

Quantification of greenhouse gas emissions from the biodegradation of garden waste

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Dissertação para obtenção do grau de Mestre em

Engenharia do Ambiente

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Abstract

The primary aim of this study was to quantify garden waste potential for GHG emissions (with focus on CH₄ and N₂O); and to identify relationships between these GHG emissions and meteorological variables in different climates. The study was carried out in two countries with contrasting climates and soil structures: Portugal with a Mediterranean climate and Scotland with a hyperoceanic climate.

A closed static chamber methodology was used for measure N₂O and CH₄ gaseous flux in three types of treatments installed in containers kept outdoors: S with soil; S+GW with soil and garden waste layered on top; and GW with only garden waste. The range of N₂O fluxes varied on a log-normal scale, ranging from slightly negative values to very high values (3 orders of magnitude). With the exception of the “control” S treatments (maximum flux of 0.54 N₂O nmolm⁻²s⁻¹ at both sites).

The percentage of the emitted CO₂ equivalent (CO₂eq) from the original C content applied to the treatments as garden waste indicates the overall impact on emissions of the composting process. Based on CO₂eq global warming potential (GWP) multipliers stated by the IPCC (2014) (25 for CH₄ and 298 for N₂O), Portugal emitted 28.47% from the treatment S+GW and 11.26% from GW, while the majority of the C remained on soils (>70%). Scotland’s treatment S+GW had a lower CO₂eq emission of 11.99%, with 58.47% emitted from the GW treatment. These results show that the overall impact on GWP of composting varies dramatically depending on management, and that CO₂ is being converted into considerably high quantities of longer lived GHGs like CH₄ and N₂O.

Cumulative CH₄ flux measurements showed sequestration in Portugal and emissions in Scotland, the effects were more pronounced in treatment S for both sites (-210.85 and 209.0519 mgCH₄m⁻²d⁻¹, respectively). The garden waste diminished the emissions for Scotland and hindered the sequestration for Portugal.

The contribution of weather conditions from each site was significant and very different relatively to the behaviour of each GHG. Portugal had constant moderate/high temperatures with peaks of rain which stimulated the GHG; Scotland on the other hand had constant rain with low temperatures with occasional rises which was the controlling factor stimulating the GHG.

Key words: Garden Waste, Nitrous oxide, Methane, Greenhouse gases

Resumo

O objetivo principal deste estudo foi quantificar a emissão de gases efeito estufa provenientes de resíduos de jardinagem (ou resíduos verdes), com especial foco nos gases CH_4 e N_2O , e avaliar o comportamento destes mesmos gases consoante diferentes variáveis meteorológicas sob diferentes climas. O estudo realizou-se em dois países com climas contrastantes e com diferentes tipos de solos: Portugal com um clima Mediterrânico e Escócia com um clima hiperoceânico.

A metodologia utilizada para a medição dos gases N_2O e CH_4 foi através de câmaras estáticas fechadas para três tratamentos diferentes em condições do exterior: S com solo; S+GW com solo e resíduo verde no topo; e GW com resíduo verde, unicamente. O alcance dos fluxos de N_2O , numa escala log-normal, variou de valores ligeiramente negativos a valores altos (3 ordens de magnitude). Com a exceção do tratamento S ($0,54 \text{ N}_2\text{O nmolm}^{-2}\text{s}^{-1}$, para ambos sítios).

A percentagem de CO_2 equivalente emitido da quantidade de C proveniente dos resíduos verdes aplicados indica que houve emissões de GEE distintos do CO_2 provenientes deste resíduo. O tratamento S+GW em Portugal emitiu 28.47% e o tratamento GW 11.26 %, a maioria do C permaneceu no solo (>70%) para ambos os casos, no entanto indica a possibilidade do solo também ter ajudado na sua emissão. O tratamento S+GW na Escócia teve uma menor emissão de 11.99% face aos 58.47% do tratamento GW o qual estará possivelmente relacionado com as altas emissões de N_2O que teve, como indicado no seu factor de emissão (4.35%).

Observou-se um sequestro no fluxo acumulado de CH_4 em Portugal e, contrariamente, na Escócia houve emissões deste gás, sendo mais acentuadas no tratamento S (-210,85 e 209,05 $\text{mgCH}_4\text{m}^{-2}\text{d}^{-1}$, respetivamente) e ao juntar o resíduo verde (S+GW) houve uma atenuação tanto para o sequestro em Portugal como para emissões na Escócia.

A contribuição das condições climáticas foi significativa em ambos os locais, e bastante diferente relativamente ao comportamento de cada GEE. Portugal apresentou temperaturas moderadas a elevadas com dias secos seguidos de picos de chuva estimulando assim a emissão dos GEE. A Escócia, por outro lado, contou com chuva constante e com temperaturas relativamente baixas com aumentos ocasionais sendo este o fator que mais estimulou os GEE.

Palavras-chave: Resíduo verde, Oxido nitroso, Metano, Gases efeito estufa

Resumo alargado

Uma sociedade em constante crescimento tem a si associado um crescimento, à mesma escala, da quantidade de resíduos produzidos. Como tal, é necessário encontrar novas estratégias para combater eficazmente este efeito. Através de estratégias como a economia circular, conceitos como, redução, reutilização, recuperação e reciclagem de materiais e energia vão ficando mais presentes no nosso dia-a-dia. Este estudo explora como os resíduos verdes ou bio resíduos provenientes da jardinagem, não sendo devidamente tratados, se podem tornar num resíduo com potencial para emitir gases efeito estufa (GEE).

Os resíduos verdes inserem-se na categoria de resíduo urbano biodegradável (RUB) e são, por definição, “os resíduos biodegradáveis de jardins e parques, os resíduos alimentares e de cozinha das habitações, dos escritórios, dos restaurantes, dos grossistas, das cantinas, das unidades de *catering* e retalho, e os resíduos similares das unidades de transformação de alimentos” (PERSU, 2016). Este tipo de resíduo pode ser produzido a grande escala em manutenções de jardins, parques públicos e privados. A sua quantidade e composição química têm uma forte dependência das localizações geográficas e estações do ano (Boldrin and Christensen, 2010) e, como consequência da falta da sua recolha seletiva, a quantificação dos resíduos verdes nos bio resíduos torna-se praticamente impossível. Este tipo de resíduo pode ser comparável com outros resíduos de culturas gerados a partir de atividades agrícolas (Duiker and Lal, 1999; Mulumba and Lal, 2008; Qiu *et al.*, 2015; Pugesgaard *et al.*, 2016). Em 2016 na Europa, emissões directas da biodegradação de resíduos agrícolas foram equivalentes a 29×10^9 kg de dióxido de carbono (CO_2 eq), em termos de potencial de aquecimento global (FAOSTAT, 2017). De facto, a degradação de matéria orgânica através de processos microbiológicos liberta quantidades consideráveis de CO_2 , metano (CH_4), e também através de processos de nitrificação-desnitrificação, óxido nitroso (N_2O).

Independentemente do destino dos resíduos verdes, estes terão sempre emissões de GEE que poderão ser aproveitadas em termos energéticos, como por exemplo, através de digestores anaeróbios para produção de biocombustível, tornando-se, assim, num possível combustível derivado de resíduo (CDR). No entanto, na maioria das vezes terminam em aterros.

No Reino Unido entre 30 a 40% dos resíduos sólidos urbanos são bio resíduos, de onde foi estimada em 2016, uma emissão de 4% dos GEE provenientes do aterro (CCC, 2018). Em Portugal, estima-se que o sector dos resíduos produza cerca de 9.6% dos GEE a escala nacional (PERSU, 2016), onde cerca de 50% dos resíduos sólidos urbanos são bio resíduos. No entanto os aterros poderão ter também um aproveitamento energético.

Estes resíduos têm ainda como utilidade gerar composto, ainda que as suas emissões quando produzidos a grande escala, são consideráveis (Andersen *et al.*, 2010).

Todos os eventuais destinos dos bio resíduos envolvem emissões e, neste estudo, é quantificada a emissão proveniente diretamente da sua biodegradação no local de formação.

O presente estudo decorreu em dois locais com clima e solos distintos: Portugal de clima Mediterrânico, e Escócia de clima hiperoceânico. Os solos de Portugal são caracterizados por serem relativamente áridos com um baixo teor de matéria orgânica, ao contrário da Escócia que possui solos húmidos e com um alto teor de matéria orgânica. O trabalho desenrolou-se entre Abril e Agosto de 2017 na Escócia (122 dias) e entre Novembro e Maio de 2017/18 em Portugal (167 dias). Foram escolhidos estes meses pela sua aproximação em termos de temperaturas e precipitação.

Os ensaios foram realizados em contentores ao ar livre e tiveram como base três tratamentos: um tratamento controlo onde se usou apenas solo (S); um segundo tratamento onde se colocou uma camada de resíduos verdes sobre uma camada de solo (S+GW) e, por fim, um tratamento só com resíduos verdes sem solo (GW).

Com o objetivo de avaliar a emissão de gases resultante da decomposição dos resíduos, fez-se a recolha dos mesmos durante os períodos atrás mencionados. E cada amostragem, foi utilizada a metodologia de câmara estática: os contentores onde estavam instalados os diferentes tratamentos foram selados durante uma hora para se poder proceder à recolha das amostras dos gases em t=0, 20, 40 e 60 min obtendo, assim, um gradiente de concentração de cada tratamento e analisados, posteriormente, através de cromatografia gasosa. Retiraram-se também os lixiviados que foram recolhidos nos mesmos dias da amostragem dos gases para quantificação dos iões amónio e nitrato ($\text{NH}_4^+/\text{NO}_3^-$).

Com as amostras recolhidas, juntamente com os dados fornecidos das estações meteorológicas, procedeu-se ao tratamento dos resultados através do programa estatístico R.

Após um mês de medições, observaram-se valores significativos de amónio nos lixiviados provenientes dos resíduos verdes no tratamento GW, devido à sua amonificação.

Em Portugal, o tratamento S+GW, subtraindo as emissões associadas ao solo (S), apresenta um factor de emissão para o N_2O de 1.25%. Na Escócia, o valor não diverge substancialmente, apresentando um factor de emissão de 0.76%. Relativamente ao tratamento GW, a Escócia apresenta um factor de emissão de 4.35%, face aos 0.69% de Portugal, no entanto, o factor de emissão para Escócia não é um valor representativo, devido à falta de drenagem deste tratamento em especial.

Assim, podemos concluir, que o comportamento das emissões de N_2O foi bastante similar em ambos os locais de estudo, ao invés do CH_4 . Portugal apresenta, sobretudo, um sequestro de metano; no entanto, ao subtrair as emissões do solo ao tratamento S+GW, o factor de emissão torna-se positivo (0.16%), concluindo assim, a correlação deste resíduo com as emissões de CH_4 . O oposto aconteceu na Escócia, onde existiram sobretudo emissões de CH_4 . O tratamento S+GW sem as emissões provenientes do solo, apresentou um fator de emissão negativo (-0.04%). Este valor negativo não nos permite concluir que possa ter havido um sequestro de metano, pois poderão ter existido menos emissões à superfície comparativamente ao tratamento S, uma vez que as maiores emissões de metano se dão nas camadas inferiores onde a carência de oxigénio é superior.

O clima teve, inquestionavelmente, uma forte influência sobre os comportamentos destes GEE. Portugal manteve temperaturas moderadas a altas, entre 15 a 25 °C, com dias secos seguidos de dias pontuais de chuva, que estimularam mecanismos como a desnitrificação e, conseqüentemente, a emissão de N_2O ; especialmente para os tratamentos com resíduos verdes.

A Escócia, por outro lado, teve a chuva como um fator constante e sem grandes oscilações, tendo a temperatura registado uma maior amplitude (5 - 20 °C). As emissões de N_2O apresentaram picos acompanhando os aumentos de temperatura, tal como o CH_4 , este também associado a dias onde a precipitação era escassa ou nula.

Em relação ao resíduo verde, este é muitas vezes deixado no mesmo local após o corte, quer amontoado quer espalhado no solo. Em locais como a Escócia, estas pilhas de resíduos verdes contribuem para as emissões de N_2O , no entanto, podem, por sua vez, contribuir também para a redução de emissão de CH_4 e aportar mais nutrientes ao solo. Contudo, e considerando o alto teor de matéria orgânica presente nos solos, este resíduo poderia ainda ter um destino mais proveitoso em termos energéticos ou para fins de compostagem. Os seus efeitos na compostagem terão de ser alvo de mais estudos, de forma a concluir efetivamente qual o seu melhor destino. Em Portugal, a presença deste resíduo no solo pode ser benéfica pelos potenciais nutrientes neles disponíveis, mas, um tratamento prévio pode auxiliar no aumento da disponibilidade dos mesmos e ajudar, assim, a combater a erosão dos solos, bem como enriquecê-los com mais matéria orgânica. Para tal, soluções como a sua recolha seletiva deveriam ser estimuladas e incentivadas para uma posterior valorização através da caracterização da sua composição.

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Table of abbreviations

C – Carbon

CH₄ - Methane

CO₂ – Carbon dioxide

DIN – Dissolved inorganic nitrogen

DON – Dissolved organic nitrogen

EF – Emission factor

GHG – Greenhouse gas

GWP – Global Warming Potential

N – Nitrogen

N₂O – Nitrous oxide

NH₃ - Ammonia

NH₄⁺ - Ammonium

NO₃⁻ - Nitrate

MSW – Municipal Solid Waste

OM – Organic Matter

SOM – Soil Organic Matter

WFPS - Water frame pore space

1 Introduction

Large quantities of organic waste (plant materials and animal waste) can be produced during the maintenance of green space areas such as gardens and public parks. The generation of this waste and its chemical composition can vary from geographical location and with seasons (Boldrin and Christensen, 2010). Grass and plant clippings, wood chip and a variety of plant materials such as roots, seeds and fruits are all often generated in large quantities in these areas. This waste can be similar to crop residue materials that are produced by agricultural activities (Duiker and Lal, 1999; Mulumba and Lal, 2008; Qiu *et al.*, 2015; Pugesgaard *et al.*, 2016), which are produced on a significant scale. Crop residues are typically left to decay or are tilled into the soil after harvest to recycle their potential nutrient contents back into the soil with an N content up to 100 kg N ha⁻¹ in some cases (Di and Cameron, 2002). Direct emissions of greenhouse gases (GHGs) from the decay of crop residues in Europe in 2016 was estimated to be equivalent to 29 x 10⁹ kg of carbon dioxide (CO₂ eq) in terms of global warming potential equivalent (GWP), with a relatively large fraction released as the non-CO₂ GHG nitrous oxide (N₂O) (93 x 10⁶ kg) (FAOSTAT, 2017).

As populations and urban sprawl grow, and the use of green space is encouraged in cities and urban areas, the amount of organic waste produced will also continue to grow. Andersen *et al.* (2010) indicates that unofficial data from EU countries suggests an increase of 100% of garden waste collection and composting between 2002 and 2008 (4 million Mg in 2002 and 8 million Mg in 2008). This will likely result in an increase in emissions of long lived GHGs such as methane (CH₄) and N₂O, at a time when the EU is actively attempting to mitigate such emissions as part of the 2015 Paris Climate Agreement.

The direct breakdown of organic matter (OM) by microbiological processes releases a considerable amount of carbon dioxide (CO₂) and methane (CH₄), while nitrogen (N) mineralisation alters nitrification-denitrification dynamics in a variety of materials (e.g. soils and composts) which results in increased N₂O emissions.

Agricultural, garden and forestry management are considered a net sink of CO₂ via the process of photosynthesis in plants and the incorporation of carbon-rich organic materials into soils. N₂O gaseous losses increase through the stimulation of nitrification and denitrification not only as a result of the available nitrogen (N), but of the availability of mineralizable carbon (C), sources provided in the green waste (Qiu *et al.*, 2015). CH₄ emissions have also been documented under well aerated conditions during mineralization (Andersen *et al.*, 2010). The importance of the production of non-CO₂ GHGs is that they have an increased GWP per volume when compared to CO₂. CO₂ has 1 GWP, while CH₄ and N₂O are 25 and 298 times, respectively, higher than CO₂ over a 100-year time frame (considering N₂O has a lifetime of 114 years) (Solomon *et al.*, 2007). Because of this, the potential GWP (ranging from positive to negative) of green spaces varies depending on a variety of aspects such as meteorological influences and management practice.

Models for GHG estimation in grasslands are predominantly CO₂ based, including the analysis of above-ground and below-ground biomass, dead wood, litter, and soil organic matter to evaluate C stock where the litter values range from 0.30 to 0.50 tonne C (tonne dm⁻¹) (IPCC, 2006a). Meanwhile CH₄ and N₂O emission estimations are difficult to model because of limited data available. CH₄ emission modelling in grasslands is linked to animal waste data or agricultural residue burning (IPCC, 2006b). Meanwhile for N₂O, several studies were conducted to analyse the environmental external factors responsible for its emissions (Hungria and Vargas, 2000; Sommer *et al.*, 2004; Wang *et al.*, 2019). Soil temperature, water content, aeration, soil type and cultivation together with NH₄⁺/NO₃⁻ losses are few indicators of the magnitude of emissions, although uncertainties remain high.

