of biostabilized material and composts not included in the Register of Fertilizer Products or the specification defined in the Galician ITR/01/08 for technosols.

6.3.2.1. FINAL PRODUCT REQUIREMENTS.

Before the application to soil, final products made from organic wastes must reach different legal requirements, variable according the normative they are influenced (Table 6.4). Some of these requirements depend on their properties (physical, chemical or biological) and others on exogenous factors (conditions of application or HM content of target soil).

Table 6.4. Comparison between different legal requirements for waste products before their application to soil in Galicia.

PROPERTIES	PARAMETER	Spanish R.D. 506/2013	Galician Decree 125/2012	Spanish R10 Decalogue	Galician ITR/01/08	EU Regulation 2019/1009	
		Commercial fertilizers	**SSTP**	**Biostabilized material**	**Technosols**	**Solid organic fertiliser**	**Organic soil improver**
Physical – chemical	Organic matter	> 35%	N.n.	≥ 25%	≥ 4%	Corg and nutrients of biological origin	95 % of biological origin
	Moisture content	< 40%	< 40% (composts) < 10% (thermic drying) < 80% (digestates)	20 – 40%	N.n.	n.d.	< 80%
	C/N	< 20	N.n.	< 20	> 12	Corg≥15%	Corg≥7.5%
	Inerts/impurities	Absence	N.n.	Impurities higher than 2 mm ≤ 3%	N.n.	n.d.	N.n.
	Ntotal	> 1%	N.n.	N.n.	N.n.	Variable	N.n.
	N organic	≥ 0,85 Ntotal	N.n.	N.n.	N.n.	n.d.	N.n.
	Macronutrients	> 1%	N.n.	N.n.	N.n.	Variable	N.n.
	Granulometry	> 90% through 25 mm sieve	N.n.	≥ 90% through 25 mm sieve Stones and gravels higher than 5mm < 5%	Stones and gravels ≤ 10% and < 50 mm	N.n.	N.n.
	Texture	N.n.	N.n.	N.n.	Silt loam or sandy loam	N.n.	N.n.
	Odours	N.n.	N.n.	N.n.	Absence	N.n.	N.n.
	Limits for specific contaminants	N.n.	N.n.	N.n.	Defined	N.n.	N.n.
	Limits for HMs lixiviation	N.n.	N.n.	N.n.	Defined	N.n.	N.n.
Presence of microorganisms	Salmonella (in 25 gr)	Absence	N.n.	Absence	Absence	Absence	Absence
	E. coli	< 1000 MPN/gr	N.n.	< 1000 MPN/gr	< 1000 MPN/gr	< 1000 MPN/gr	<1000 MPN/gr
Specific raw materials [a]	Furfural	0,05 %	N.n.	N.n.	Variable, depending on the type of raw material	N.n.	N.n.
	Polyphenols	0,8%	N.n.	N.n.		N.n.	N.n.
	Benzo-(a)-pyrene	N.n.	< 1 (mg/kg)	N.n.		N.n.	N.n.
	PAH $_{16}$	N.n.	N.n.	N.n.		N.n.	N.n.
	Size (inert materials)	N.n.	< 25 mm	N.n.		N.n.	N.n.
Stability	Self-heating test	N.n.	N.n.	Class III (or higher)	n.d.	N.n.	N.n.
	O_2 consumption index	N.n.	N.n.	N.n.	n.d.	N.n.	N.n.
Toxicity	Acute toxicity test (OECD 207)	N.n.	N.n.	N.n.	Fulfilment	N.n.	N.n.
	Terrestrial plants growth test (OECD 208)					N.n.	N.n.

Table 6.4.(continuation). Comparison between different legal final product requirements before their application to soil in Galicia.

PROPERTIES	**PARAMETER**	**Spanish R.D. 506/2013**			**Galician Decree 125/2012**		**Spanish R10 Decalogue**	**Galician ITR/01/08**	**EU Regulation 2019/1009**	
		Commercial fertilizers			**Treated wastes**		**Biostabilized material**	**Technosols**	**Solid organic fertiliser**	**Organic soil improver**
	Element	**Compost classification**			**Soil pH**					
		CLASS A	**CLASS B**	**CLASS C**	**< 7**	**≥ 7**				
HMs content (mg/kg.)	Cd	0,7	2	3	20	40	3	0.5	1.5	2
	Cu	70	300	400	1000	1750	400	200	300	300
	Ni	25	90	100	300	400	100	140	50	50
	Pb	45	150	200	750	1200	200	100	120	120
	Zn	200	500	1000	2500	4000	1000	250	800	800
	Hg	0,4	1,5	2,5	16	25	2,5	0.5	1	1
	Cr	70	250	300	1000	1500	300	150	N.n.	N.n.
	Cr (VI)	u.d.l.	u.d.l.	u.d.l.	n.r.	n.r.	N.n.	0.1	2	2
	As	n.r.	n.r.	n.r.	n.r.	n.r.	N.n.	100	40	40
Soil application conditions		Indirectly specified (CGAP)			Directly specified		To specify in authorization request	Partially specified	N.n.	
Target soil HMs analysis		N.n.			Yes		< 5 t d.m ha^{-1} : Literature references > 5 t d.m ha^{-1} : Soil analysis	N.n.	N.n.	
Raw materials treatment		N.n.			Specified		N.n.	N.n.	N.n.	

N.n. Not necessary; u.d.l. under detectable limits; [a] Presence related to the characteristics of input materials.

There are no specifications for manures, except the voluntary application of CGAP.

In terms of the recirculation of nutrients, CE promotes closed loops of organic wastes as sources of amendments of fertilizers (Toop *et al.*, 2017). Considering this, regulations directly related with this topic are Galician Decree 125/2012 and Spanish R.D. 506/2013. Comparatively and regarding quality assessment as fertilizers, legal requirements of SSTP are much laxer than for the other products. Aspects such as nutrients content, C/N ratios or impurities are irrelevant. Thus, it can be inferred that Galician Decree 125/2012 is not finally aimed to obtain a fertilizer but a material ready to its disposal to soil, specifically with no adverse effects on the environment. At this respect, the presence of microorganisms, stability or toxicity are omitted by the Galician normative, in which the final safety conditions rest on mandatory treatments as methods to achieve the hygyenization. However, treatments not always ensure fertilization in safety conditions (Zhang *et al.*, 2019).

With respect to the HMs content and considering acidic soils, which are the majority in Galicia, limits are considerable higher, and thus more permissive, for SSTP than for any other product, even for these of class C commercial fertilizers. Considering that the total amount of SSTP applied to soil is partially determined by their N and/or P content and that no minimum content of these nutrients is required, it could be possible that soils could receive great amounts of SSTP with low nutrient and organic matter content, but with variable, from low to very high HMs content. In the case of manures, there is no current legal limitation about their HMs content with fertilization purposes despite it can be considerably high. Finally, the recent Regulation 2019/1009 establishes more stringent limits and the upcoming EU fertilizers will be more stringent than present class B Spanish fertilizers. This will lead to a more careful selection of those raw materials intended to be used, alone or in combination, as fertilizers. Thus, in accordance with (Chojnacka *et al.*, 2019), under a CE perspective it will be necessary to introduce selective waste collection, increase the efficiency of nutrient recovery and obtain a more concentrated form with good bioavailability.

Biostabilized materials, and more clearly technosols, are not primary intended for fertilization or agronomic purposes. In the fist case, materials are non-quality biotransformed products that in other Autonomous Communities (e.g. Valencia in SE Spain) regional laws that allowed their use as fertilizers were judicially denounced against the Spanish Constitutional Court by environmental organizations.

6.3.2.2. APPLICATION PRACTICES.

The addition of organic materials to soil must be submitted to different conditions which can be very different from each other (Table 6.5). The most restrictive buffering distances were established for SSTP whereas they are not defined for biostabilized materials. Similarly to final products requirements, HM content in soils is considered as a limiting factor for some products.

Table 6.5. Conditions to be considered prior to soil application of products according to legislation. Conditions for manures are the same as for commercial fertilizers but they are optional. No conditions established for EU fertilizers regulation.

PARAMETER	DETAILS			Spanish R.D. 506/2013 Commercial fertilizers	Galician Decree 125/2012 Treated wastes	Spanish R10 Decalogue Biostabilized	Galician ITR/01/08 Technosols
Distances (m)	Water bodies[a]	Public supply	Yes	> 30 - 50	> 200	No buffering distances established	Prohibited for groundwaters, header and river banks
			No	> 2 -10	> 50		
		Traditional bathing areas		Not considered	> 250		
		Water tanks and closed conduits		Not considered	> 15		
	Buildings	Residential, industrial, sport or recreational areas		Not considered	> 250		No buffering distances established
		Agricultural		> 100	> 100		
	Elements of cultural interest			Not considered	> 250		
	The Way of Saint James			Not considered	> 30		
Terrain requirements	Slope			< 20%	≤ 25 %	No references	No references
	Forestland conditions			No references	Cleared of scrub and tree spacing	No references	Prohibited for climax forests, protected and singular natural areas, meadows, etc.
	Land uses			Agricultural or forest land	Defined in SIXPAC[c]	Agricultural or forest land	
Quantitative limits (kg/ha year)	Nitrogen			N or P are not considered. Limit is 5.000 d.m. basis (Class C fertilizers).	45 -250 [b]	N and P, not considered. Need to justify if higher than 5.000 d.w. basis (agricultural use).	No references
	Phosphorous				50 - 100 [b]		
	Limits of HMs in soils			Not established	Established	Established	Not established
Agronomic techniques	Consideration of periods of appropriate fertilization			Yes	No	Case by case study. Detailed description required in the authorization request	No
	Considerations for fertilization near water courses, steeply sloping, water saturated, flooded, frozen or snow-covered soils			Yes	Prohibition on water saturated soils		Prohibition on water saturated soils
	Guidelines on crop rotation and minimum quantity of vegetation cover during certain periods			Yes	Prohibited periods after SSTP application		No
	Recommendations to control nutrient losses to water bodies			Yes	No		No
	Consideration of pollution prevention with irrigation systems			Yes	No		No
	Mandatory fertilization plans			Yes	No	Yes	No

[a]Mandatory and binding report from Hydraulic Agencies needed. [b] Ranges dependent on different crop cultivation (arable and woody crops, natural or non planted forage utilization areas, forest areas). In italics for R.D. 506/2013, direct consideration in the legal text. [C] Agricultural Plots Geographical Information System (https://sixpac.xunta.es).

The agricultural application of biostabilized materials or technosols should be carried out after a case by case study assessed by the regional Agency.

Approaches of Galician Decree 125/2012 and Spanish R.D. 506/2013 are markedly different. Protective buffering distances are higher for SSTP. Decree 125/2012 also considers other singular elements to protect and increases the total soil target surface by raising land slope limit to 25% (20% for commercial fertilizers), allowing forestland application (two thirds of total surface of Galicia) as well as defining susceptible plots allowed for receiving SSTP (in practice, this is carried out through land uses established in the Agricultural Plots Geographical Information System, which makes all uses permitted, with the exception of water bodies and unproductive areas).

Regarding MPL, enforcement of regulations can be a difficult task (specially when organic wastes are applied in a liquid form) as non-compliance can only be determined by observing some act of violating rules (Ortolano *et al.*, 2009). More frequently, the consequences of these acts become apparent as physical disturbances in the environment, sometimes reported in the media.

Galician Decree 125/2012 establishes the maximum loading rate by lowest value of the following 3 calculations: a) SSTP HMs load (kg ha^{-1} year^{-1}, same tabulated values than SS Spanish normative); b) maximum N loads (kg ha^{-1} year^{-1}, tabulated values depending on great groups of crops); c) maximum P loads (kg ha^{-1} year^{-1}, tabulated values depending on great groups of crops). R.D. 506/2013 only limits to 5 t ha^{-1} year^{-1} the class C fertilizers and derives the fertilization conditions (for all fertilizers) to the CGAP, intended primarily to avoid nitrates pollution from agriculture practices. In this manner, in spite that the state legislation makes the CGAP compulsory for commercial quality composts, the Galician normative does not requires it for SSTP application and makes it optional for manures.

Similarly, agronomic techniques are only established for Spanish commercial fertilizers. In the rest of cases (Table 6.5), they are expressed in the form of prohibitions (SSTP and technosols) or subjected to case study (biostabilized material).

6.3.3. GALICIAN SEWAGE SLUGE REGULATION.

6.3.3.1. IMPLICATIONS ON WASTE RECOVERY.

SS is a waste characterized by its high levels of HMs, usually higher than materials from other sources (López-Mosquera *et al.*, 2005). In Europe, the question regarding whether the extension of SS Directive onto other organic wastes, when sufficiently justified, was discussed in Sludge and Biowaste Working Document (EC, 2010). In Galicia, with the publication of Decree 125/2012, such doubts were elucidated by making extensible the rules for SS to other organic waste intended to be applied to soil as fertilizer. Thus, Galician Decree fixes the same mandatory conditions for raw materials whose properties might be completely different from SS.

As a consequence, these mandatory conditions could represent an obstacle to the multiple beneficial effects derived from the addition of organic amendments on soil (Diacono and

Montemurro, 2010) or a loss of opportunity that represents the waste valorisation versus others less desirable in the model hierarchy in waste management (landfill disposal or incineration). In Galicia, the recycling of organic wastes, with no previous treatment, proved positive effects on soil fertility. Mussel shell can act as a substitutive of lime, avoiding environmental effects arising from lime extraction (Álvarez *et al.*, 2012a, 2012b), or can be used as pollution control agent in the copper-enriched vineyards soils (Garrido-Rodríguez *et al.*, 2013). Mussel shell was also added to soils in combination with cattle slurry, enhancing their biological and chemical properties with no adverse effects (Paz-Ferreiro *et al.*, 2012). Similarly, ash with charcoal from biomass plants (Santalla *et al.*, 2011) and mixtures with other organic wastes (Pousada-Ferradás *et al.*, 2011) can act positively as fertilizers and liming agents for agricultural and forestry use. Lowering solubility of HMs, alkaline wastes reduce the risks of water pollution (Pousada-Ferradás *et al.*, 2012). Scientific literature contains other additional references to the recovering of organic wastes with beneficial agronomic purposes in the region (Pérez-Cruzado *et al.*, 2011; Seco-Reigosa *et al.*, 2014; Merino *et al.*, 2016; Solla-Gullón *et al.*, 2008). Thus, these practices are no longer feasible after the promulgation of Decree 125/2012, since it required mandatory treatment before their valorisation as a fertilizer in agricultural soils. The economical costs of these treatments suppose additional costs that could discourage the recovery of the nutrients and OM contained in wastes. On the other hand, some allowable treatments may not be technically necessary with certain streams of wastes (thermal drying, e.g., in the case of ashes).