This study was carried out to investigate the GHG emissions as a result of the management of clippings from grasslands in two countries with contrasting climatic conditions, Portugal and Scotland. Plant materials left to decay on soils after harvest or mowing (and the associated decay of dead root materials) are a considerable source of N for grassland soils (Whitehead, 2000). However, statistics on garden waste quantities is scarce in all member states (MS) of Europe, partly due to lack of separate collections of bio-waste (Eurostat, 2005).

In Scotland, and excluding rural areas, only food waste is considered for bio-waste separate collection. Scottish Government (2010) intends to set a limit on the biodegradable content of waste that can be landfilled to protect the environment against GHG emissions, reducing to 1.26 million tonnes which still requires a diversion of 530,000 tonnes of biodegradable municipal waste.

Portugal has so far only implemented bio-waste collection for some business and public gardens, while the separate collection has been only for pilot studies in civic amenity sites (EC, 2015). In accordance with the Green Growth Commitment (GGC), Portugal aims to reduce disposal in landfills of biodegradable urban waste from 63% to 35% by 2020 (against the reference year of 1995); increasing the rate of preparation of waste for reuse and recycling from 24% to 50% (Républica Portuguesa, 2014).

This study intends to investigate emissions of GHGs as a result of grass clipping degradation in Portugal and Scotland. Portugal is characterized by a Mediterranean climate, dry hot summers and cold wet winters with an average rainfall of 800 mm per year, whereas Scotland has an Oceanic climate with less variation in temperature between mild summers and winters and with an average rainfall of 920 mm per year.

As this study is focused on the GWP potential of the grass clipping degradation, CO₂ emissions will not be taken into account, as its contribution to global warming is not considerable due to its biogenic origin (Christensen *et al.*, 2009) (i.e. CO₂ emissions cannot be larger than CO₂ uptake of the original plant materials, therefore GWP of CO₂ is not an issue). However, as N₂O and CH₄ do contribute significantly to GWP the focus will be on these gases. Because of its powerful GWP and long atmospheric lifetime, this study will pay special attention to N emission deriving from the garden waste decomposition.

There have been previous studies focused on GHG emission from mulching (Mulumba and Lal, 2008; Wang *et al.*, 2019), leaf litter (Mchale *et al.*, 1998), compost from garden waste (Andersen *et al.*, 2010) and crop residues (Baggs *et al.*, 2003; Qiu *et al.*, 2015; Pugesgaard *et al.*, 2016). In contrast to the previous mentioned studies which involve other factors such as fertilizers, laboratory conditions, or simply have a different focus: N mineralization, Volatile Organic Compounds (VOC); this study aims to:

- a) Quantify garden waste potential for GHG emissions, with focus on CH₄ and N₂O, in outdoor conditions;
- b) Identify relationships between GHG emissions and meteorological variables in different climates;

2 Literature Review

2.1 Greenhouse gases

After the Industrial revolution in the 19th century, human activities have significantly altered the balance of trace gases in the lower atmosphere (IPCC, 2013). A number of these gases (a.k.a. greenhouse gases (GHGs)) increase atmospheric temperatures via the greenhouse effect (Solomon *et al.*, 2007). The impact of the individual GHG species are defined by Global Warming Potential (GWP), which determine their strength as a GHG in comparison to CO₂. Figure 2.1 describes the main sources of the different GHG, under this topic the sources involved would be emissions from “Waste and other”, “Agriculture” and “Forest and peat fires”.

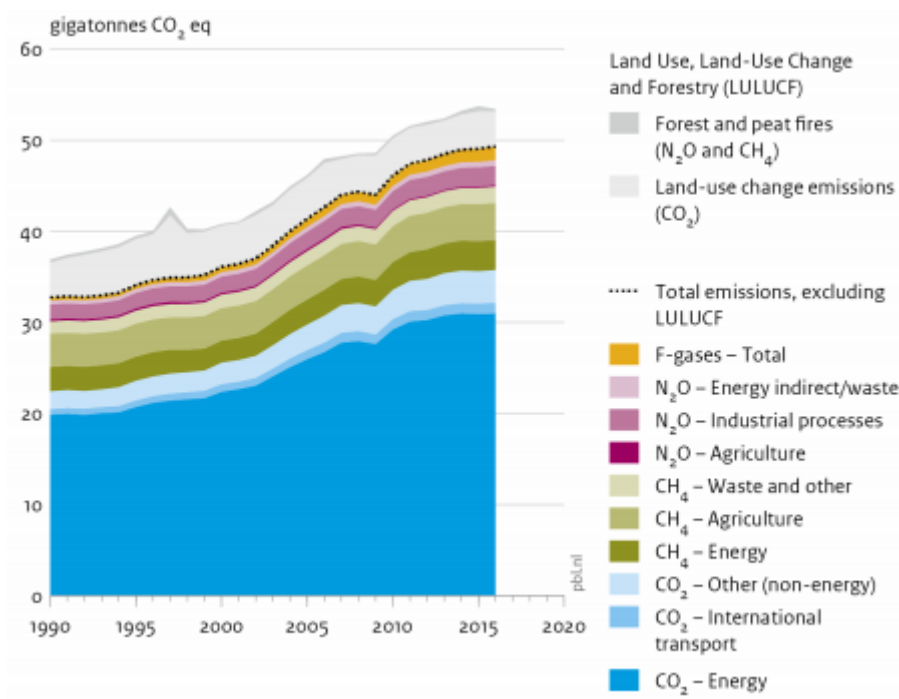


Figure 2.1 Global GHG emissions, per type of gas and source, including LULUCF. Source: Edgar v.4.3.2 (EC-JRC/PBL, 2017)

Atmospheric CH₄ concentrations increased by approximately 150% beyond the pre-industrial level (IPCC, 2007) reaching 1834 ppb in 2015 (Reay *et al.*, 2018); with an estimated contribution of approximately 70% attributed to biogenic sources (Conrad, 2009): wetlands, landfills and livestock production. Nevertheless, a large fraction of CH₄ produced is rapidly consumed by microorganisms before it enters the atmosphere (Frenzel, 2000; Reeburgh, 2003), specially during aerobic methane oxidation (methanotrophy) as regarded in Figure 2.2:

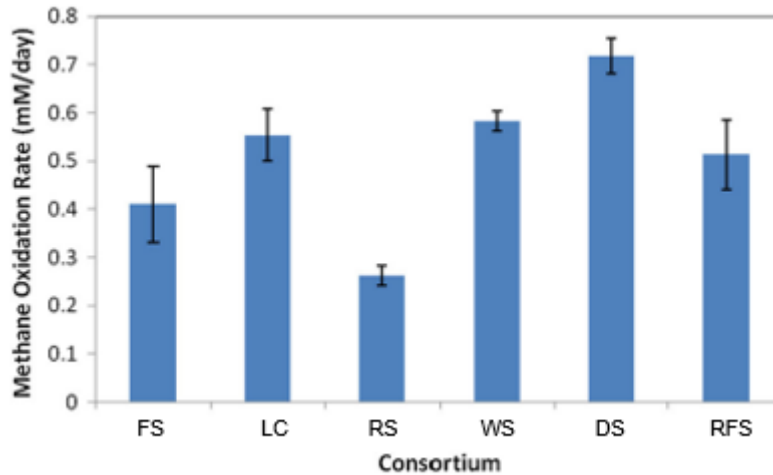


Figure 2.2 Methane oxidation rate of methanotrophs from different ecosystems (Forest Soil, Leafy Compost, Riverbed Soil, Wetland Soil, Dumpsite Soil and Rice Field Soil, respectively). Source: Brindha and Vasudevan, 2017

N inputs to the ecosystems are also increasing with human activities. During the first decade of the twentieth century, the worldwide demand for N-based fertilizers far exceeded the existent supply. It was only in 1912 when the first commercial plant produced industrially synthesized ammonia (NH_3) via the Haber-Bosch process to meet the needs of the growing world population, which has subsequently increased globally by 78% since 1970 due to a rapidly increasing population, and led to an increase of anthropogenic reactive nitrogen (Nr) in the environment by 120% (Galloway *et al.*, 2008). Agricultural demand for nitrogen fertilizers' application, livestock production and land use changes are considered to be the main sources of Nr pollution. The "nitrogen use efficiency" (NUE) in crop production is considered to be less than 50% in most farm productions in the world (Lassaletta *et al.*, 2014) and the actual fraction emitted by the nitrogen-based fertilizers is still uncertain (Davidson, 2009) considering the wide range of environmental external variables and the different applied agricultural techniques.

Crop residues were reported to be highly correlated with N_2O emissions rather than inputs of N from manure/fertilizer (Pugesgaard *et al.*, 2016), although more investigation is needed for residue composition and quantity analysis (Baggs *et al.*, 2003). Moreover, not only the quantification rates of N_2O are difficult to determine but its spatial and temporal variation (Cowan *et al.*, 2015).

2.2 Garden waste policy and management

Garden waste in EU Waste Frame Directive 2008/98/EC is inserted in the bio-waste definition “biodegradable garden and park waste, food and kitchen waste from households, restaurants, catering and retail premises and comparable waste from food processing plants”. The lack of separation of bio-waste makes it practically impossible to directly measure the mass of garden waste generated as there would be a need for collection, sorting, processing and transport from the source until the treatment/recycling facilities.

The actual fraction of bio-wastes from Municipal Solid Waste (MSW) classified as recycled by the EU are the amounts reported to Eurostat as the digested or composted material (EEA, 2013) as shown in Figure 2.3. where Portugal recycled around 13% and UK 17% with the difference of bio-waste collection at the households.

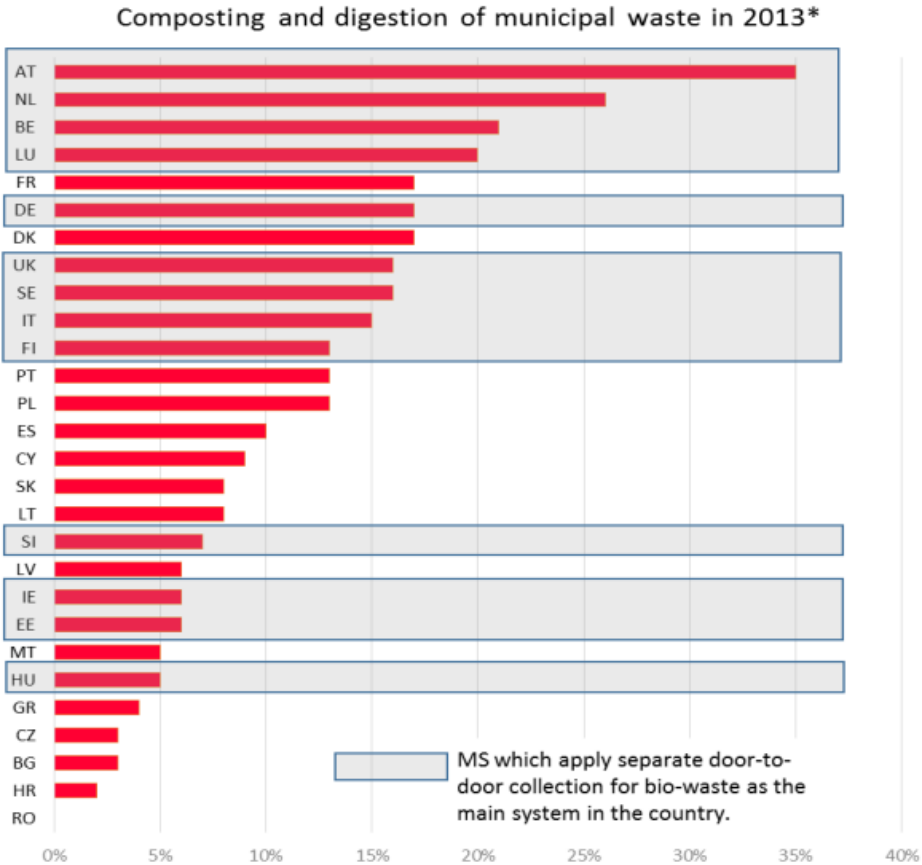


Figure 2.3 Composting and digestion rate of municipal waste in 2013 together with the municipal states who apply a door to door collection of biowaste (EUROSTAT, 2019)

In order to transition to an efficient circular and green economy, generated waste needs to be minimised at a variety of scales from a wide range of sources. For this particular waste, its decline in production indicates a reduction of green areas. As the main idea is to have an increase of green spaces specially in urban areas, it is important to understand how to profit the most from it. In this sense it is important to prioritize and develop actions which can be applied to achieve these goals.

As population tends to grow so does the waste production and reducing its GHG emissions will become more complicated. A good solution is to lead the emissions into a positive GHG flux balance, in other words, to benefit from the emitted gases in a controlled manner instead of ending in a landfill. Thereby, a number of treatments and pre-treatments is performed, with different efficiencies:

Mechanical-Biological Treatment (MBT)

MBT is a complement to other further treatments, works as a pre-treatment where it sorts biodegradable and non-biodegradable waste from a mixed waste stream and then applies a biological treatment to address the waste into a next suitable treatment (UK Government, 2013).

Anaerobic Digestion

Anaerobic digestion of bio-waste can be advantageous considering the CH₄ and CO₂ emissions from the biodegradation to produce biogas and replace the use of fossil-fuels. After digestion, the digestate goes through a posttreatment to filter the liquid and separate the solids. This solid fraction, after stabilization, can be directly used as an organic amendment or compost (Fruteau de Laclos *et al.*, 1997). The methane yield will be highly dependent on the waste composition, considering bio-waste being the “vegetable-garden-fruit” (VGF) fraction of the MSW the garden waste may hinder the process because of its lignocellulosic content requiring always a pre-treatment.

Composting

Composting involves the microbial oxidation of OM turning the waste into a humus-like material. This activity is also becoming a solution for garden waste in Europe, allowing to partially replace fertilizers or peat compost, thus avoiding the associated emissions of GHG from the fertilizers and the damage made to peatlands ecosystem. Although the GHG emission from composting in open vessels (windrow composting) is still a disadvantage (Andersen *et al.*, 2010), which is the case for several member states of Europe, at a smaller scale is also done for households. Contrary in the compost heat recovery systems (CHRS) (closed reactors) producing compost and recover energy at the same time for on-site purposes, helps to diminish the GHG flux about -10 kg CO₂ eq/tonne of the MSW (Smith *et al.*, 2001). Figure 2.4 shows how much of the MSW ends as a compost: UK, having a surface almost 3 times higher than Portugal, produced 6 times more waste than Portugal in 2017 having 16% of it ending in compost while Portugal composted 20% of the total MSW generated.

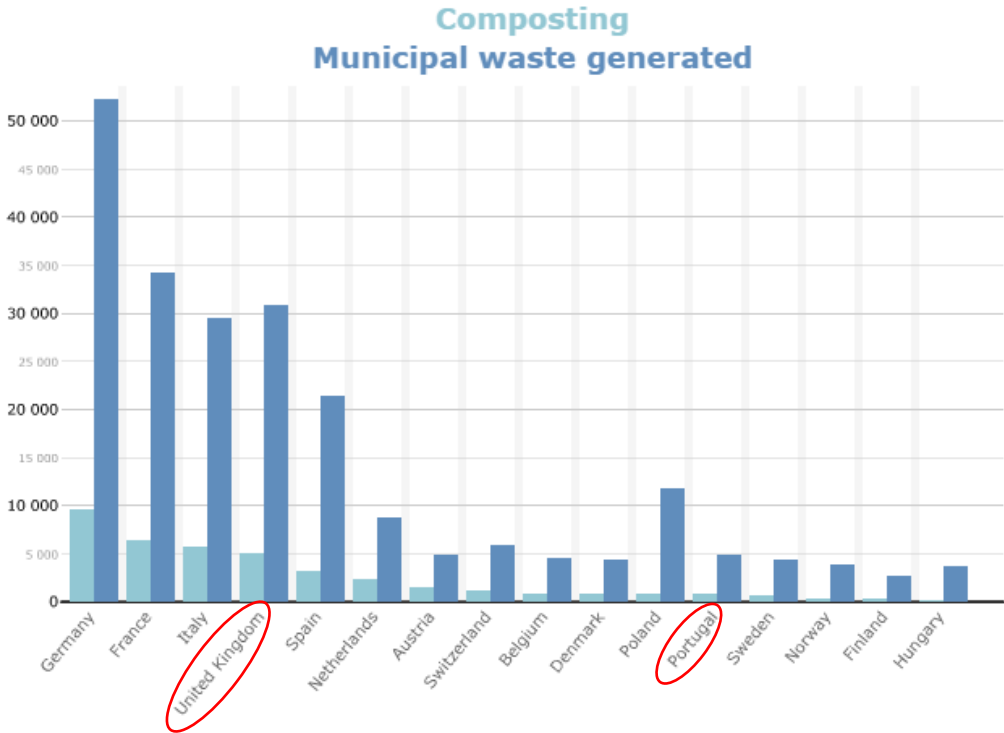


Figure 2.4 Compost production and MSW generation based on OECD data from 2017. Units: Tonnes, Thousands.