6.3.3.2. HEAVY METALS RESTRICTIONS IN SOILS.

Regarding HMs limits in soils, SS Galician Decree 125/2012 took the same values than the Spanish R.D. 261/1996 (transposition of the Nitrates Directive) despite soils as well as climates in Galicia are very dissimilar from those in other parts of Spain, especially in the southeast areas, the driest in Europe.

At a supranational scale, the implementation of EU legislation may differ widely (EC, 2014) as most Directives and Regulations are legislative documents that need to be applicable throughout the wide range of climates, soils, ecosystems and agricultural practices present in the EU (Vrebos *et al.*, 2017). De Clercq (2001) exposed that bordering countries may face environmental concerns in a completely different manner from a legislative approach. Thus, of interest for this case study, the North Portuguese and Galician soils, both in adjacent territories (Figure 1c), present greater similarities than other Spanish soils (EC, 2005).

However, differences in legal HM soil limits exists between Portugal and Galicia/Spain (Table 6.6). Whereas Galician/Spanish legislation only distinguished between acidic and basic soils, Portuguese legislation (Diário da República, 2009) introduced an intermediate 5,5 – 7,0 pH range for moderate acidic soils with more tolerant limits. Such soils could be assimilated to those of Galicia where agriculture practices, as liming, led to a raise in pH (Conde-Cid *et al.*, 2018). This means that in Portugal, the possibility of recovering organic waste, because of the natural HM concentration in soils, is expanded. The limits fixed in Portugal for moderate acidic soils would be above the natural Galician HMs (Table 6.6). In the end, Portuguese normative considered a strongly acidic range (pH<5,5), representative of Galician forestland soils. In this last case, Portuguese legislation presents the same values (except for Cr) than Galician/ Spanish legislation (Table 7). For pH>7 limits in Portugal are less restrictive than in Galicia/Spain, but as in Galicia, Portuguese soils are mainly acidic.

Table 6.6. Comparison among different legislative HMs limits (mg kg^{-1}) in soils for wastes valorisation and reference values in Galician soils (Macías and Calvo de Anta, 2009).

Normative	Soil pH	Cd	Cu	Ni	Pb	Zn	Hg	Cr
Europe [a]	6 – 7	1 -3	50 – 140	30 – 75	50 – 300	150 – 300	1 – 1.5	-
Galicia/Spain	<7	1	50	30	50	150	1	100
	>7	3	210	112	300	450	1.5	150
Portugal	≤5,5	1	50	30	50	150	1	50
	5,5<pH≤7	3	100	75	300	300	1,5	200
	>7	4	200	110	450	450	2	300
Galician soils reference values[b]		0,11	20,61	55,83	29,32	60,29	0,07	80,25

[a] If sludge were applied in soils with pH<6, EU Member States should take into account the increased mobility of HMs and, where necessary, reduce the limit values they have fixed in accordance with Annex I A. [b] Reference values (Macías and Calvo de Anta, 2009).

In Galicia, MPL of HMs in soils may face the recycling of the SSTP as the mean soil concentration are close (Hg, Cr) or higher (Ni) than the stablished limits (Table 6.6). Even thresholds for Cu, Pb, and Zn can be achieved in natural soils when settled under determinate rocks (see italicized bold values in Table 1). Only soils settled on sediments and granites would be plenty appropriate for the recovery of organic amendments as fertilizers (Barral and Paradelo, 2011; Figure 6.2). This legal approach can limit the recovery of organic wastes as fertilizers, compromising the action proposal of reusing organic wastes that can be returned to the soil as fertilisers included in the Galician CE Strategy (Xunta de Galicia, 2019). Of course, this limitation do not works in the absence of controls on the compliance of the established rules or if controls result inefficient. As indicated, enforcing rules is a difficult task and non-compliance is very possible (Ortolano *et al.*, 2009).

Average of natural Cr content in Galician soils rounds the 80% of its MPL and Ni content presents a higher value (55,83 mg kg-1) than the MPL (Table 6.6). Regarding this Ni value, previous studies in A Coruña province determined soil Ni oscillations in the wide range of 3,05 – 2.239 ppm, with average values of 118,24 ppm (Carballas *et al.*, 1965), almost double than the value reported for Galicia in 2009 (Table 6.1). This could be due to particularities in lithologies of A Coruña province. In Galicia, the HM distribution in soils is highly dependent on the geological material they are settled (Carballas *et al.*, 1965; Macías and Calvo de Anta (2009).

It also should be noted that HMs content on agriculture soils might exceed their natural levels due to previous agricultural activities (Roudposhti *et al.*, 2016). At this respect, Mosquera-Losada *et al.* (2017) suggested that over 90% of the Galician soils are suitable to receive SS under the current HMs regulations. This was because the soil samples studied by Mosquera-Losada *et al.* (2017)

were under the baseline levels of Galicia (Macías and Calvo de Anta, 2009) and thus concluded that SS fertilization was possible without a significant increase of the usual levels of HMs if SS contained low HMs level and adequate doses are applied. In comparison, other authors found higher levels of HMs on agricultural soils, and evidence of contamination by Cu and Zn due to the traditional use of animal manures as fertilizers (Paz-Gonzalez, 2000; López-Alonso, 2000).

In the main wine production areas of Galicia, covering a 33.273 ha of land, Fernández-Calviño *et al.* (2009) found total Cu concentrations that largely exceeded (from a factor of 2 to up to 5) the 50 mg kg^{-1} threshold defined in Table 6.6. Current regulation would restrict the recovery of regional treated wastes because of the HMs content in these vineyard soils. This is a key consideration as soils in the vineyards of the region are characterized by a low OM content (Fernández-Calviño *et al.*, 2009) and on the other hand, Cu immobilization by OM is a common technique that results in reducing Cu soil solution and subsequently, the toxic effects on microbiota (Kabata-Pendias and Mukherjee, 2007). In this particular case, in the region crushed mussel shell has shown beneficial effects in reducing Cu bioavailability and enhancing soil properties (Garrido-Rodríguez *et al.*, 2013; Fernández-Calviño *et al.*, 2017).

Conversely, from a legal point of view these vineyards would admit inorganic fertilizers, commercial amendments or manures, despite HMs accumulation in soil by MSW composts (Domínguez *et al.*, 2019) or manures (Feng *et al.*, 2018; Lipoth and Schoenau, 2007; Tiecher *et al.*, 2013), or even result in toxicity for cattle manure as reported by López Alonso *et al.* (2000) in Galicia.

In the same manner, inorganic fertilizers might content HMs in upper concentrations to those marked in regional legislation for treated wastes, as in Cd reported by Loganathan and Hedley (1997). For this particular element, Cd, the so recent Regulation (EU) 2019/1009 on fertilizers has already been questioned as its dispositions are considered insufficient alone in reducing the Cd accumulation in EU soils (Marini *et al.*, 2020). In the meantime, in Galicia there are no restrictive limits for the use of inorganic fertilizers although some European countries have developed legislative restrictions in their heavy metal content, both for agriculture and forestry application (e.g. Finland, (Ministry of Agriculture and Forestry, 2011)).

6.3.4. CHARACTERISTICS OF ORGANIC MATERIALS.

6.3.4.1. DATA COMPILED.

Data from organic materials produced in Galicia was collected (Table 6.7). Regarding commercial fertilizers, 51 fertilizers were accounted (8 corresponding to class A, 35 to class B and 8 to class C). After data screening, 27 were considered for quantitative prospection since nutrients and HMs values were available (subgroups I to IV in Table 6.7). The 24 items removed were excluded due to the absence of NPK information (or provided in a too broad range, e.g. 2-22% N) and secondly, HMs values matched the legal limit threshold linked to the respective class, suggesting data not based on real analytical results but considered values in the absence thereof. These deficiencies affected 8 class C fertilizers and another 16 belonging to class B. Medium values are offered after grouping fertilizers in two ways: HMs content (class A or B) and type of fertilizer (organic fertilizer or amendment).

Data for SSTP is concerned to various facilities registered in Galicia according to Decree 125/2012, presenting two different management systems: anaerobic digestion and lime stabilization. Mean values correspond to information declared to the regional Agency in 2017 (subgroups SSTP1 to SSTP3 in Table 6.7).

The search for treated wastes from peer-reviewed articles (P-R articles) concluded with the selection of 76 characterizations, from which only 50 were considered. 26 items were discarded for two reasons: very incomplete characterization of the interest properties (19 removed) and duplicates since same properties resulted in more than one different paper (7 removed). Selected items were clustered into subgroups V to XII considering initial raw materials and/or type of applied treatment as indicated in Table 6.7.

At a first glance it can be observed similar total HMs values between commercial fertilizers and P-R articles (103±40%). Both groups are very dissimilar from SSTP and comparisons established revealed important differences: a) 13,8±13,5% of average values of P-R articles, <10% of total content of P-R articles in the case of Ni, Pb or Hg and from 18 to 32% for Cu, Cd and Zn; b) <13% of total HMs and <3% of Ni, Pb, Hg and Cr of anaerobic SS from P-R articles; c) only 26-60% of Cu, Cd and Zn of composted SS from P-R articles. Ni, Cr or Pb concentrations of 0 mg/kg in SSTP are confusing when characterizations of natural phytomass from the region presented higher values (Arias *et al.*, 2019, 2017) thus, and in the absence of supplementary information on raw materials that resulted in the SSTP, these values (subgroups SSTP1 to SSTP3 according to Table 6.7) were excluded from further analysis.

Table 6.7. Characteristics of organic materials produced in Galicia (HMs in mg kg^{-1}).

Organic material	Subgroup	n	TS %	VS %	N%	P%	K%	Cd	Cu	Ni	Pb	Zn	Hg	Cr
Commercial fertilizers (Spanish R.D. 506/2013, n=32)[a]														
Class A (7 org. amendment +1 org. fertilizer)	I	8	66,1	51,3	2,0	0,69	1,24	0,34	46,8	14,1	12,2	92,7	0,23	19,5
Class B (17 org.amendment +7 org fertilizer)	II	19	71,3	47,9	2,4	1,06	1,05	0,76	147,5	18,5	30,6	366,1	0,32	23,7
Organic amendment (7 class A + 17 class B)	III	21	66,6	45,6	1,9	0,77	0,87	0,60	121,7	18,3	30,8	246,4	0,28	25,1
Organic fertilizer (1 class A + 7 class B)	IV	6	80,8	60,2	3,3	1,59	1,94	0,75	103,7	13,2	5,3	420,5	0,35	12,9
Total fertilizers	I-IV	**27**	**69,8**	**48,9**	**2,24**	**0,95**	**1,11**	**0,64**	**117,7**	**17,2**	**25,1**	**285,1**	**0,29**	**22,4**
SS Treated Products (Galician Decree 125/2012)[b]														
SSTP-Anaerobic digestion	SSTP1	n.a.	21,26	57,50	6,00	0,12	0,80	0,00	50,00	0,00	0,00	412,00	0,00	0,00
SSTP-Lime stabilization 1	SSTP2	n.a.	34,40	13,20	0,12	0,03	0,04	1,00	3,00	1,00	1,00	19,00	0,00	3,00
SSTP-Lime stabilization 2	SSTP3	n.a.	26,90	8,40	1,16	0,00	0,02	0,00	7,00	0,00	3,00	41,00	0,00	0,00
Mean SSTP	SSTP1-3	**n.a.**	**27,5**	**26,4**	**2,43**	**0,05**	**0,29**	**0,33**	**20,0**	**0,33**	**1,3**	**157,3**	**0,00**	**1,0**
Peer-Reviewed Articles (n=50)[c]														
Anaerobic SS	V	8	38,7	n.a.	2,95	1,27	0,24	1,17	185,3	51,1	144,3	1197,5	n.a.	60,2
Composted SS	VI	5	54,5	32,7	1,55	0,89	1,73	0,62	77,7	35,8	41,5	262,5	0,12	48,7
MBT (biostabilized MSW)	VII	3	63,6	45,9	1,63	0,21	1,74	3,37	493,0	62,9	199,6	788,5	0,58	79,1
OFMSW compost	VIII	3	75,0	51,9	2,00	0,25	2,42	0,89	129,3	31,0	130,3	436,7	n.a.	31,7
Local compost	IX	8	37,5	59,1	2,16	0,52	1,46	0,65	32,9	21,8	19,7	143,9	0,08	50,3
Green waste compost and various	X	9	61,2	63,9	2,16	0,36	0,67	0,17	22,9	7,9	12,3	130,3	0,04	9,7
Green waste and pig slurry compost	XI	8	33,3	56,6	2,09	0,30	0,12	0,12	15,7	14,2	2,7	72,4	0,03	18,4
Solid fraction pig manure compost	XII	6	33,4	51,3	1,74	2,05	1,44	0,13	153,5	12,9	9,6	2190,7	0,01	8,6
Mean (literature review)	V-XII	**50**	**42,8**	**55,1**	**2,12**	**0,85**	**1,00**	**0,70**	**106,8**	**26,5**	**54,0**	**612,3**	**0,06**	**35,4**

[a] MAPA, 2018. [b] Xunta de Galicia, 2018. [c] Arias *et al.*, 2017; Arias *et al.*, 2019; Barral Silva *et al.*, 2007; Comesaña *et al.*, 2017; Domínguez *et al.*, 2019; Estévez-Schwarz *et al.*, 2009; Ferreiro-Domínguez *et al.*, 2018; Forján *et al.*, 2018; Illera-Vives *et al.*, 2013; López-López and López-Fabal, 2016; López-Mosquera *et al.*, 2011; López-Mosquera *et al.*, 2008; Mato *et al.*, 2019; Moldes *et al.*, 2007; Mosquera-Losada *et al.*, 2019; Mosquera-Losada *et al.*, 2010a; Paradelo *et al.*, 2017; Paradelo *et al.*, 2008; Rigueiro-Rodríguez *et al.*, 2018; Vázquez *et al.*, 2015a, 2015b, 2017; Vázquez and Soto, 2017. n.a Not available.

Table 6. 8. Heavy metal concentration indicator (CI_{HM}: relative HM concentration to Class A limit concentration of commercial fertilizers) for subgroups I to IV (commercial fertilizers) and subgroups V to XII (peer-reviewed articles).