Even though Portugal had a higher percentage of composted material, it is important to understand the actual fraction of biowaste in the MSW, and in the following table (Table 2.1), which gives an idea of the amount of bio-waste which can be found in the MSW in European countries, it is possible to see the higher potential for compost that Portugal has in respect to UK. Keeping in consideration that this table is based on 2008 to 2010 data, the tendency for generated waste per capita has been slightly decreasing: from 2011 to 2017 Portugal and UK produced, respectively, -0.6 % and -4.68 % kg (EUROSTAT, 2019).

Table 2.1 - Bio-waste share in municipal waste in 28 European countries in 2008–2010. Source: (EEA, 2013)

% of bio-waste in total municipal waste	Countries
Less than 20%	Lithuania, Norway and Slovenia
Between 20 % and 30 %	Bulgaria, Denmark, Ireland, Hungary, Latvia and Switzerland
Between 30 % and 40 %	Germany, France, Italy, Sweden, United Kingdom, European average
Between 40 % and 50 %	Austria, Belgium, Czech Republic, Estonia, Finland, Luxembourg, the Netherlands, Poland, Romania and Spain
Between 50 % and 60 %	Greece, Portugal, Slovakia
Between 60 % and 80 %	Malta

The application of organic amendments, like the green waste compost, the digestate from anaerobic digestion, or even applying directly green waste on top of soils (mulching), are practices with positive impacts when it comes to preventing soil erosion, increasing moisture conservation and fertilisation effects (Mulumba and Lal, 2008). Favourable effects of residue mulching on soil organic carbon (SOC), soil water retention and percent water-stable aggregates have been reported for the surface layer (Duiker and Lal, 1999). Mulching the top soil will also prevent runoffs, loss of moisture content of the soil, can be a protection for seedlings and other benefits (Rathore *et al.*, 1998). However, the actual GHG emissions from decaying matter, particularly during composting process, are recognized for being considerable but not well quantified (Baggs *et al.*, 2003; Dalal *et al.*, 2008; Skiba *et al.*, 2012; Verdi *et al.*, 2018).

2.2.1 Biowaste and GHG

As aforementioned, green waste belongs by definition in the biowaste section. Its evaluation and statistical analysis in municipalities it is still scarce as a result of its poor valorisation as a waste. As so, in this section the data its related to all the waste integrated in the biowaste definition.

In section 2.2, discussing treatments for MSW management, landfill wasn't stated as one of the options because of its noxious consequences. Biowaste in landfills increasesGHG emissions as a result of its biodegradation, Table 2.2 indicates CH₄ as a major constituent from the gas composition from landfills. Concurrently, Figure 2.5 shows the associated GHG emissions in CO₂ eq. from landfill, among others, throughout the years in the UK.

Table 2.2 Composition of landfill gas. Source: Themelis and Ulloa, 2007

Composition of landfill gas	
Compound	Average concentration (%)
Methane (CH ₄)	50
Carbon dioxide (CO ₂)	45
Nitrogen (N ₂)	5
Hydrogen sulphide (H ₂ S)	< 1
Non-methane organic compounds (NMOC)	2700 ppmv

In 2016 in the UK, 4% of the GHG emissions mainly comprising methane, came from the decomposition of biodegradable waste in landfill sites (CCC, 2018). In the same year in Scotland, 1.15 Mt of biowaste went to landfill (Zero Waste Scotland, 2019), even though its reduction has been considerable as regarded in Figure 2.5.

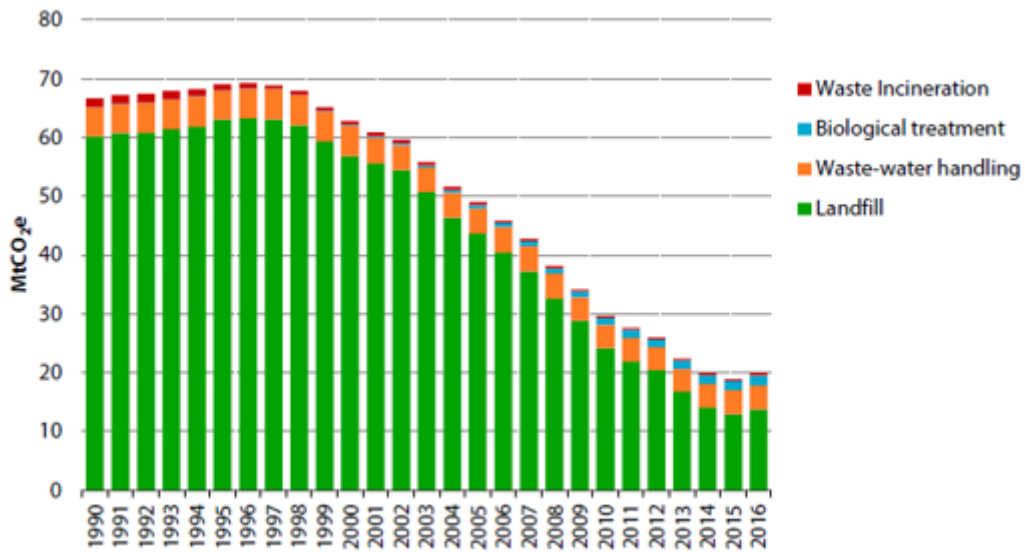


Figure 2.5 GHG emissions from waste by source in UK (1990-2016). Source: (CCC, 2018)

In Portugal the waste sector, including waste water, is responsible for the 9.6% of the national GHG emissions (PERSU, 2016). The lack of separate collection of biowaste in Portugal leads to its deposition in a landfill incrementing its GHG emissions.

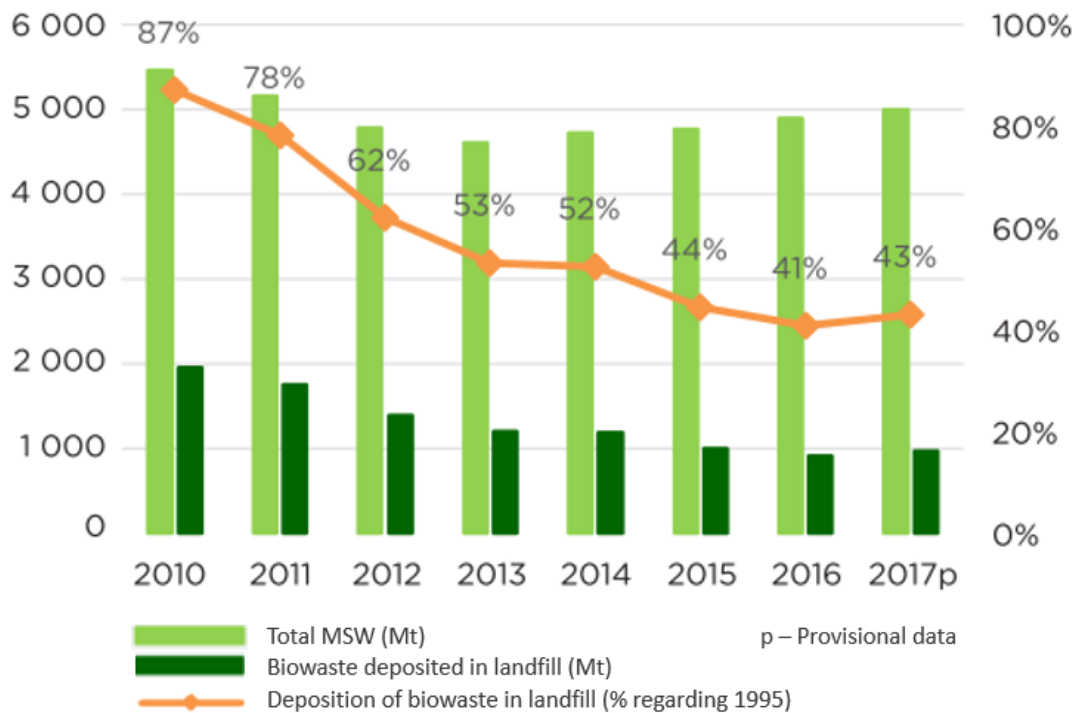


Figure 2.6 MSW and bio-waste in landfills in Portugal. Source: Fernandes et al., 2018.

In table 2.1, about 50% of the MSW in Portugal is biowaste and together with figure 2.6 suggests that 50% of the biowaste produced ended in a landfill. Even so, the amount of biowaste produced is highly uncertain when there's no separate collection of this type of waste.

2.3 Nitrous Oxide (N₂O)

Soils are the largest source of natural and anthropogenic N₂O. Although agricultural soils are considered the most significant source of anthropogenic N₂O emissions due to fertiliser application, non-agricultural soils are gaining importance as disturbance of natural N cycles becomes more apparent in the environment. N₂O impacts, as mentioned in the succeeding chapters, are highly variable and unpredictable in both terrestrial and aquatic systems (Gruber and Galloway, 2008).

It should be emphasized that the largest loss of nitrogen from terrestrial soils tends to be through ammonia (NH₃) volatilisation and production of inert dinitrogen (N₂) via denitrification. However, NH₃ emissions are typically a result of high N concentrations in the soil (i.e. fertiliser events and deposition of animal waste) and warm weather, while N₂ is the final product of denitrification, limited in some instances due to the lack of the N₂O reductase enzyme in bacteria resulting in N₂O as the final product.

Garden waste composition is an important factor to be analysed because of the available N which can be provided to the soil and its consequential N-loss through gas emissions. The N content varies from season to season as described in Figure 2.7 where N content is highest during summer and autumn months corresponding to when grass clippings or leaves are the major constituents.

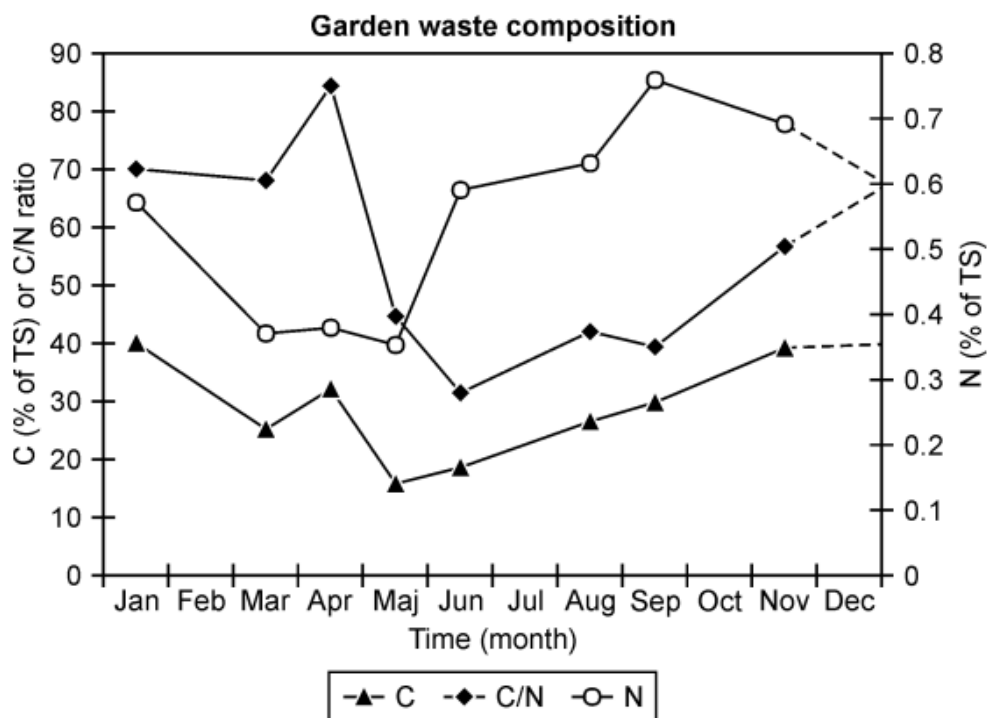


Figure 2.7 Seasonal variation in carbon and nitrogen content, and C/N ratio of garden waste in Netherlands (Boldrin and Christensen, 2010). Please note different scales for y-axis.

Thus, the N-gas focused in this study will be N_2O due to its GWP and related impacts discussed in section 2.4.

2.4 Nitrogen net sink

Nitrogen pollution is predominantly diffuse pollution, lacking of a specific point of discharge. Its loss can be under different forms: gaseous, leachate and particles deposition either wet or dry; largely due to mechanisms like soil erosion, leaching, ammonia volatilization, ammonia oxidation and denitrification (Thomson *et al.*, 2012).

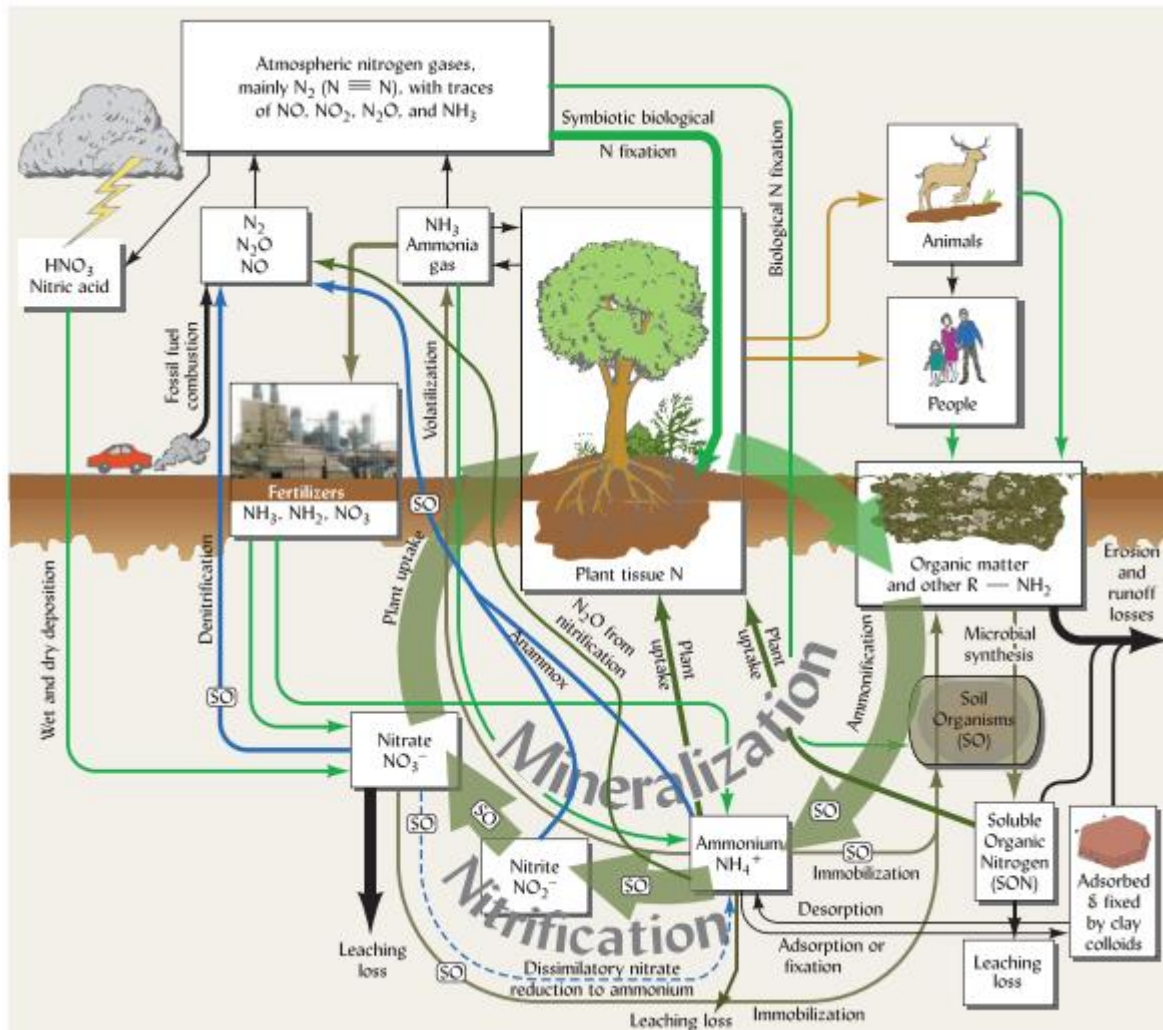


Figure 2.8 This figure shows N complexity through its many valence states and phases (gas, liquid, and solid). The arrows represent processes by which one form is transformed into another. Note the processes by which nitrogen is lost from the soil and by which it is replenished (bright green arrows). The blue arrows represent anaerobic processes. Soil organisms, whose enzymes drive most of the reactions in the cycle, are represented as rounded boxes labeled "SO." (Weil and Brady, 2016)

Agriculture land is an important source of diffuse pollution, accounting for about 50% of all the ammonia that is volatilised worldwide (Sommer *et al.*, 2004).