Subgroup [a]	Cd	Cu	Ni	Pb	Zn	Hg	Cr	Mean CI_{HM}	Mean CI_{HM}/x_{VS} [b]	Mean CI_{HM}/x_N [b]	Class	Class: HM>0,6 [c]
I	0,486	0,669	0,564	0,271	0,464	0,575	0,279	0,472	0,92	23,6	A	A: Cu
II	1,443	2,561	1,332	1,231	1,970	1,400	1,011	1,564	3,29	68,0	B	B: Zn
III	1,114	2,056	1,092	1,013	1,390	1,075	0,760	1,214	2,71	63,9	B	None
IV	1,500	2,181	1,296	0,922	2,202	1,575	1,031	1,530	2,52	47,8	B	B: Zn
I-IV	1,200	2,087	1,140	0,991	1,593	1,200	0,827	1,291	2,67	58,7	B	B: Zn
V	1,671	2,647	2,044	3,207	5,988	0,000	0,860	2,345		79,5	>C (C except Zn)	C: Cd [d], Pb
VI	0,886	1,110	1,432	0,922	1,313	0,300	0,696	0,951	2,91	61,4	B	None
VII	4,814	7,043	2,516	4,436	3,943	1,450	1,130	3,619	7,88	222,0	>C (C, except Cd,Cu)	C: Ni, Pb, Zn
VIII	1,271	1,847	1,240	2,896	2,184	0,000	0,453	1,413	2,72	70,6	B	B: Pb, Zn
IX	0,929	0,470	0,872	0,438	0,720	0,200	0,719	0,621	1,05	28,7	A	A: Cd, Ni, Zn, Cr
X	0,243	0,327	0,316	0,273	0,652	0,100	0,139	0,293	0,46	13,6	A	A: Cd [d], Zn
XI	0,171	0,224	0,568	0,060	0,362	0,075	0,263	0,246	0,44	11,8	A	None
XII	0,186	2,193	0,516	0,213	10,954	0,025	0,123	2,095	3,96	116,7	>C (B, except Zn)	B: None
V-XII	1,000	1,526	1,060	1,200	3,062	0,150	0,506	1,215	2,20	57,3	C (B, except Zn)	B: None

[a] Material code according Table 6.7. [b] X_{VS} and X_N are the fraction of VS and N on dry basis (%/100). [c] Other HM near the limit of the indicated Class. [d] Cd if outliers are considered.

6.3.4.2. COMMERCIAL FERTILIZERS.

A regression analysis of data from commercial fertilizers suggests significant ($p <0,05$) but weak (R^2 ranged from 0,15 to 0,46) correlations between various parameters. Extending the analysis to those commercial fertilizers firstly excluded because of their limitations, correlations are much stronger, but this is caused by the fact of assigning the maximum values of each class and thus, results are not considered valid. Among HMs correlations, it is highlighted Ni with Hg and Cr as well as Cu with Zn ($R^2 > 0,3$). Cu presents correlations with the largest number of metals (Ni, Pb, Zn and Hg). On the other hand, VS correlate with N, K, and Ni, but not with P, and N, P, and K correlate with each other. The strongest correlation occurs between P and K ($R^2 = 0,46$, $p < 0,000$).

Among subgroups, N content is slightly higher in class A than B fertilizers (subgroups I and II with respective average values of 2,0 and 2,4%, significantly not different, $p = 0,4$), and clearly higher for organic fertilizers compared to organic amendments (subgroups IV and III with respective average values of 3,3 and 1,9%, significantly different, $p < 0,000$). P/N and K/N showed global mean ratios of 424 mg P gN^{-1} and 495 mg K gN^{-1}, and for the indicated subgroups they varied in the respective ranges of 349-477 and 448-628, but not significantly ($p > 0,09$). This indicates that the commercial fertilizers present similar NPK ratios.

Relative to HMs, class B fertilizers presented higher concentrations than class A, in a factor ranging from 1,2 to 4,0 depending on the metal considered (average value of 2,3), while organic fertilizers and organic amendments showed more similar contents (average ratio of 0,92) although variable among metals relations (range from 0,17 to 1,71). On the other hand, comparing HMs and N content (HM/N ratios) for organic fertilizer was lower than that of organic amendments (ratio 0,53, range 0,1-1,0), while class B fertilizers (subgroup II) provide almost twice HMs (average ratio of 1,9, range 1-3,3) than those of class A (subgroup I).

Therefore, when trying to minimize the HMs entry into the soil, class A fertilizers are obviously preferable but most of them correspond to amendments and not with fertilizers. In addition, Class B fertilizers would provide less HMs per unit of N than Class A amendments, but this may be caused by the removal of entries with higher values (those equal to the class limit, considered inaccurate). In short, the fact that a significant percentage of items rescued from the national database (MAPA, 2018) are unreliable or lack several parameters, makes it impossible to draw certain conclusions about the relative contribution of HMs, nutrients and organic matter to soils.

6.3.4.3. PEER-REVIEWED ARTICLES.

In relation to subgroups V to XII corresponding to P-R articles (Table 6.7), Figure 6.5 describes their HMs content in relation with upper limit of class A commercial fertilizers which would be represented by a value of 1,0 in the vertical Y axis. Subgroups X and XII present mean values and 75% percentiles lower than limits for Class A in all cases, as well as subgroup IX although in this case the third quartile is over the unit value in most cases. Subgroups VI and VIII overcome the class A limit and would be mostly under the class B limit (relative value to class A of 3,4 and range from 2,5 to 4,3, depending on the metal considered). Remaining subgroups, VI, VII and XII clearly overcome class A and even class B limits, showing a class C quality or worse. This question is shown against a majority of metals (subgroups V and VIII), or only attributed to Zn (subgroup XII).