Besides agriculture, natural land also contributes largely to global N₂O emissions (6 Tg N yr⁻¹) (Thomson *et al.*, 2012). Altogether, the soil contributes approximately 57% to the total annual global emission (IPCC, 2006c).

The N gas emissions (NH₃, N₂O, NO_x) can have detrimental implications such as acid rains and increasing the ozone in the tropospheric layer and damaging the stratosphere. In the lower atmosphere N₂O it is a relatively inert gas but in the stratosphere it is broken down by UV light, producing oxygen radicals and thus ozone (O₃), which filters out ultraviolet radiation from the sun. Ozone in the troposphere acts like a GHG, damages the plants and is bad for human health (Ramanathan *et al.*, 1985).

Organic wastes, whether applied to agricultural soils or left behind, are a source of nutrients (such as N and phosphorus (P)) for plant uptake. However, a large fraction of it is not readily available, and stays in pools interconnected by several possible mechanisms regulated by the environmental conditions. Nutrients can be lost to the atmosphere as beforementioned, leached or be assimilated in the OM, preventing plant uptake.

N when leached (predominantly under as NO₃⁻), can cause several effects on waterbodies and soil's productivity. N leaching, together with other macronutrients transported into waterbodies may cause eutrophication. It has been shown that poor management of organic wastes (such as garden wastes and manure) can cause algal blooms and the consequent decline of aquatic ecosystems if washed into drainage systems during storms via decreasing oxygen availability (Strynchuk, *et al.*, 1999; Smith and Schindler, 2009).

Both NH₄⁺ and NO₃⁻ can also cause acidification of the soil in different ways: NH₄⁺ can decline soil buffer capacity by displacing base cations (Na⁺, Ca⁺, K⁺, Mg²⁺) and once is consumed by root systems it releases H⁺ into the soil. NO₃⁻ has a tendency to leach and with it basic cations and metal cations, causing mobilisation of Aluminium (Al) (Gundersen *et al.*, 2006; Tian and Niu, 2015).

The nitrogen cascade (Figure 2.8) involves the cycling of N amongst the different natural compartments such as air, soil, living organisms and water. The following subchapters will focus on the main N pathways in the different natural compartments present in the study.

2.4.1 Soil N balance

Nitrogen budgets seek to summarize the complex agricultural N cycle by documenting the major flow paths of N in various dynamic N pools, based on the principle of mass conservation (Eq. 2.1) (Meisinger *et al.*, 2008):

$$N_{\text{inputs}} - N_{\text{outputs}} = \Delta N_{\text{soil}} \quad [2.1]$$

Meisinger (1984) made the division between systems for N balances based on “whole crop” vs. the “aboveground crop” approach.

Nitrogen can be found in soils in different forms of biomass such as in soil organisms and microorganism, or trapped in organic matter and/or clay substrates under organic and inorganic forms (Cameron *et al.*, 2012).

2.4.2 N – Fixation

N-Fixation is the conversion of atmospheric N (N_2) to a form of reactive nitrogen in the biosphere. This process happens in nature through biological nitrogen fixation; but the primary anthropogenic route is through the synthetic chemical Haber Bosch process.

- Chemical (Haber Bosch)

The industrial process that produces ammonia (NH_3) from molecular hydrogen (H_2) and molecular nitrogen (N_2) under high pressures and temperatures (20 MPa and $500^\circ C$) with a contribution of, approximately, 3% of the global emissions of CO_2 (Smith *et al.*, 2012; Cai *et al.*, 2017).

- Biological Nitrogen Fixation (BNF)

Several natural agents carry out this biological process, including actinomycetes in forest ecosystems, cyanobacteria in wetlands and rhizobacteria in grasslands and agricultural soils in symbiosis with *Fabaceae* (Weil and Brady, 2016).

Soil moisture is an important factor for N-fixation, as there needs to be sufficient water in the soil to activate cyanobacterium activity. However, over hydration may lead to depletion of energy reserves necessary for N fixation. Where moisture content fluctuates between wet and dry, the N-fixation rates in soils can increase (Belnap, 2001). The temperature is also vital for microorganism activity, the optimum for N-fixation is $20-30^\circ C$ but activity has been observed between -5 and $30^\circ C$ (Belnap, 2001).

The optimal pH for N-fixation and microorganisms activity is approximately 7 and above (Davey and Marchant, 1983; Hungria and Vargas, 2000), yet if the pH is above 8 there's a depression in microbial activity (Granhall, 1970)

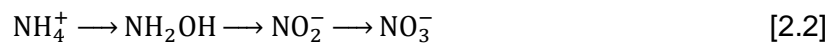
2.4.3 Nitrification

Norton and Stark (2010) describe nitrification as a biological conversion of reduced nitrogen (N) in the form of ammonia (NH_3) or ammonium (NH_4^+) or organic N to oxidized N in the form of nitrite (NO_2^-) or nitrate (NO_3^-).

The conversion of N from a cation to an anion state may improve plant uptake in some cases (Tang and Rengel, 2003), although both forms are available for the plants the anion is more mobile in soils due to its capacity to not get adsorbed in the soil matrix (Vareennes, 2003).

Nitrification can be described in two steps (Arp and Stein, 2003) where the key element are the ammonia oxidizing bacteria (AOB), also described as chemolithotrophs because they can derive all their energy for growth from the oxidation of the ammonia to nitrite (Arp, 2009).

The first step result, carried out by the *Nitrosomonas* bacteria, is hydroxylamine (NH₂OH) which is then catalysed by hydroxylamine oxidoreductase (HAO) converting NH₂OH into nitrite. The nitrite ion is then oxidized by Nitrite oxidizing bacteria, like *Nitrobacter* and converted into nitrate ions completing the nitrification process (Vareennes, 2003) as presents in Eq. 2.2:

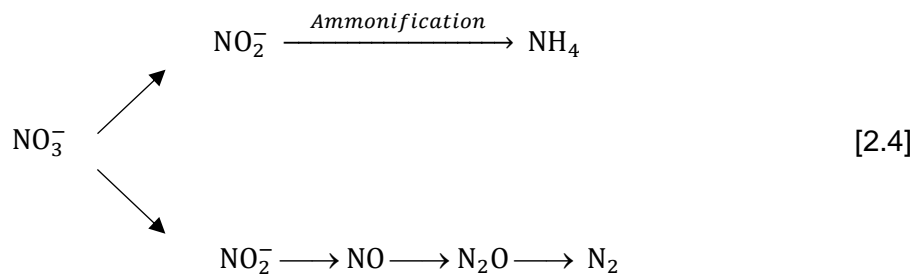


This last procedure is carried out by autotrophic bacteria but some heterotrophic bacteria (and also fungi) can carry out parts of the process, more commonly designed as heterotrophic nitrifiers (Prosser *et al.*, 2007). These rates are typically lower because they cannot obtain energy from the oxidation of the organic and inorganic forms of N.

The nitrification process produces nitrogenous gaseous losses as a by-product from the microbial activity. N₂O produced at a global level from nitrification processes has a significant impact over the greenhouse effect and the ozone layer (Hutchinson and Davidson, 1993; Gødde and Conrad, 2000). The gases produced by the AOB are NO, N₂O and NO₂, which can also be consumed by AOB (Arp and Stein, 2003).

2.4.5 Denitrification

Denitrification is most active under anaerobic conditions where there are high concentrations of both oxidised nitrogen compounds (NO_3^- , NO_2^-) acting as terminal electron acceptors in the absence of oxygen, to be reduced into gaseous oxides (NO , N_2O), which may themselves be further reduced to dinitrogen (N_2). NO_3^- can also be reduced to NH_4^+ via NO_2^- , with N_2O being produced, this process is designated as nitrate ammonification and can take place in the same environmental conditions as denitrification (Eq. 2.4) (Canfield, Kristensen and Thamdrup., 2005; Thomson *et al.*, 2012).



As well as biological denitrification described above, there's also the chemical denitrification or chemo denitrification based on the reduction of nitrite ions, which are unstable in acidic environments, through oxidation of organic N by NO_2^- with N_2 gas as output (Christianson and Cho, 1983).

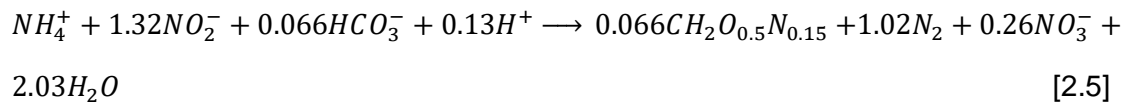
Soil moisture fluctuation influences the denitrification through the aeration of the soil, meaning if the soil moisture is higher than the field capacity the denitrification rates will increase due to the anoxic conditions developed; contrarily to nitrification, above 60% WFPS denitrification is the predominant process in the production of N_2O emissions (Müller and Sherlock, 2004).

The addition of organic C compounds to the soil eases the complete denitrification process inducing anaerobiosis through stimulation of O_2 demand, reducing emissions of N_2O and NO and emitting directly N_2 (Vallejo *et al.*, 2004).

2.4.6 Anammox

Anammox stands for anaerobic ammonium oxidation and in this case ammonium and nitrite are biologically converted, directly, to N_2 and N_2O gas; N_2O can be inhibited by nitrite presence (Strous *et al.*, 1999; Thomson *et al.*, 2012)

Anammox is inhibited by the presence of nitrite, higher than 0.1 g per litre (Strous *et al.*, 1999). Strous *et al.* in 1998 developed the stoichiometry based on the mass balance (Eq.2.5):



2.4.7 N- MIT (Mineralization-Immobilization Turnover)

Mineralisation occurs during organic matter decomposition. Microorganisms use complex organic compounds as a source of energy and transform them into smaller more readily available compounds (Jansson and Persson, 1982).

N mineralization divides into three processes carried out by heterotrophic microorganisms and autotrophic bacteria focused on the nitrification. The heterotrophic perform the aminization, transforming the complex nitrogenous organic compounds into simpler ones like amines, which then are used to be turned into ammoniated compounds through the ammonification (Eq. 2.6) (Tisdale and Nelson, 1985; Rodrigues and Coutinho, 2000):



But immobilization can occur when the products from mineralization are reused by microorganisms, integrating the compounds in its tissues or in non-cellular organic matter (humus) making nitrogen unavailable for plant uptake.

Mineralization and immobilization can happen at the same time, reason why is referred as Mineralization-Immobilization Turnover (MIT).

Tisdale (1958) indicates the different C/N values to determine MIT. C/N between 20:1 and 30:1 is the perfect ratio for an efficient plant N uptake. For residues with high rates of C/N applied to the soil, as shown in the first plot from Figure 2.10, there is an immobilization of mineral N because of the N content consumed by microbial activity, leading to the depletion of the soluble N in the soil and consequently creating a nitrate depression period affecting the possible plant uptake. The underneath plot describes what happens when the residues have a low rate of C/N, meaning there is more N content than necessary, therefore the soluble N content in the soil increases.

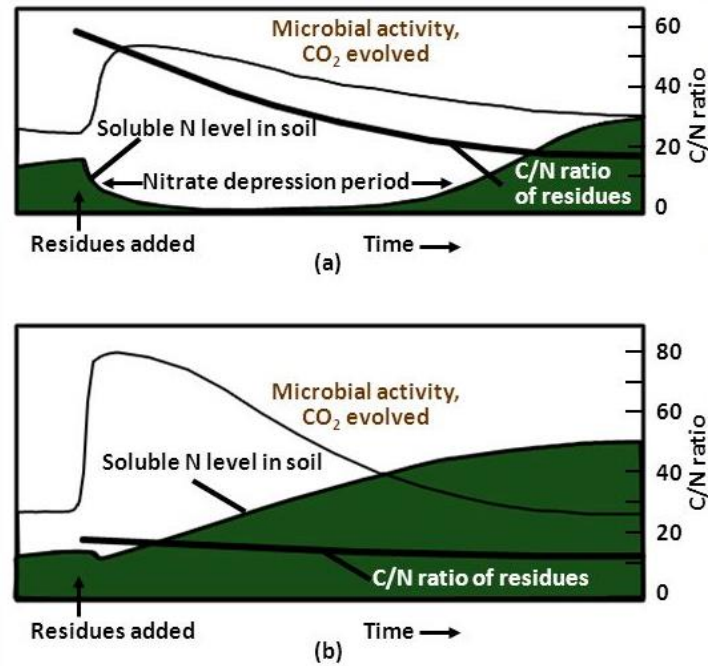


Figure 2.10 Mineralization-Immobilization turnover explained by residues added with different C/N ratio. Source: Weil and Brady, 2016

2.4.8 Plant uptake

Inorganic N is preferred for plant uptake, typically in the form of NH_4^+ and/or oxidized NO_3^- rather than other dissolved organic N (DON) forms (e.g., urea, amines, proteins, and nucleic acids) which are absorbed in smaller quantities or are mineralized into inorganic forms by microorganisms (Nacry *et al.*, 2013). Although van Breemen (2002) suggested that more investigation is needed in DON plant uptake specially in N-limiting environments. The referred inorganic forms are very dynamic, and can be consumed as fast as they are produced, especially in well aerated soils with neutral pH (Jones *et al.*, 2004).

2.4.9 Soil-Water

The soil-water content and water filled pore space (WFPS) of soils influences the ratios of $\text{N}_2\text{O}:\text{NO}:\text{N}_2$ emissions as demonstrated in the hole-in-the-pipe (HIP) model (Davidson and Verchot, 2000). Moving water can work as a transport of oxygen throughout the soil system, it also has the important part of transporting NO , N_2O and N_2 out of the soil.

Generally conditions can be summarised into three situations: a dry well aerated soil, where oxidative process is predominant, with NO production higher than N₂O or N₂; a wet soil with poorly aerated soil thus the most reductive oxide is the dominant product, N₂O; and a very wet soil that creates anaerobic conditions so nitrogen oxide forms are consumed by the nitrifiers, releasing mostly N₂ as a result (Davidson and Verchot, 2000). Due to the heterogeneous nature of soil, all of these processes can occur in tandem in macrosites within the soil structure, making identification of the dominating process at any given location difficult and highly spatially variable.

2.4.10 N-Leaching

NO₃⁻ leaching is directly related to the concentration of N in the soil, and consequently the rates of nitrification-denitrification, which in turn is dependent on soil moisture and rainfall/irrigation that regulates the soil aeration being this essential for nitrification rates.

NO₃⁻ leaching will also depend on temperature, as lower temperatures reduce production of NO₃⁻ (Russell *et al.*, 2007). Soil type is also important, as if it is a poorly structured sandy soil there'll be more macropores helping on the aeration of soils and consequently decreasing denitrification rates and facilitating the water movement which increases NO₃⁻ leaching (Cameron *et al.*, 2012). On the other hand, clay soils can fix N in their small pores, reducing leaching but also reducing accessibility to microorganisms.

2.5 Methane (CH₄)

Methane is a heat trapping gas with the most abundant reactive trace gas in the atmosphere and its sources can be either natural or anthropogenic. The natural sources considered significant are the oceans, termites' activity and wetlands. Wetlands are the main natural source of CH₄, with an emission of 177 and 284 Tg year⁻¹ (Reay *et al.*, 2018) but its high diversity (swamps, bogs, forest floods, etc) and spatial variability makes the CH₄ emission evaluation a challenge. A novel source has been also reported, Keppler *et al.* (2006) estimated an CH₄ emission of 1–7 Tg yr⁻¹ for plant litter under aerobic conditions suggesting that sunlight has a significant influence on the methanogenesis (Bloom *et al.*, 2010). Nevertheless, bio-waste can have a substantial impact in CH₄ emissions as it can be regarded in the following figure (Figure 2.11) in "Residential (biomass)" together with the other 11 top anthropogenic global sources of methane.

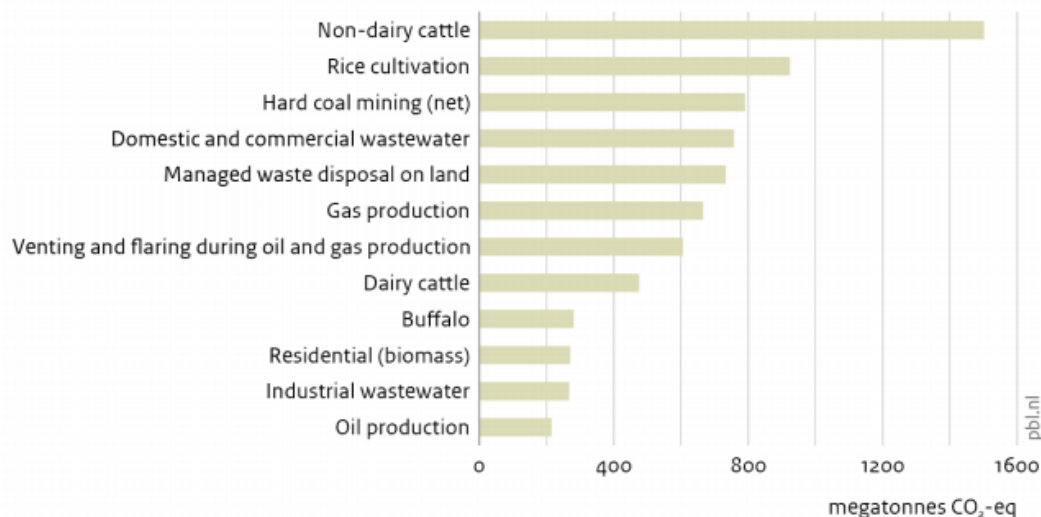


Figure 2.11 Global CH₄ emissions by source in 2016 presented in megatonnes of CO₂ equivalent. Source: (CCC,2018)

2.6 Methane net sink

The main sinks for CH₄ emitted into the atmosphere can be divided in three categories:

Non biological oxidation of CH₄ by UV-created hydroxyl (OH) radicals in the troposphere is the most important sink, destroying circa 90% of the CH₄ present in the atmosphere (with a concentration of approximately 1.7 ppm) (Smith *et al.*, 2003). Secondly, is stratospheric chemical reactions, which is less dense and not as vertically mixed by convection. These characteristics will allow CH₄ to enter from below and being consumed by chemical reactions, with OH radicals in the lower stratosphere and by reaction with chlorine radicals or oxygen atoms in the upper stratosphere (Jardine *et al.*, 2004).

The third main sink for atmospheric CH₄ removal takes place in the ground-atmosphere interface, where about 6% is oxidised and consumed by microorganisms in aerobic soils (Dalal *et al.*, 2008).

The balance of methane in the soil dwells between what is consumed by oxidation (methanotrophy) and what is emitted in anaerobic conditions (methanogenesis), if the activity of methanotrophic bacteria and methanogenic bacteria is positive it works as a source of emission (Le Mer and Roger, 2007)

Watanabe *et al.*(2007) stated that the majority of methane produced is biologically from anaerobic decompositions under anoxic conditions with very low redox potential, carried out by methanogenic archaea. A good example of these environments would be the lakes and the wetlands.

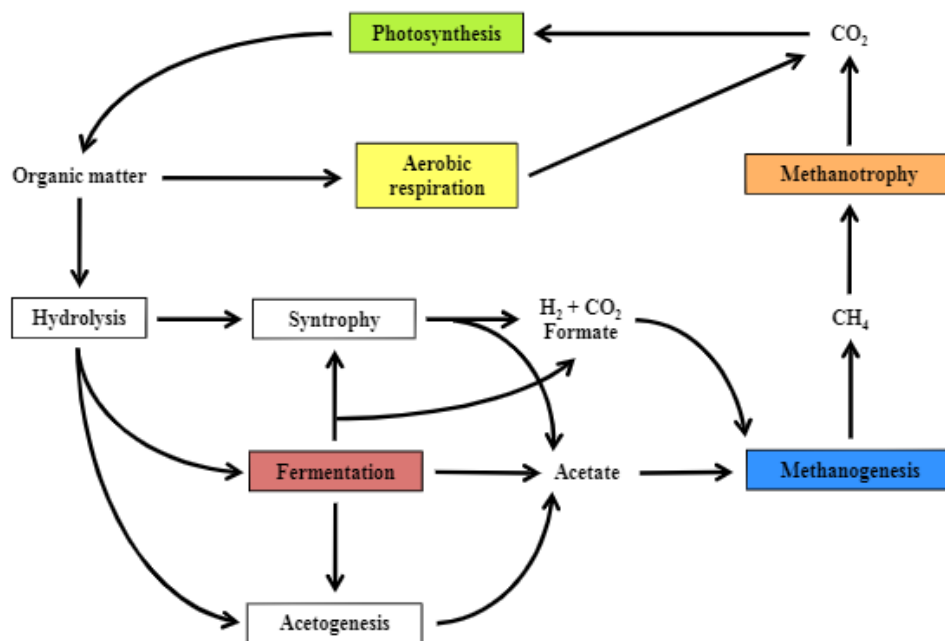


Figure 2.12 Soil methane cycle based on Loic Nazaries et al (2013)

2.6.1 Methanogenesis

Methanogenesis occurs in anaerobic conditions by methanogenic bacteria doing anaerobic digestion of organic matter, these are decisive factors for CH₄ production (Dalal et al., 2008).

Methanogens produce methane as metabolite in energy production through two different pathways (Lai, 2009):



(Acetotrophic methanogens)

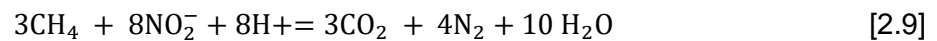


(Hydrogenotrophic methanogens)

Although methanogenesis takes place under anaerobic conditions, there are some studies showing that is imprudent to discard the hypothesis of CH₄ formation under aerobic conditions (Messenger et al., 2009; Althoff et al., 2010).

2.6.2 Methanotrophy

Methanotrophic bacteria can be found in well-aerated surface soils and oxidize CH₄ to generate energy and fix CO₂ into organic compounds, contributing up to 10% of global CH₄ oxidation (Smith *et al.*, 2003; Lowe, 2006) but biological CH₄ oxidation is also done by anaerobic archaea in association with anaerobic bacteria. In mesophilic anaerobic conditions, NO₂⁻ can work as an inhibitor for the methane oxidation, consisting in a mechanism of nitrite-dependent anaerobic oxidation of methane theory (Ettwig *et al.*, 2010). The following equation [2.9] is adapted from Ettwig *et al.*, 2010:



$$(\Delta G^\circ = -928 \text{ kJ mol}^{-1} \text{ CH}_4)$$

There are also references concluding that NH₄⁺ has a strong influence as an inhibitor of atmospheric CH₄ oxidation, which can suppress soil CH₄ consumption by up to 70% (Boeckx *et al.*, 1996; Hütsch *et al.*, 1996; Gullledge *et al.*, 1998).

3 Materials and methods

This experiment was carried out in two locations; a) Easter Bush, Midlothian (UK) (55°51'50.1"N 3°12'44.0"W) in 2017 and b) Lisbon Portugal (38°42'50.8"N 9°11'12.4"W) 2017/18. To quantify the GHG emissions from garden waste materials at a home-scale, several measurements were carried out in boxes/pots with different treatments established outdoors.

3.1 Site description

Edinburgh, Scotland, has a temperate hyperoceanic climate characterized by cold winters with an average temperature of 4 °C and cool summers with an average temperature of 14 °C, and its average annual precipitation is 920 mm, evenly distributed.

Lisbon, Portugal, has Mediterranean climate characterized by cold wet winters with an average temperature of 11 °C and dry hot summers with an average temperature of 23 °C, and an annual precipitation of approximately 800 mm (IPMA, 2019).

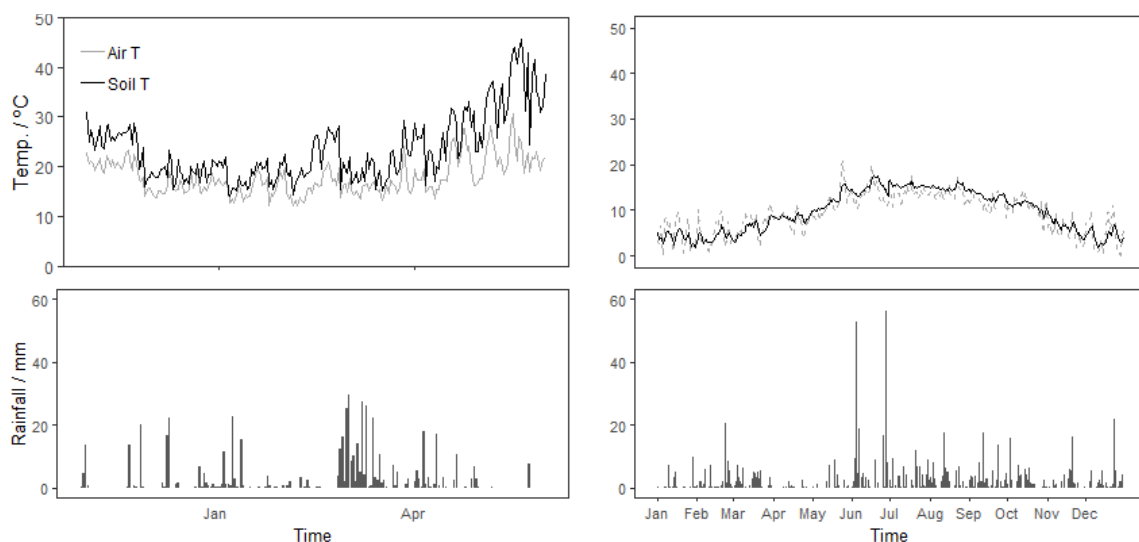


Figure 3.1 Air and soil temperature (°C) and precipitation (mm), for Portugal from November 2017 to May 2018 (left) and Scotland from January to December 2017 (right) based on data from meteorological stations during experiment..

In order to ensure that the samples reflect local microbial activity, measurements took place between April and August of 2017 (122 days) in Scotland, and between November and May of 2017/18 (167 days) in Portugal, to reflect the peak from growths season.

The substrates for the experiment were collected from both sites using the same experimental approach. In Scotland, the sample was taken from a grassland with Eutric Cambisol. The soil in Lisbon is a Haplic Vertisol with loamy clay texture (FAO, 1998).

Table 3.1 - Soil type and grass species properties measured from Portugal (November, 2017) and Scotland (May, 2017).

Parameters	Lisbon, ISA	Edinburgh, CEH
Soil	Haplic Vertisol	Eutric Cambisol
pH	7.6	6.5
C:N	19.73	11.72
Grass	Panicum Repens L.	Lolium Perenne L.
MC (%) ¹	60.25	79.03
N content (%)	1.83	2.57
C content (%)	86.10	61.75

2: Moisture Content

3.2 Field experiment

Both systems were set up outdoors throughout the study.

Three different treatments were applied in both sites: a control treatment with a soil layer (S), a second treatment with the same substrate layer plus covered by garden waste (S+GW) and a third treatment with only garden waste decomposing and no soil (GW).

In Scotland, the systems were assembled in transparent plastic boxes (78 x 56 x 43 cm), each box composed by a gravel layer to improve water drainage, topped with a layer of filtering textile and then covered with the respective treatment. This system was composed by 3 replicates for each treatment.

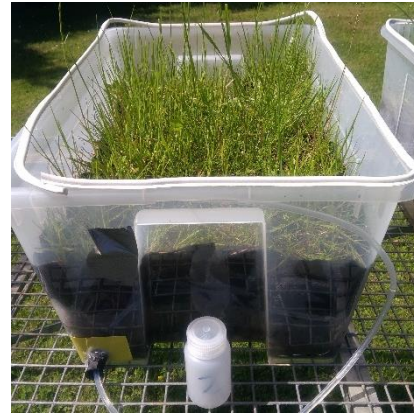


Figure 3.2 Boxes assembled in Scotland for treatment with soil and garden waste (left) and with soil and no garden waste (right)

In Portugal, the same methodology was applied with different materials. Kick-Brauckmann-pots (25.5 x 28 Ø cm) were used rather than boxes to also facilitate the water flux, thereby disregarding the need for a gravel layer. This system, because of the smaller area available per pot, was composed by 5 replicates for each treatment to provide a better estimate of the spatial variability.



Figure 3.3 Kick-Brauckmann-pots assembled in Portugal for the different treatments

Table 3.2 Outline of the assembled systems for each treatment for Scotland and Portugal with the respective applied garden waste. *Available volume for measurements

Site	Treatments	Replicas	V (m ³)*	Garden Waste (Kg)
Scotland	S	3	0.036	0
	S+GW	3	0.036	1
	GW	3	0.053	1.2
Portugal	S	5	0.017	0
	S+GW	5	0.017	0.1
	GW	5	0.017	0.4

3.3 Measurements

3.3.1 Flux measurements

Gaseous flux measurements were carried out once or twice a week, depending on the meteorological events, through a static gas chamber methodology (Hutchinson and Mosier, 1981) followed by a gas chromatography lab analysis.



Figure 3.4 Lid used for air measurements with a fan in Scotland

In Scotland, the boxes were sealed with a lid, containing neoprene sponge attached to the underside, and a fan to improve air mixture. The lid was closed with clips for a better sealing system. In Portugal the sealing was achieved with a plastic lid. All chambers were sealed during 60 min to obtain a concentration gradient for the GHG flux. Four samples were collected from each plot through a 100 mL syringe at $t = 0, 20, 40$ and 60 min and flushed into a 20 mL glass vials using 2 needles so air could flow through by pressure, flushing the vial with 500 % of its volume.

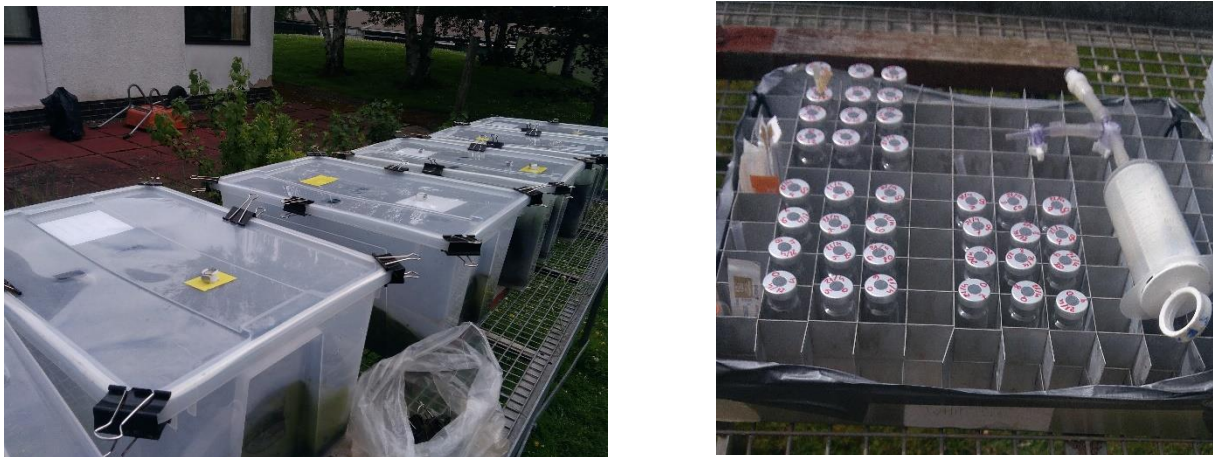


Figure 3.5 Sealed boxes ready for mensuration and the vials to collect the gas samples

The samples were then analysed using a Hewlett Packard 5890 series II gas chromatograph (Agilent Technologies, Stockport, fitted with an electron capture detector). The GC can have associated errors when it comes to the calibration curve and with sample concentration values close to the limit can result in anomalous values. Four sets of four calibration standards were used per GC run of 108 samples to improve quality control.

The concentration rate of gas flux from the soil was calculated according to Eq. 3.1:

$$F = \frac{dC}{dt} \times \frac{\rho V}{A} \quad [3.1]$$

Where F is the gas flux emitted from the soil ($\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), dC is the change in concentration in $\text{mol}\cdot\text{mol}^{-1}$, dt the change in time in s, ρ the air density in $\text{mol}\cdot\text{m}^{-3}$, V the chamber volume in m^3 , and A the surface available in the chamber for measurement in m^2 .

The gas concentration measurements reported by the GC were then used to calculate fluxes with the statistical program Rstudio. The RFlux package (a custom program (RFlux) written by Dr Peter Levy (Centre for Ecology and Hydrology, Edinburgh, UK) which adds compatibility between the HMR package and the GC output) was used to obtain the chamber fluxes. Cumulative flux was then calculated using trapezoidal integration between daily mean fluxes taken from the different treatments using a custom code written in R.

3.3.2 Leachate

The water and gas samples were collected in tandem. In Portugal, the leachate was collected in a bottle at the end of the pot and, for Scotland, through a tube at the end of the box, to trace NH_4^+ / NO_3^- . These concentrations were measured with a SEAL AQ2 discrete analyser (SEAL Analytical, US).



Figure 3.6 Water samples in Scotland where samples 1,2,3 belong to treatment S; 4,5,6 to treatment S+GW; 7,8,9 to treatment GW

3.3.3 Meteorological data

Both sites have a permanent measurement station providing air temperature, soil temperature, soil radiation and rainfall. In Scotland, the station recorded each 30 minutes while in Portugal where daily measurements. The variables for Scotland and Portugal where, respectively, air temperature recorded at 1.8 and 1.5 m altitude, soil temperature 0.3 and 0.5 m depth, soil radiation ($\text{J}\cdot\text{m}^{-2}$) and rainfall (mm).

3.3.4 Statistical analysis

N_2O emissions along with leachates data (NH_4^+ / NO_3^-) were log-mean transformed before analysis because of its wide range and uneven distributions of values.

The statistical analysis was performed in the software R using the following tools:

A multiple linear regression (MLR) to analyse the N_2O flux emissions with several predictor variables and its respective F-Global test to see the effectiveness of the constructed model when the coefficient of determination (R^2) is dubious.

$$R^2 = (\sum_{k=1}^n (\hat{y} - \bar{y})^2) / (\sum_{k=1}^n (y_k - \bar{y})^2) \quad [3.2]$$

To obtain the best fitted model there was an elimination of variables that don't contribute to the linear distribution with an Akaike Information Criterion analysis (AIC).