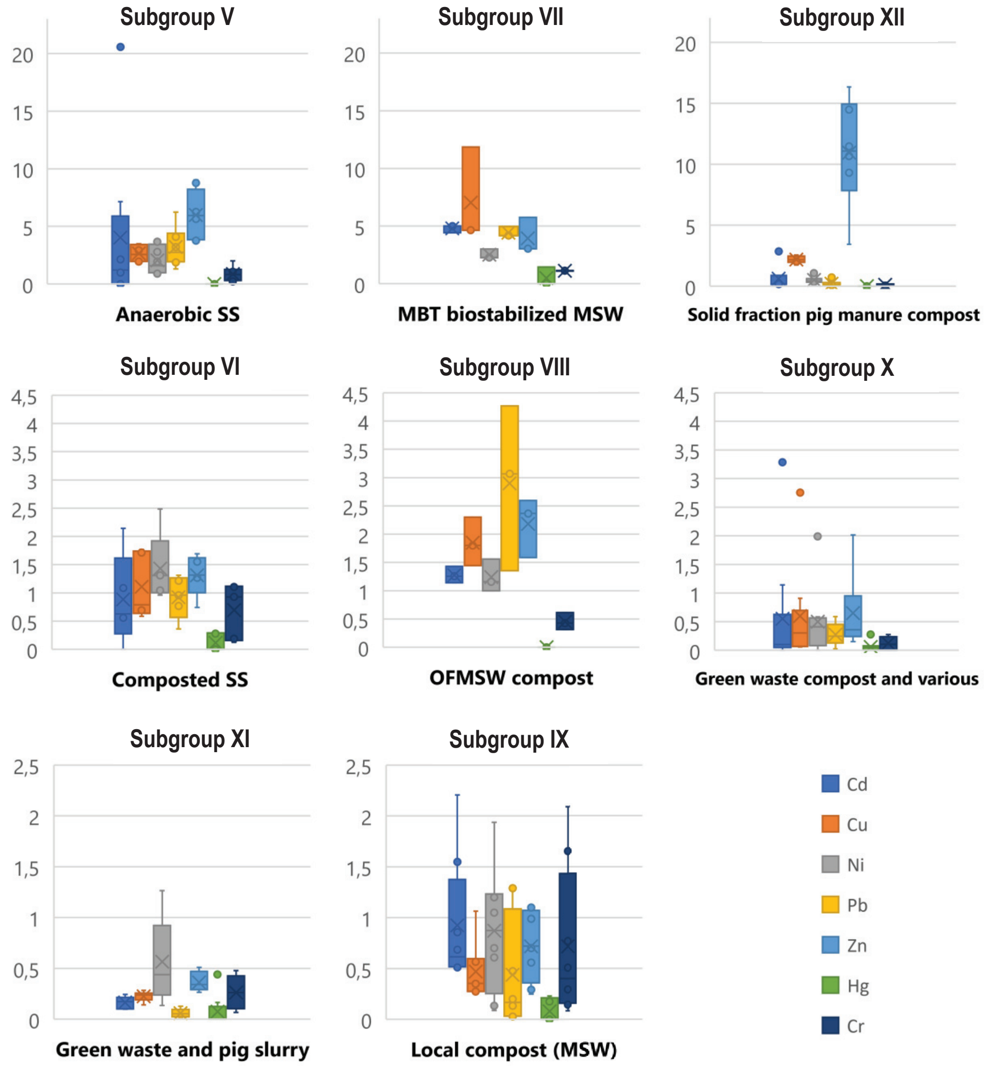

Figure 6.5. Boxplot with characterizations of treated wastes extracted from P-R articles (relative HMs content in relation to commercial fertilizers class A limit (value=1)). In the boxplot a cross represents the mean value and the horizontal line the median.

Outliers (corresponding to subgroups V (Cd), X (Cd, Cu, Ni) and XII (Cd)) were removed to obtain the average values contained in Table 6.7, as well as further analysis (Table 6.8 and Figure 6.6).

Considering HMs as a whole, there is correlation with Pb and the rest of metals, and weaker with Cu, Ni e Zn. Nevertheless, these correlations are influenced by the heterogeneity of wastes from very diverse origin and thus, results must be considered as estimates. For instance, in subgroup XII, the solid fraction pig manure compost presents very high concentrations of Zn and Cu whereas the rest of HMs considered are quite low, thus affecting clearly the aforementioned correlations (Figure 6.5).

6.3.4.4. INDICATORS TO CIRCULAR ECONOMY CONTRIBUTION.

The recovery of nutrients from bio-products processed from waste constitutes a priority of CE and thus it is necessary to develop quality parameters (EU, 2015). These parameters should measure the nutrient capacity (fertilizer properties), the addition of organic matter (amendment to improve soil quality and carbon sequestration) and the introduction of potentially toxic substances (such as HMs in high concentrations).

N is the most demanded nutrient for most crops and the most widely used indicator in the evaluation of intensive agriculture (Ruiz-Martinez *et al.*, 2015). At the other end, HMs are the common limiting factor in the normative affecting the addition of organic materials to soil (Table 6.4) and indexes relative to their addition to soil from organic wastes applied as fertilizers in agriculture have been also developed (Lopes et al., 2011). Under a CE context, a good indicator would be the HM/N ratio which would evaluate the HM input in relation to fertilizer capacity. Another indicator would be the HM/VS ratio. The information selected in Table 6.7 contains HMs, N, and SV data for almost all entries, except SV in the case of data from P-R articles, in which only 31 of 50 entries contain this information. The use of the HM/VS index should be accompanied by a high stabilization of the organic material, an aspect that is not always guaranteed and for which there is no quantitative information for most entries.

In order to account on a simple indicator, the concentration of each heavy metal was transformed into the respective concentration relative to the upper limit of the class A commercial fertilizers. In this way, each metal is characterized by a concentration indicator (CI) comparable to that of the other HMs depending on the relative risk assigned by the respective normative. The CI values for each HM and subgroup are presented in Table 6.8. The average of all CI values provides an unique chemical quality index (pollution) for a determined material. The equations that define these indices are:

$\mathbf{CI_{HMi}}$ = Conc. HMi concentration / Class A limit HMi; i= Cd, Cu, Ni, Pb, Zn, Hg, Cr

$\mathbf{CI_{HM}}$ = SUM (HMi concentration / Class A limit HMi) / SUM (i); SUM (i) = 7

Considering these indexes, a material could be considered class A when:

$CI_{HMi} < 1$, for every single metal i

In this way it can also be applied, as necessary but not sufficient condition:

$CI_{HM} > 1$

A similar procedure can be carried out to know the quality of the material, but depending on the limits of all classes, A, B and C (data not shown). This allows the material to be classified within the corresponding quality class. The limits for classes B and C vary slightly from one metal to another, reaching mean values relative to class A of 3,4 ± 0,6 (Class B) and 4,9 ± 0,8 (Class C). On the other hand, the limits for Decree 125/2012 vary more widely, with an average value relative to Class A of 19,8 ± 10,6 (case of soils with pH <7) and 32,7 ± 18,9 (soils pH> 7), while the new EU Regulation 2019/1009 is 3,1 ± 0,9 (see Figure 6.6, upper part).

According to Table 6.8, the commercial fertilizers correspond to classes A and B. We must not forget that due to the lack of analytical data for many of the materials registered in the database, many of the materials included in the analysis were excluded from this analysis. same. In the set of selected samples, the metal closest to the class limit is Zn (class B), and Cu (class A).

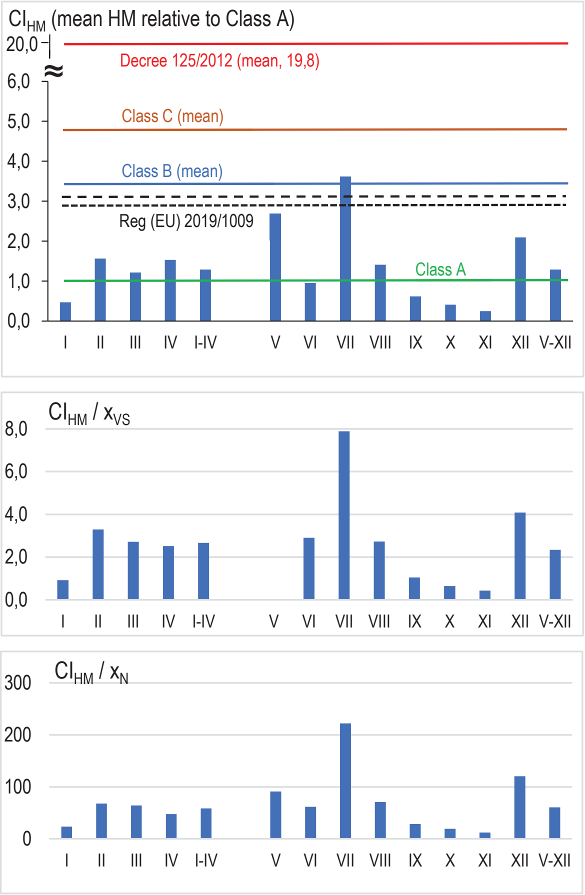

Figure 6.6. HMs concentration indicator (CI$_{HM}$, including diverse normative limits) and ratios between this indicator in SV and N for the different subgroups (Table 6.7).

The information obtained from the P-R articles is broader, and presents all the qualities depending on the type of materials. Subgroups IX (local composting of OFMSW), X (compost from green waste and other materials such as some manures or algal waste) or XI (Green waste with pig slurry) reach class A. Cd and Zn are the metals closest to the class limit, followed by Ni and Cr. Two types of materials have class B: VI (Composted SS) and VIII (industrial composting of FORM), the last with Pb and Zn near the limit value of class B. None of the materials could be classified as class C, with three types exceeding this class due to Zn (V: SS digestate; XII: compost from solid fraction of pig manure) or to Cd and Cu (VII: MBT biostabilized MSW). SS digestate and biostabilized MWSW also presented higher concentrations of Cd and Pb, and Ni, Pb and Zn, respectively, which were close to the class C limit.