Analysis of variance (ANOVA) was also done in order to detect the effect of the factors over a response variable. It was constructed based on 2 factors (Site and Treatment) with 95% of probability without interaction between factors.

4 Results

4.1 Gaseous emissions

4.1.1 Non-cumulative

The non-cumulative N_2O and CH_4 fluxes for Portugal and Scotland, in each treatment, are presented in the following figures (Figure 4.1 and Figure 4.2), respectively.

At both sites, N_2O fluxes from the control treatments which contained only soil (S) do not show any statistically relevant fluctuation. The treatment that contained soil and grass waste (S+GW) in Portugal showed a peak in N_2O emissions after the first month of the experiment ($1.09 \pm 0.35 \text{ N}_2\text{O nmolm}^{-2}\text{s}^{-1}$ at the 15th of Dec) followed by a steep decline; and Scotland, for the same treatment, showed also a peak after the first month ($2.4 \pm 1.14 \text{ N}_2\text{O nmol/m}^2\text{s}$ at the 16th of May) overpassing the highest emission from Portugal, as shown in Appendix A.1 where it can be more perceptible.

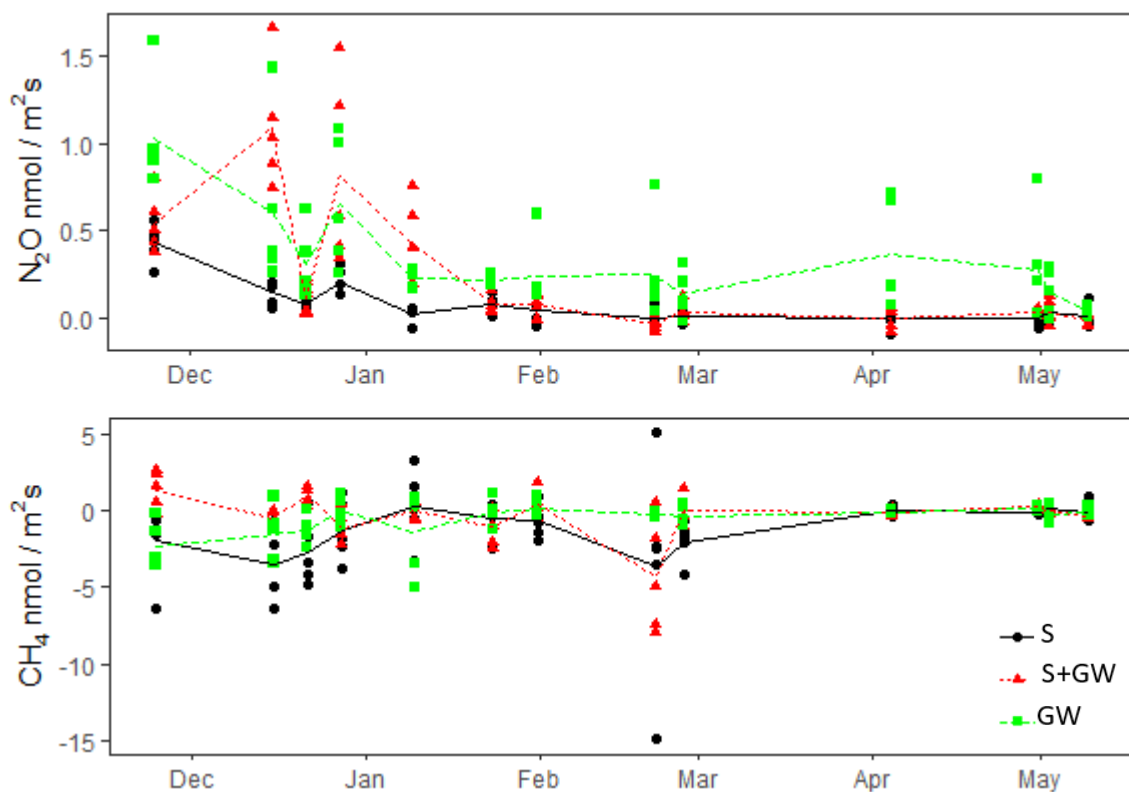


Figure 4.1 Non cumulative gaseous emissions of N_2O (above) and CH_4 (below) for Portugal. Each individual flux measurement belongs to a plot ($i=5$) for each treatment (S, S+GW and GW) with a concentration obtained for $t=60$ min in all measurements ($n=13$).

After two months the treatment containing only grass waste (GW) in Scotland reached the highest emissions measured ($3.33 \pm 5.17 \text{ N}_2\text{O nmolm}^{-2}\text{s}^{-1}$ at the 19th of Jun), a peak 5 times higher for any of the measured in Portugal, with a nonlinear continuous fluctuation. Meanwhile, for the same treatment, in Portugal, it had high emissions at the beginning ($1.03 \pm 0.32 \text{ N}_2\text{O nmolm}^{-2}\text{s}^{-1}$) and gradually decreased.

In Portugal there is a clear sequestration of CH_4 overall, but on the 21st of February in treatment S, individual measurements showed the highest emitted value and the highest consumption for methane, 5 and $-14.8 \text{ CH}_4 \text{ nmolm}^{-2}\text{s}^{-1}$, respectively. The standard deviation of its mean can point out clearly this discrepancy, $-3.61 \pm 7.13 \text{ CH}_4 \text{ nmolm}^{-2}\text{s}^{-1}$, also observable in Appendix D.2.

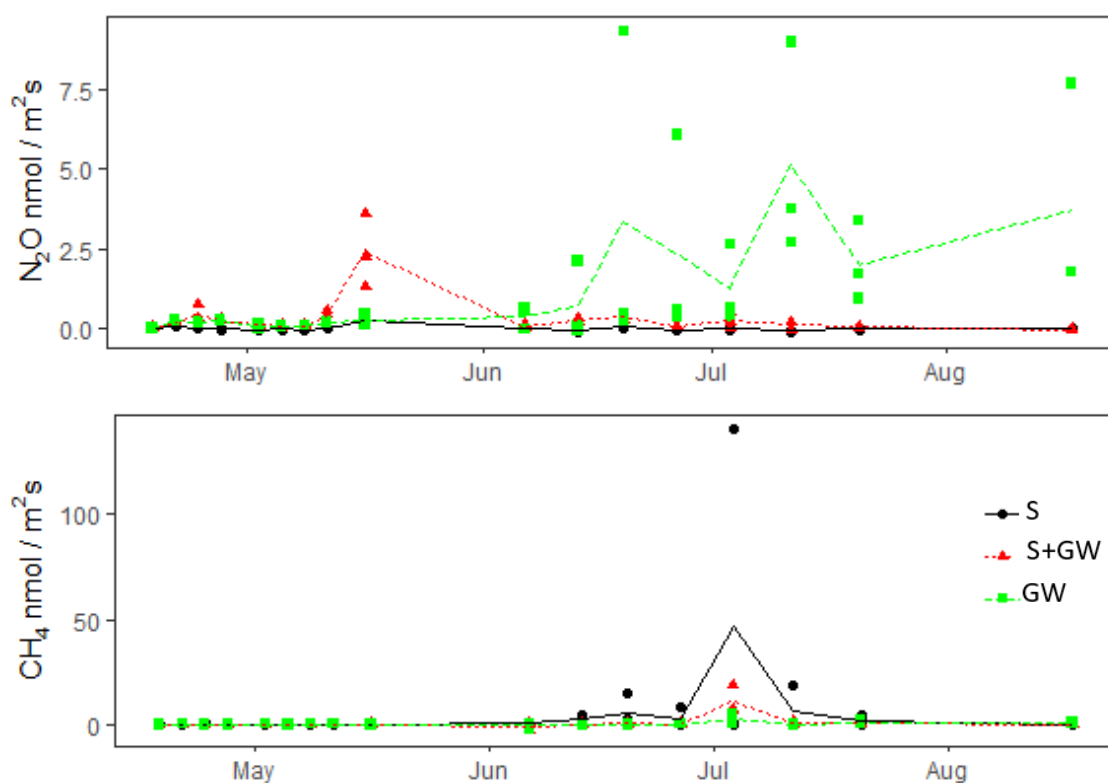


Figure 4.2 Non cumulative gaseous emissions of N_2O (above) and CH_4 (below) for Scotland. Each individual flux measurement belongs to a plot ($i=3$) for each treatment (S, S+GW and GW) with a concentration obtained for $t=60 \text{ min}$ in all measurements ($n=17$).

In Scotland there's a wide discrepancy between plots within the same CH₄ measurement in the control treatment (S), with a particular peak on the 3rd of July for an individual plot of 140.2 CH₄ nmolm⁻²s⁻¹, just after a high rainfall event on the 29th of June for all the treatments. This same plot presents higher emissions in each measurement than the other plots of the same treatment S. Subsequently, this high emission is considered to be an anomaly and is not included in the analysis, reducing its emitted mean from 46.96 ± 72.2 to 28.31 ± 62.53 CH₄ nmolm⁻²s⁻¹ with a still relatively high SD; in Appendix A.2 it is possible to examine the Scotland's CH₄ graph without this sample.

Treatment S+GW in Portugal also showed a methane consumption on the 21st of February for the majority of the plots (-4.33 ± 3.63 CH₄ nmolm⁻²s⁻¹). In Scotland this same treatment, after the anomalous value from treatment S, had the highest emissions 10.88 ± 6.20 CH₄ nmolm⁻²s⁻¹ at the same date (3rd July). Even though GW had the least relevant emissions for CH₄ for both sites, in Scotland its emissions also rose on the 3rd of July relatively to the other days.

4.1.2 Cumulative

A cumulative N₂O flux graph gives a good representation of the flux emissions throughout the study (Figure 4.3).

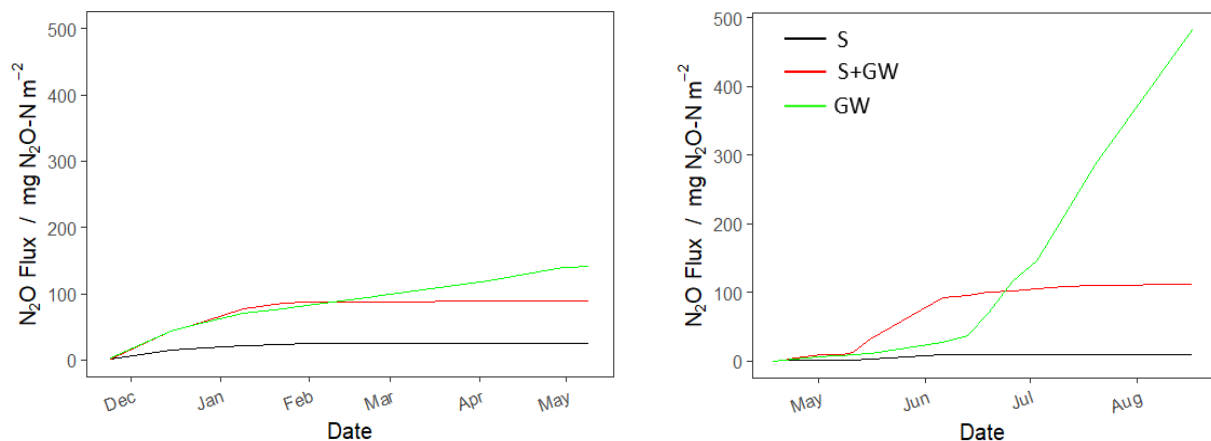


Figure 4.3 Cumulative N₂O flux for the different treatments (Black – S; Red – S+GW; Green – GW) for Portugal (left) and Scotland (right); obtained with the flux mean of each treatment for each measurement.

Treatment S emitted relatively low amounts of N₂O in comparison with the other treatments. The S+GW treatment in Portugal had continuous emissions until its stabilization while in Scotland there is a more accentuated peak, also after the first month, and then it stabilizes as well. Quantitatively speaking there were approximately the same amount of emissions for both sites in treatment S+GW (90 mg N₂O-N m⁻²) although Portugal had one more month of measurements.

The behaviour for the treatment GW was significantly different between sites, Portugal emitted gradually until its stabilization just as treatment S+GW and Scotland after a couple of months started its emissions with a tendency to increase. Emissions of N₂O did not stabilise from the GW treatment in Scotland before the end of the experiment, over 3 months after the grass was cut.

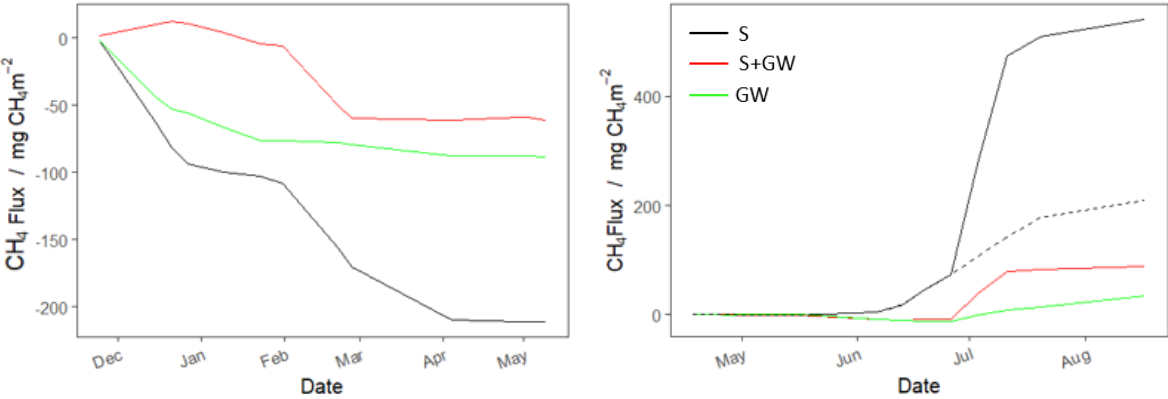


Figure 4.4 Cumulative CH₄ flux for the different treatments (Black – S; Red – S+GW; Green – GW) for Portugal (left) and Scotland (right); obtained with the flux mean of each treatment for each measurement.

With regard to CH₄ (Figure 4.4), the experiment in Portugal showed in general, a sequestration of CH₄, especially for treatment S which was also the treatment which emitted the highest CH₄ from the measurements in this site. Treatments S and S+GW are isometric in nature, an opposite behaviour with few exceptions as 5th and 21st of February. It should be noted that due to the method of generating the cumulative flux (linear interpolation) the negative flux could be an artefact of measurement errors from slightly negative chamber flux data close to a detection limit; however, the consistency of the observations lend legitimacy to the measurements.

Scotland treatment S had higher CH₄ emissions regarding the treatment S+GW. If the anomalous measurement for S in 3rd July is removed, as aforementioned, its cumulative emissions decrease substantially.

Based on the cumulative flux for each non-CO₂ GHG (previously mentioned), and the respective GWP, together with the C content applied (see Table 3.1) to the treatments it was estimated the percentage of the emitted CO₂ equivalent from the C applied (Table 4.1).

Table 4.1 Percentage of the emitted tonnes of CO₂ equivalent per tonne of C input in each treatment. Based on the cumulative flux from each non-CO₂ GHG times its respective GWP (currently adopted by the UNFCCC national emissions reporting) per input of C content in each treatment.

Treatments	Scotland (%)	Portugal (%)
S+GW	11.99	28.47
GW	58.47	11.26

N₂O GWP aided in elevating these results as it presents a GWP of 298, for CH₄ the GWP is 25 as adopted by the UNFCCC national emissions reporting.

4.1.3 Emission Factors

The nitrogen content (Table 3.1) was combined with cumulative N₂O flux to calculate the emission factor as a percentage of N input for each treatment (Table 3.2). It was subtracted from the treatment with soil and applied garden waste (S+GW) the cumulative flux from the treatment S for a better understanding of the effect of the garden waste emissions.

Table 4.2 Emission factors for Scotland (SCT) and Portugal (PT) for N₂O based on the N content of the biomass from each site (see Table 3.1) and the cumulative emissions from each treatment for a 3-month period. To treatment S+GW was subtracted the cumulative emission value from treatment S.

Treatment	SCT (mgN ₂ O m ⁻² d ⁻¹)	EF (N ₂ O) %	PT (mgN ₂ O m ⁻² d ⁻¹)	EF (N ₂ O) %
S	10.26	-	25.70	-
(S+GW) - S	101.61	0.76	63.90	1.25
GW	481.95	4.35	141.11	0.69

Treatment S does not have an emission factor considering there was no garden waste applied, thus no N input.

The treatment with higher emissions factor for N₂O in Scotland were the piles of garden waste (GW) with moderate distinction from the treatment S+GW. Portugal had a higher emission factor for S+GW than GW; it should be taken into consideration the amount of garden waste applied in each treatment (Table 3.1) versus its emissions, where treatment S+GW had almost half of GW emissions but less than half of the applied waste.

The following table (Table 4.2) also presents emission factors but for CH₄, where treatment S also doesn't have an emission factor due to the lack of C input.

Table 4.3 Emission factors for Scotland (SCT) and Portugal (PT) for CH₄ based on the C content of the biomass from each site (see Table 3.1) and the cumulative emissions from each treatment for a 3-month period. To treatment S+GW was subtracted the cumulative emission value from treatment S.

Treatment	SCT (mgCH ₄ m ⁻² d ⁻¹)	EF (CH ₄) %	PT (mgCH ₄ m ⁻² d ⁻¹)	EF (CH ₄) %
S	209.0519	-	-210.85	-
(S+GW) - S	-120.42	-0.04	150.02	0.16
GW	33.45	0.01	-88.67	-0.02

CH₄, as seen before, shows an opposite behaviour from one site to another. Scotland's treatment S+GW minus the cumulative emissions from S give a negative EF suggesting a sequestration because of the garden waste. The opposite can be seen for Portugal where the subtraction of treatment S to S+GW gives a positive EF.

4.2 Leachates

All three treatments in Portugal show a peak in leachates production after the first month, in 21st of Decembre (Figure 4.5), where was registered a heavy rainfall (200mm) after a relatively dry period with an average temperature of 16 °C. Treatment S and S+GW at this date had a higher leach of NO₃⁻ rather than NH₄⁺ (Appendix B.1) with losses of 3.1 and 7.3 N-NO₃⁻ mgNL⁻¹, respectively. On the other hand, treatment GW had a considerable peak of ammonium of 276 N-NH₄⁺ mgNL⁻¹.

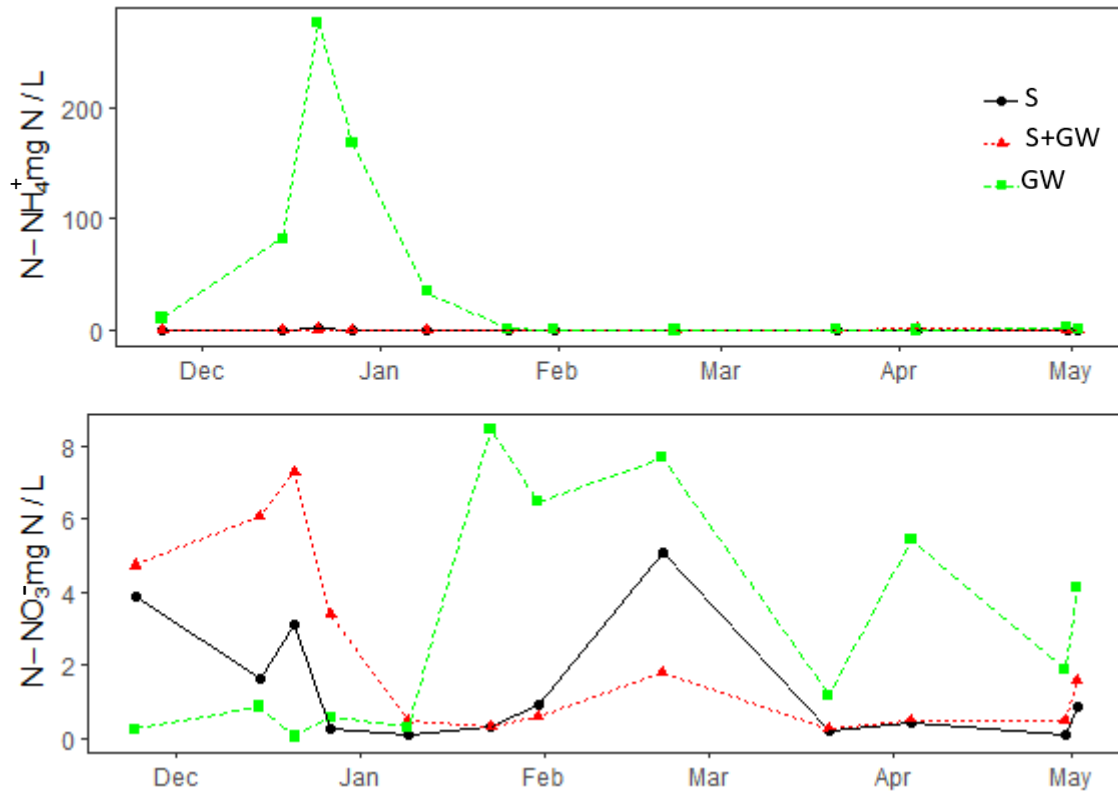


Figure 4.5 NH_4^+ (above) and NO_3^- (below) present in water samples for Portugal in each treatment (S, S+GW, GW) presented by the mean from the replicas ($i=5$) of each treatment.

The NH_4^+ in leachates in Scotland for treatment S and S+GW (Appendix B.1) fluctuated always in accordance, characterized by peaks followed by drops contrasting to NO_3^- (Appendix B.2) which doesn't show any considerable concentration except for treatment GW (Figure 4.6).

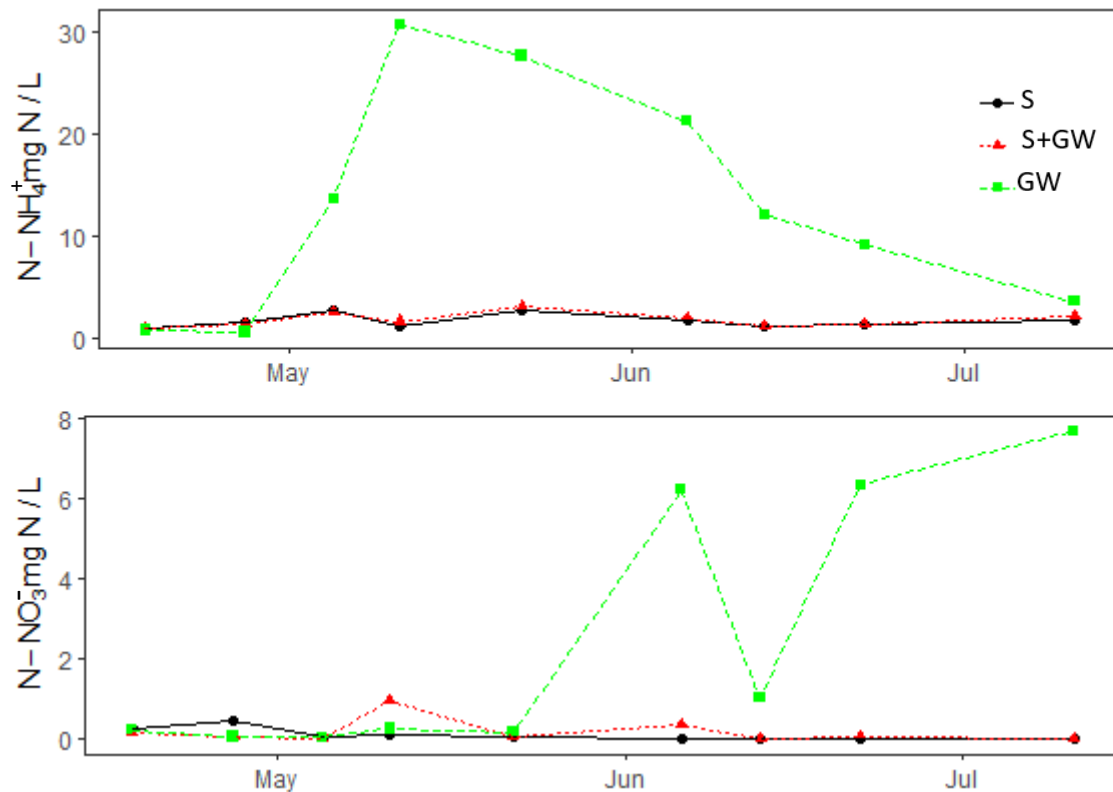


Figure 4.6 NH_4^+ (above) and NO_3^- (below) present in water samples Scotland in each treatment (S, S+GW, GW) presented by the mean from the replicas ($i=3$) of each treatment.

The treatment GW shows similarities between sites. Both reached a peak of NH_4^+ followed by its decrease and subsequent increase of NO_3^- . With the difference that in Portugal there's only a peak for NH_4^+ and in Scotland NH_4^+ levels maintain until the end, even though Portugal peak was approximately 10 times higher in treatment GW.

4.3 N-flux statistical analysis

Statistically significant effects between the response variables and the factors "Site" and/or "Treatment" with no interaction between them are shown in Table 4.4.

Table 4.4 ANOVA two-way test with no interaction for N₂O flux emissions and leachates (NH₄⁺, NO₃⁻)

Response variable	Explanatory variable	DF	Sum of Sq	Mean Sq	F-value	Pr(>F)
N ₂ O flux	Site	1	0.00	0.003	0.004	0.952
	Treatment	2	15.89	7.943	11.526	7.64e-05
NH ₄ ⁺	Site	1	12.328	12.328	21.379	2.69e-05
	Treatment	2	0.003	0.001	0.003	0.997
NO ₃ ⁻	Site	1	22.160	22.160	59.179	4.98e-10
	Treatment	2	1.496	0.748	1.997	0.146

Regarding N₂O flux, the high F-value (11.526) in respect to the low p-value (6.86×10^{-10}) indicates there're high effects between "Treatments". In Appendix C1 an interaction plot shows the lines are not in parallel indicating there's a similarity in the behavior, between Portugal and Scotland, in the way that each treatment affects the N₂O flux. Meanwhile the interaction plot between sites and N₂O flux mean for each treatment (Appendix C2) shows there's a significant mean change between each treatment in each site, but there's no sign of effect of this factor over N₂O flux.

This doesn't exclude the "Site" factor not interfering with the N-cycle, it concludes there's no difference between treatments in the way that each site affects N₂O flux. Which is the opposite for the leachates. NH₄⁺ and NO₃⁻ both suggest the factor "Site" has an effect over these, as it is visible by their respective high F-value and the correspondent low p-value.

In Figure 4.7 is possible to see how the conditions of a site interfere with the N₂O gaseous losses through the correlation between weather variables and log-normal N₂O mean flux.

4.3.1 Relation between N₂O flux and weather/soil properties

For a better understanding of the relationship of the site with the results, a study of their correlation was proceeded.

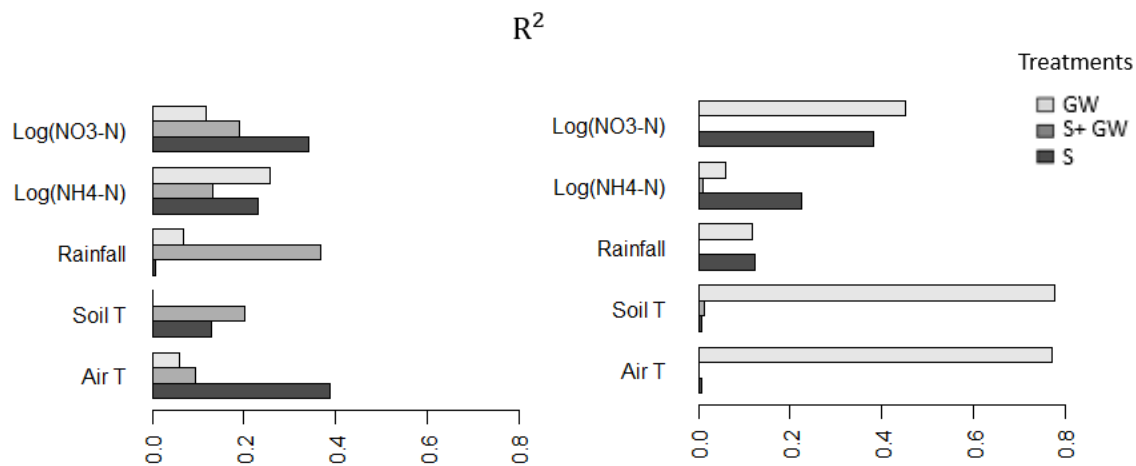


Figure 4.7 Variance in $\log(N_2O)$ flux in linear regression with different variables for Portugal (left) and right for Scotland (right)

The correlations in Portugal are fairly poor, the strongest correlation observed is between $\log(N_2O)$ and air temperature for treatment S with a determination coefficient of 38% followed by the correlation between $\log(N_2O)$ and rainfall in treatment S+GW (37%).

Scotland also presents very low correlations with treatment GW as the exception, indicating high correlations with Soil and Air temperature and NO_3^- with a R^2 of 78%, 77% and 45% respectively.

Knowing that the factors don't act as individual but in group as a system, its analysis as a whole is necessary. The selection of a model was based on the AIC's lowest value.

The logged data has negative values so it was transformed into $\log(x+1)$ to account for negative values.

Table 4.5 Best fitted models for each treatment in both sites with $\log(N_2O \text{ flux})$ as the response variable

Predictors		R ² (%)	Radj (%)	AIC
Portugal				
S	Mean Air T week + Mean Soil T week + $\log(NH_4^+)$	76.46	58.80	-4.17
S+GW	Mean Air T week + Mean Soil T week + Rainfall week + $\log(NO_3^-)$	84.94	69.89	-2.31
GW	Mean Air T week + Mean Soil T week + Rainfall week	35.19	7.41	-9.64
Scotland				
S	Mean Air T week + Mean Soil T week + Rainfall week	74.6	49.19	20.48
S+GW	Mean Air T week + Rainfall week + $\log(NH_4^+)$	17.4	65.2	5.41
GW	Mean Soil T week + Rainfall week + $\log(NH_4^+)$	84.29	72.50	-1.67

The weekly rainfall mean seems to be the most frequent predictor in the best fitted models, although it didn't show high individual correlations in any of the cases (Figure 4.7). The "week" variables represent the cumulative data.

In general, all models explain a large portion of the variance of the N_2O flux, showing the importance of the meteorological variables over N_2O flux behaviour. It was only treatments GW in Portugal (~35%) and S+GW in Scotland (~17%) which didn't show high correlations within the models.

An extensive number of parameters used doesn't specifically signify an improvement in the model, yet in general the multiple linear regression provides a better fit than the individual correlations (Table 4.2 and Figure 4.7).

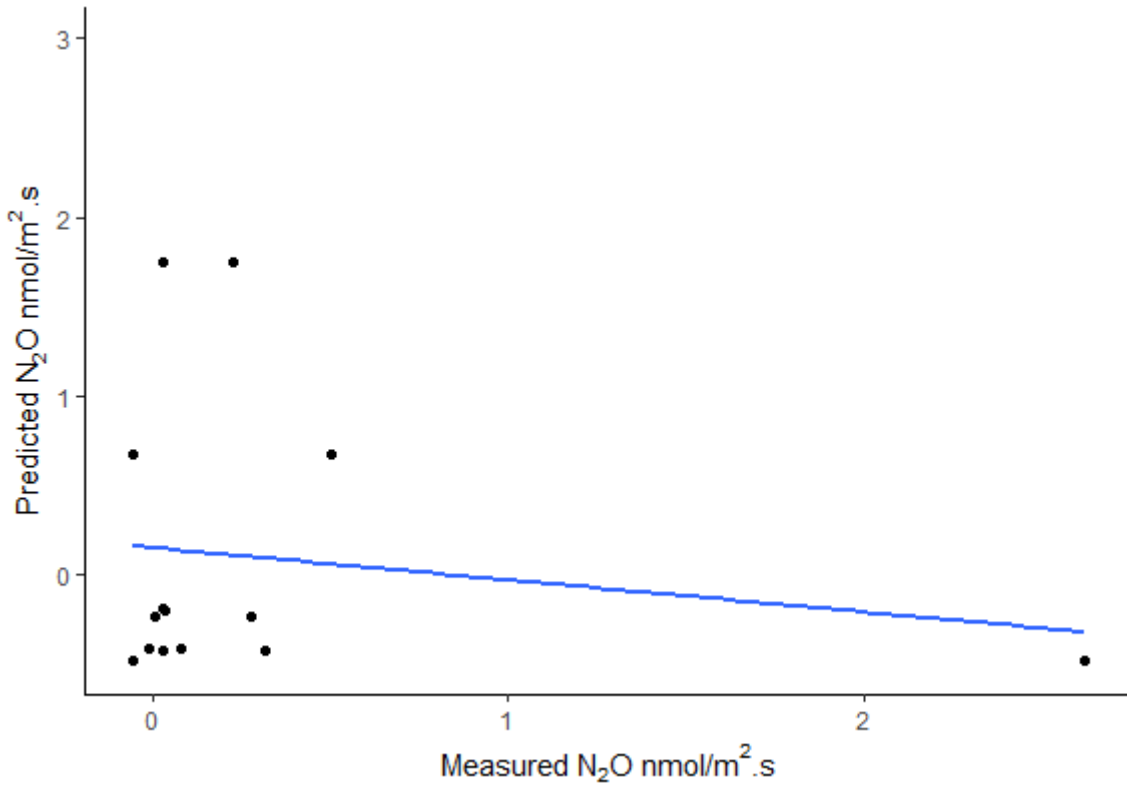


Figure 4.8 Scotland's treatment GW measured N_2O flux plotted against predicted flux based on the best regression model with the lowest AIC value (Table 4.2).