Although heavy metal pollution is always an undesirable aspect of organic products selected from waste, their use in agriculture and soil restoration is motivated by the benefits derived from their nutrient and organic matter content. Thus, the SV and N content are positive factors that can be considered indicators of a greater contribution to the CE when these materials are reused. The quotient between CI_{HM} and the content in VS or N offers us an indicator of adequacy to CE, which will be higher the lower the quotient. The results for these indices are shown in Table 6.8 and Figure 6.6. CI_{HM} / VS varies between 0,4 (high CE contribution) to 8 (low CE contribution) and CI_{HM} / N varies from 12 to 222, for the materials indicated in Table 6.8.

The differences between the CI_{HM}/VS and CI_{HM}/N indices for the different materials are mainly due to the HM content but also to the SV and N values. In the materials considered, no correlation is observed between CI_{HM} and the N and VS parameters (R^2 = 0,00 and 0,105, respectively), while these two correlate weakly (R^2 = 0,390). However, the two synthetic identifiers, CI_{HM}/VS and CI_{HM}/N, show a strong correlation with each other (R^2 = 0,966), so they could be used indifferently. Due to the lower variability in SV and N content than in heavy metals, the CI_{HM}/VS and CI_{HM}/N indices follow the trends already shown by the qualities of materials such as Classes A, B and C already described, although the effects of high concentrations of a single metal appear diluted.

6.4. FINAL REMARKS AND CONCLUSIONS.

The flexibility of Member States to adapt the EU legislation may be affected by various administrative and competential boundaries where different overlapped normative indirectly regulates the use of organic wastes in soils. None of these regulations or their contextual frameworks are focussed on environmental aspects of soils health while efforts to reconsiderate the withdrawn Soil Framework Directive (EC, 2004) are demanded (Marini *et al.*, 2020). The underlying scope of most of the related normative was to protect human beings from pollutants.

Nowadays, SS Directive is considered out of date (Fijalkowski *et al.*, 2017) and has never been adapted to technical and scientific progress with regard to HM limits in sludge and soil (EC, 2014). The last reviewing draft dates from nearly two decades ago (EC, 2000). Revisions intended to extend its scope to emerging pollutants and establish more stringent limits for HMs. Currently, the content remains unaltered as no consensus could be reached about limit values for HMs in sludge and soil (EC, 2014). In Spain, it was transposed by R.D. 1310/1990 (BOE, 1990) although the Spanish CE Strategy (MAPAMA, 2019) plans to review its content as there is evidence that part of the SS was not properly managed before its application on soil (aspects to face would be related to hygienization, stabilization and others to ensure the environment protection (MAPAMA, 2019)). At a regional scale and according to Galician Decree 125/2012 if wastes are turned into SSTP, their application to soil is conditioned by the HMs content of the target soil, factor that might be exclusive by natural factors. To circumvent this inconvenient, a legal shortcut would invite SSTP to reach the commercial fertilizers requirements, in which case the natural HMs content in soils would not be a limiting factor. Another debatable aspect of Decree 125/2012 would be connected with the mandatory treatments for certain flows of wastes. Organic matter may influence the chemical properties of the soil by reducing Al toxicity and increasing the retention of cations in the soil exchange complex of soils of the region. If organic matter accounts non-acid pH it also reduces HM solubility, and therefore reduces their bioavailability, specially important in Galicia, location characterized by acidic soils and high precipitations. Different local studies proved the beneficial effects of organic amendments recovery to soil but these practices don´t fit Galician legal requirements. In Galicia, adapted legislation to main groups of soils (Macías *et al.*, 2006) and related main climatic areas as they might influence biochemical soil properties (Paz-Ferreiro *et al.*, 2010) could favour the recirculation of nutrients in nature and valorisation of wastes. Suggestions of Barral and Paradelo (2011) on the Spanish State compost legislation could be extended to other organic materials in Galicia or proposals in the region on varying the HMs limits to fulfil bioeconomy and circular economy requirements (Rigueiro-Rodríguez *et al.*, 2018) should be reconsidered. Finally, Decree 125/2020 might blur the limits between fertilization and disposal (of treated wastes) as neither quality standards for SSTP nor tests of its agronomic efficiency are required. For this reason, it could be possible to get rid of important amounts of those (treated) wastes with low HMs content and scarce agronomic interest. This creates an undesirable scenario that must be avoided (prevent soils from being mere receptors of (treated) wastes).

Unlikewise SS Directive, Nitrates Directive is not intended to be revised although several authors indicated it would be necessary, suggesting under certain circumstances N loading rates much higher than currently established (Schröder *et al.*, 2007; Zavattaro *et al.*, 2016). In Spain, the distribution of administrative powers and/or lack of coordination between Regional Governments and Spanish Central State created some difficulties in its implementation and different timing (Izcara Palacios, 1998; Soler-Rovira *et al.*, 2001). Galicia solved this implementation concluding in the absence of NVZ and thus, no binding limits of N from agrarian sources. In this way, there are not also legal limits for HMs of targeted soils or manures while these issues should be respected for SSTP, biostabilized products or organic commercial fertilizers (besides for the latest, application of CGAP becomes mandatory). For this reason, and comparatively with other materials, legislation seems to involve a more indulgent approach with manures. The time of the review of Galician normative at this respect does not seem very remote since the intensification of livestock production and the important decrease in the useful agricultural area experienced in the last two decades. Manures represent the major fraction of organic wastes produced in the region and different models from direct application to soil will be needed in the future to deal with these wastes.

Regarding commercial fertilizers and as announced in the CE Action Plan, the EU revised (and repealed) the Regulation (EC) 2003/2003 on fertilizers by Regulation (EU) 2019/1009 (Marini *et al.*, 2020). Despite being a recent normative, Regulation (EU) 2019/1009 has already been questioned as it is aimed to satisfy the highest agricultural land productivity while safeguarding human beings from contaminants (Marini *et al.*, 2020). Under a mimetic vision, Spanish CE Strategy contemplates the revision of current R.D. 506/2013 on fertilizers and it is expected to be adapted to Regulation (EU) 2019/1009. Nevertheless, different authors insist on the need of integrated and complementary policy instruments to protect and conserve soils health (Marini *et al.*, 2020).

In productive soils and to reduce dependence on non-renewable resources, CE demands a shift in current policies related with the addition of organic wastes to soil, aimed mainly in protection against pollution. The efficient recirculation of nutrients from organic wastes and the obtaining of fertilizers with high agronomic interest while achieving healthier soils must play a key role. At a bottom scale, regional normative on recycled wastes intended to be used as fertilizers should be adapted to specific particularities (even local or sectorial). Regulations should open pathways to synergies between wastes rich (at least) in organic matter and abundant acidic soils with high (natural or anthropogenic) HMs content. Local literature about recycling of wastes should also be considered as there is scientific evidence of beneficial effects on Galician soils and as their mandatory treatment might discourage their recycling facing other alternatives as landfilling. Current regulations permissive with the application of treated wastes to soil without a minimum requirement of nutrients or organic matter seems to confront the CE principles and should also be refocused. Normative should be adapted to main streams of organic wastes at local or regional scale and adjusted to the properties (and capabilities) of the main groups of soils of the region. Results and other debatable situations (mandatory application of CGAP for high quality fertilizers when its optional for manures, mandatory HMs limits in soils for SSTP whereas manures or inorganic fertilizers are exempted, etc.) obtained from this case study can evoke those of other states with a decentralized structure where regulations from different legislative sources coexist or soil fertilization is ruled by tangential normative.

Disconnection between scientific evidence and its translation to environmental policy was previously reported (Barraza *et al.*, 2016; Margalida *et al.*, 2015; Young *et al.*, 2014). The question that emerges is whether the legislation should adapt to science or science to legislation. The Spanish Circular Economy Strategy outlines as one of the primary objectives to promote mechanisms to enhance the exchange of information and coordination among public administrations, the scientific and technological community, and economic and social agents to favour the transition to a circular model (MAPAMA, 2019).

In the organic wastes recycling, regulations lags behind the state-of-the-art in terms of control of pollution and many organic compounds of recent concern are not currently covered by regulations

(Wassenaar *et al.*, 2018). In the near future, it may be predictable the increasing appearance of new limiting factors for organic recovery on soils, some of them with risky consequences if releases are not regulated (Bengtsson-Palme and Larsson, 2016; Fijalkowski *et al.*, 2017; Qian *et al.*, 2018; Zhang *et al.*, 2019). Indicators for the evaluation and monitoring of the objectives of the CE, such as those proposed here, will be necessary. Regulations yet to come should deal with these upcoming issues at the time of solving current mismatches that call into question the inspiring principles of the circular models of current and future policies.

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CAPÍTULO VII

CONCLUSIÓNS

7. CONCLUSIÓNS.

As investigacións levadas a cabo nesta tese enfocáronse a residuos vinculados ao sector primario de Galicia. Cuestións diversas como a súa abundancia localizada, condicionantes normativos ou a progresiva redución da superficie agraria utilizada impoñen unha necesidade, que os traballos realizados pretenden amosar como oportunidade, de búsqueda de modelos de xestión respectuosos co ambiente no marco dunha economía circular. En relación aos obxectivos inicialmente formulados, nos seguintes paragrafos resúmense as conclusións máis relevantes.

Durante a compostaxe de residuos agroforestais (Capítulos II e III):

→ A fitomasa procedente do monte, ben en forma de especies de matogueira, ben resultante do mantemento e explotación do froito de plantacións de castiñeiro supón un abundante recurso susceptible de ser empregado con éxito como estruturante en procesos de compostaxe.

→ A matriz conformada pola fitomasa orixinada nas plantacións de castiñeiros, en combinación con xurro de porcino, é incapaz de acadar a etapa termofílica en volumes de 340 L. Este inconvinte é solventado con tamaños de pila de aproximadamente 2.5 m^3.

→ Dos lodos procedentes da industria de taboleiros de fibras de media densidade non existían referencias previas ata o momento.As experiencias aquí expostas amosan a súa compostabilidade.

→ O emprego destes lodos como aditivo e o das follas e ourizos de castiñeiro como estruturante, diminúe as as perdas de N (factor de 2.3 con respecto á mostra de mato sen lodo e únicamente do 8.9%, respectivamente). Analogamente, comprobouse unha redución de *E. coli* e *Salmonella sp*. por baixo dos umbrais do R.D. 506/203 sobre produtos fertilizantes (factor de aproximadamente 8 con respecto á mostra de mato sen lodo e practicamente hixienizado para follas e ourizos de castiñeiro). Estas dúas cuestións (redución das perdas de N e hixienización) parecen conferir un valor engadido a estes materiais e invitan a ensaios expecíficos para confirmar estes extremos.

→ Nas condicións baixo as que se efectuaron os traballos, obtívose un compost con contidos de N comprendidos entre 1.7 e2.4%, estable aproximadamente nun mes e con valores de metais pesados por baixo dos marcados pola normativa.

→ Con humidades de partida próximas ao límite de lixiviación, acadáronse ratios de xestión do xurro comprendidos entre os 1.8 e 2.5 L por kg de materia seca de estruturante. Estes valores de referencia poden ser superados mediante a conformación de pilas de maior volume e a diminución do tamaño de partícula do estruturante. O delourado dos materiais é unha práctica, simple e de escasos requerimentos, recomendable para incrementar as cantidades de xurro xestionadas. A compactación conduxo a incrementos de temperatura significativos.

Durante os ensaios de degradabilidade de composts e residuos orgánicos mediante a DBO_5 (Capítulo IV):

- → O método da DBO_5 pode ser empregado para determinar a estabilidade de mostras de compost da fracción orgánica de residuos sólidos urbanos. O limiar de estabilidade proposto é de 25 mg de DBO_5 g SV^{-1}, por riba do cal a mostra pode calificarse como inestable.
- → Para residuos agroforestais as correlacións entre os resultados da DBO_5 cos métodos SOUR e Rottegrade son bos pero non a un nivel estatísticamente significativo, atribuíndose á natureza recalcitrante destes materiais e a súa baixa biodegradabilidade asociada.
- → Ensaios convencionais para a medición da estabilidade do compost como os test SOUR ou Rottegrade deberían ser redefinidos para substratos sólidos agroforestais. É necesario establecer as condicións de operación para a súa posta en práctica, fundamentadas en boa medida no aporte de inóculo (ensaios baseados no consumo de O_2) ou a incorporacion de estruturante e/ou inóculo (ensaios baseados no autoquecemento).

Durante os ensaios de dixestión anaerobia de residuos da industria forestal de taboleiros de fibras de media densidade (Capítulo V):

- → A produción de metano da auga previa ao tratamento físico-químico da industria e do lodo resultante deste tratamento, xeraron 4.0 L CH_4/L e 21.4 mL CH_4/g respectivamente.
- → Apreciouse toxicidade nestes dous materiais debido aos sólidos en suspensión e compostos solubles, requirindo dilucións. Esta toxicidade non foi apreciada na auga á saída do tratamento físico-químico pero a produción de metano descendeu ata 0.8 L CH_4/L.
- → A sedimentación da auga previa ao tratamento físico-químico permite a eliminación de sólidos superior ao 80%. Este proceso propiciou a produción de 4.0-4.8 L CH_4/L a concentracións de ata 80% desta auga (mentres que en ausencia de sedimentación a toxicidade foi apreciada a concentracións do 40%).

Durante o estudo dos condicionantes normativos implicados na aplicación de residuos orgánicos ao solo no marco dunha economía circular: (Capítulo VI):

- → Existe unha ampla variedade de normas que regulan a aplicación ao solo de residuos de orixe orgánica sen que exista unha lexislación específica que xire sobre a conservación e mellora dos solos.
- → Estercos, lodos de depuradora e residuos orgánicos xerados en Galicia, fertilizantes comerciais, tecnosolos ou materiais estabilizados son materiais que poden ser aplicados directamente ao terreo e sobre os cales distintos estándares deben ser acadados.
- → A normativa debería adecuarse aos principais fluxos de residuos producidos na Comunidade, ás súas particulares propiedades e a dos solos destinatarios.

→ A economía circular esixe o deseño de indicadores que se axeiten aos múltiples enfoques sobre os que esta pode estar dirixida. No caso concreto da aplicación de materiais con orixe orgánica e a mellora dos solos produtivos, propuxéronse ratios avaliativos baseados en parámetros tanto positivos (nitróxeno e materia orgánica) como negativos (metais pesados).