A linear regression between observed and predicted from the best fitted model was done to see if it could be improved somehow. There's a clear subsection of performance between 0 and 1 for the actual results. The standard error, which measures the accuracy of predictions through the vertical distance from the regression line, in general, is small apart from two observations. If these two observations are deleted it is possible to determine a better fitted model, although this regression is completely influenced by one measurement as noted by the dot with approximately 3 N_2O nmolm⁻²s⁻¹ (7th of Jul).

5 Discussion

The results show that N₂O emissions for treatments S and S+GW behaved similarly at both sites. Emissions of N₂O and CH₄ remained relatively low from the soil with no waste (S), meanwhile S+GW had a peak after the first month possibly attributed to the ammonification from the garden waste applied for the treatment; as it is known that decaying plant matter stimulates N₂O emissions (Arp and Stein, 2003). Although treatment GW didn't show any pattern due to the high deviation given (Appendix D.1), it produced substantial N₂O emissions when compared to the other treatments throughout the experiments, which came undoubtedly from the organic waste. Portugal emissions were generally lower than Scotland's, even though a wetter period was expected for Portugal, possibly resulting in higher N₂O emissions.

Measurements in Portugal showed higher NO₃⁻ traces in water samples denoting higher rates of nitrification, which can be predicted, by taking into consideration, the low OM content found in these soils hinders water retention and, consequently, leaves the pore spaces filled with air.

Measurements in Scotland pointed to denitrification with higher NH₄⁺ concentration present in leachates, input of N together with highly available C in soils create the perfect conditions for denitrification and, taking also into account, the high soil moisture in Scotland site due to the continuous rain helps denitrification by developing anaerobic microsites (Müller and Sherlock, 2004).

The peak of NO₃⁻ in Portugal for all treatments could indicate nitrification, although it coincides with a sudden drop of N₂O flux in the 21st of Dec, suggesting a denitrification interruption by the cease of rain creating dry conditions in contrast to the previous (15th Dec) and following (9th Jan) measurements. Thus, allowing nitrate to pool and N₂O emissions to slow down. Extended dry periods tend to stop microbiological activity and a sudden rain after this period reactivates this microbial community using all the N and C available releasing great amounts of CO₂, NO and N₂O. This effect is named as pulsing effect, and may explain measurements observed in Portugal in treatment GW regarding the high ammonium concentrations.

The nitrate concentration present for treatment S and S+GW in Portugal may have had an influence in the CH₄ sequestration, in anaerobic conditions it can work as limiting factor for the methane oxidation (Ettwig *et al.*, 2010). Nevertheless, for biodegradation to take place methanogens activity is necessary, the sequestration in treatment S+GW was not an expected result but it is possible to assume there's a negative balance between the production by methanogenic bacteria and consumption by methanotrophic bacteria creating a sink environment (Le Mer and Roger, 2007).

High latitude soils with peatlands, like Scotland, are a significant deposit of fixed carbon hence relatively large fractions of C content in the soil (high SOM); also, conditions are characterized by being poorly drained soils promoting anaerobic conditions (Lai, 2009). Thus, it is sensible that we observe CH₄ emissions for Scottish soils; especially for treatment S and S+GW when temperatures were higher (17-25°C) and soil moisture was elevated (>45%).

Emission factor, when deducting treatment's S emissions from S+GW for CH₄, was negative for Scotland (-0.04%) suggesting the garden waste helped in sequestration, or rather diminishing its emissions. For Portugal the CH₄ emissions from S+GW, deducting also S emissions, were positive (0.16%), pointing to be correlated to the biodegradation process. Methane presents low EFs but this gas is usually produced in less aerated large piles of waste. Our waste was relatively well aerated in comparison, which may be the reason why uptake is observed. N₂O often forms closer to the surface whereby there's more emissions than CH₄ for treatments with garden waste.

The garden waste biodegradation presented different results in between treatments and in between sites. When the soil was left exposed to the climate conditions its N₂O emissions were scarce in contrast to the CH₄ emissions, which emitted the most (sequestered in Portugal's case). The quantity of garden waste left to decay showed to be positively correlated with N₂O emissions, resulting in having the GW piles emitting the most. Meanwhile the opposite happened for CH₄, decreasing its emissions, or sequestration for Portugal, along with the increase in quantity of decaying biomass.

The percentage of emitted CO₂eq from the garden waste shows how these non-CO₂ GHGs can cause environmental impacts by the way the waste is managed. When left behind in households, in heaps, it can show different outcomes depending on the site. Portugal emitted up to 28.47% from the C content from the garden waste, still, more data on the waste composition is needed as it differs between seasons and so its C and N content may be higher and therefore stimulate or hinder emissions.

On the other hand, Scotland emitted 58.47% of the C content present for treatment GW. Although, this treatment, waterlogged several times, consequentially enhancing the N₂O emissions which had a larger contribution to the emitted percentage due to its GWP. Scotland's S+GW treatment emitted 11.99%, a large portion remained on the soil and on a further stage of the waste's biodegradation could show higher emissions, but there were effectively non-CO₂ emissions from the waste.

In Portugal there is a large amount of this waste being produced but not properly handled as it is possible to analyse in Table 5.1 where it shows what is actually collected and the potential collected green waste. What is not quantified is more likely to end in landfills, which emissions, when there's no gas recovery, in Europe, are in the regions of 1.80 tonnes CO₂e/ tonnes of MSW (OECD, 2012). A number not far ahead of 0.5847 tonnes CO₂e/ tonnes of garden waste from treatment GW in Scotland.

Table 5.1 Amount of green waste collected and its potential collection from separate collection in 2017, Portugal. Based on data from APA 2016

Green waste				
Region	Collected		Potential	
	Tons	kg per capita	Tons	kg per capita
North	0	0	25200	7.3
Center	0	0	896	0.49
LVT	0	0	51152	14.24
Alentejo	0	0	5247	10.66
Algarve	15138	34.36	18305	41.55
Total	15138	1.54	100801	10.28

There are several advantages from collection and quantification of this MSW, instead of ending in landfills where is produced circa Mt of CH₄ annually world-wide, from which only 12% is captured (Themelis and Ulloa, 2007; Ermolaev, 2015). Mulching municipal parks/garden's soils with this type of residue could be a favourable solution as it provides N-content and increases the soil C stock; its use for anaerobic digestion as a co-substrate has been proven to increment the production of biogas (Fitamo *et al.*, 2016); composting garden waste in small and large scales is considered to be a climate-smart sustainable agricultural land management in adapting to the effects of global climate (Andersen *et al.*, 2010; Boldrin and Christensen, 2010; van Amstel, 2012; Ermolaev, 2015) where emission factors for N₂O and CH₄ are respectively 0.13 gN₂Okg⁻¹ and 0.21 gCH₄kg⁻¹.

However, additional measures are being developed. For instance, there's the Action plan for the municipality of Lisbon for PERSU 2020 which includes measures for Green waste valorisation from municipal parks, where it promotes its MBT and its further use *in loco* to improve soil quality as well as its composting.

In Maia (Portugal) there's an advance in the strategic plan for MSW by collecting the bio-wastes door-to-door, after a successful pilot-project at Águas Santas in 2018, meant for organic fertilizer after its composting, with future implementation in Lisbon (SICN, 2019)

Meanwhile in Edinburgh, Scotland, the garden waste collection services (kerbside collection and Recycling Centres) represent around 25% of the current recycling performance to increase the collection frequency which serves to reduce waste arisings overall. These actions have helped in reducing the biowastes in landfills corresponding to a reduction of emissions by 75% (42Mt CO₂) together with the capture of landfill gas, and by 2021 the landfilling of biodegradable municipal waste is intended to be phased out (Scottish Government, 2018).

6 Conclusions

Considering the hypothesis initially formulated, the conclusions may be divided into two sections:

a) Quantification of garden waste potential for GHG emissions, with focus on CH₄ and N₂O, in outdoor conditions

The garden waste led to higher N₂O emissions when left in a pile on the soil in comparison with the bare soil. The waste tended to emit and leach more nutrients after 1-month period as a result of its mineralisation. The emissions of N₂O were clearly derivative from the organic waste decomposition as was possible to observe from treatment GW reaching emissions of 9.3 N₂O nmolm⁻²s⁻¹ in Scotland with a tendency to increase.

CH₄, contrarily, had higher emissions from the treatment S for both Portugal and Scotland. The emissions from soil with no garden waste tended to act very differently according to the site. The results show that the presence of garden waste had non-significant emissions until the three-month period, after which, there was sequestration for Portugal (-14.83 CH₄ nmolm⁻²s⁻¹) and an emission for Scotland (18.89 CH₄ nmolm⁻²s⁻¹). The garden waste showed a tendency to reduce CH₄ emissions in northern-soils like in Scotland, and to hinder sequestration in other places like Portugal. Although in a more advanced stage of its biodegradation the results could indicate otherwise.

For Portugal the use of this waste could be beneficial to the soil organic carbon content, as the majority of the waste's C content remained in the soil (>70%) for both treatments. Its disposition should be scattered, to avoid high N₂O and CH₄ emissions. Scotland, showed a considerable CO₂eq emissions from large heaps (GW treatment), the equivalent of 58.47% of the original CO₂ uptake in the starting garden waste. But as mentioned before, further research is needed to obtain a better understanding of its biodegradation and underlying processes for N₂O and CH₄ production.

b) Identify relationships between GHG emissions and meteorological variables in different climates;

The high/moderate temperatures of Portugal together with rainfall were unquestionably correspondent to the higher emissions of N₂O, distinctively for treatments S+GW and GW. Overall there were fluctuations in the first 3 months of measurements followed by a stabilization.

Scotland showed punctual peaks of N₂O emission, rather than fluctuations in treatments with garden waste. The accountability lies on the constant soil moisture from the constant rain with point rises in temperatures resulting in denitrification in these plots. Meanwhile the emission peaks of CH₄ from the bare soil plots (S), were also associated to soil temperatures higher than normal, between 16 and 20 °C with no rain events.

In general, for Portugal, CH₄ had negative flux measured, above all for treatment (S), after rain with soil temperature between 15-25°C. Not being enough as indicators for this apparent sequestration a more detailed study on this case is needed just as for other treatments. It is evident that each treatment behaves differently according to the weather conditions, but it is also possible to find similarities in how the garden waste is disposed.

7 Future study needs and perspectives

Future studies may alter methodology and measurement design to improve understanding of the processes that occur during composting. Based on the work carried out in this project, I would recommend that the following actions are considered.

1. Our study suggests that the garden waste GHG emissions are strongly linked to the weather conditions, soil composition and to the biomass composition. Further work should better identify the carbon and nitrogen content of the waste materials and soils prior to composting, following changes in these over time. As our experiments were box based, we could not take soil samples regularly without damaging the experiment. Field trials would be better suited to carry out larger scale research that would allow measurements to be made that can follow nutrient pools changing over the duration of the experiment.
2. The composting did not finish to completion during the time available to run the experiment. Increasing the experiment time to at least 1 year after degradation begins would allow better quantification of complete emission factors.
3. The emissions from the boxes were measured sporadically, with days between measurements. An automated measurement approach would allow a better temporal analysis of the gas fluxes, thus allowing a better understanding of the underlying microbial activity.

References

- Althoff F., Jugold A. and Keppler F. (2010) 'Methane formation by oxidation of ascorbic acid using iron minerals and hydrogen peroxide', *Chemosphere*. Elsevier Ltd, 80(3), pp. 286–292. doi: 10.1016/j.chemosphere.2010.04.004.
- van Amstel A. (2012) 'Methane. A review', *Journal of Integrative Environmental Sciences*, 9(SUPPL. 1), pp. 5–30. doi: 10.1080/1943815X.2012.694892.
- Andersen J. K., Boldrin A., Samuelsson J., Christensen Thomas H., Scheutz C. (2010) 'Quantification of Greenhouse Gas Emissions from Windrow Composting of Garden Waste', *Journal of Environment Quality*, 39(2), p. 713. doi: 10.2134/jeq2009.0329.
- APA (2016) *PERSU 2020: Plano Estratégico para os Resíduos Urbanos*.
- Arp, D. J. (2009) 'Nitrification', *Encyclopedia of Life Sciences*, pp. 1–6. doi: 10.1002/9780470015902.a0021154.
- Arp, D. J. and Stein, L. Y. (2003) 'Metabolism of Inorganic N Compounds by Ammonia-Oxidizing Bacteria', *Critical Reviews in Biochemistry and Molecular Biology*, 38(6), pp. 471–495. doi: 10.1080/10409230390267446.
- Baggs, E. M., Rees, R. M., Smith, K. A., Vinten, A.J.A. (2003) 'Nitrous oxide emissions following application of residues and fertiliser under zero and conventional tillage', *Plant and Soil*, 254(2), pp. 361–370. doi: 10.1023/A:1025593121839.
- Belnap, J. (2001) 'Factors Influencing Nitrogen Fixation', *Biological soil crust: structure, function, and management*, 150, pp. 241–261.
- Black, A. S., Sherlock, R. R., Smith, N. P., Cameron, K. C., Goh, K. M. (1985) 'Effects of form of nitrogen, season, and urea application rate on ammonia volatilisation from pastures', *New Zealand Journal of Agricultural Research*, 28(4), pp. 469–474. doi: 10.1080/00288233.1985.10417992.
- Bloom, A. A., Messenger, David J., Palmer, Paul I., Reay, David S., McLeod, Andy R., Lee-Taylor, Julia, Madronich, Sasha (2010) 'Global methane emission estimates from ultraviolet irradiation of terrestrial plant foliage', *New Phytologist*, 187(2), pp. 417–425. doi: 10.1111/j.1469-8137.2010.03259.x.
- Boeckx, P., Van Cleemput, O. and Villaralvo, I. (1996) 'Methane emission from a landfill and the methane oxidising capacity of its covering soil', *Soil Biology and Biochemistry*, 28(10–11), pp. 1397–1405. doi: 10.1016/S0038-0717(96)00147-2.
- Boldrin, A. and Christensen, T. H. (2010) 'Seasonal generation and composition of garden waste in Aarhus (Denmark)', *Waste Management*. Elsevier Ltd, 30(4), pp. 551–557. doi: 10.1016/j.wasman.2009.11.031.
- van Breemen, N. (2002) 'Natural organic tendency', *Nature*, 415(6870), pp. 381–382. doi: 10.1038/415381a.
- Brindha, R. K. and Vasudevan, N. (2017) 'Methane oxidation capacity of methanotrophs isolated from different soil ecosystems', *International Journal of Environmental Science and Technology*. Springer Berlin Heidelberg, 15(9), pp. 1931–1940. doi: 10.1007/s13762-017-1546-1.
- Cai, R., Minteer, Shelley D., Pita, Marcos, Leech, Dónal, De Lacey, Antonio L., Milton, Ross D., Abdellaoui, Sofiene (2017) 'Bioelectrochemical Haber-Bosch Process: An Ammonia-Producing H₂/N₂ Fuel Cell', *Angewandte Chemie International Edition*, 56(10), pp. 2680–2683. doi: 10.1002/anie.201612500.
- Cameron, K. C., Di, H. J. and Moir, J. L. (2012) 'Nitrogen losses from the soil/plant system: a review', 162, pp. 145–173. doi: 10.1111/aab.12014.

- Canfield, D. E., Kristensen, E. and Thamdrup., B. (2005) *Advances in Marine Biology, Advances in Marine Biology*. Elsevier.
- Christensen, T. H., Gentil, Emmanuel, B., Alessio, L., Anna W., Weidema, Bo P., Hauschild, M. (2009) 'C balance, carbon dioxide emissions and global warming potentials in LCA-modelling of waste management systems', *Waste Management and Research*, 27(8), pp. 707–715. doi: 10.1177/0734242X08096304.
- Christianson, C. B. and Cho, C. M. (1983) 'Chemical Denitrification of Nitrite in Frozen Soils', *Soil Science Society of America Journal*, 47(1), p. 38. doi: 10.2136/sssaj1983.03615995004700010007x.
- Ciais, P. and Sabine, C. (2013) 'Carbon and Other Biogeochemical Cycles', *IPCC Climate Change 2013: The Physical Science Basis*.
- Committee on Climate Change (2018) *Reducing UK emissions 2018 Progress Report to Parliament*. Available at: www.theccc.org.uk/publications.
- Conrad, R. (2009) 'The global methane cycle: Recent advances in understanding the microbial processes involved', *Environmental Microbiology Reports*, 1(5), pp. 285–292. doi: 10.1111/j.1758-2229.2009.00038.x.
- Cowan, N. J., Norman, P., Famulari, D., Levy, P. E., Reay, D. S., Skiba, U. M. (2015) 'Spatial variability and hotspots of soil N₂O fluxes from intensively grazed grassland', *Biogeosciences*, 12(5), pp. 1585–1596. doi: 10.5194/bg-12-1585-2015.
- Dalal, R. C., Allen, D. E., Livesley, S. J., Richards, G. (2008) *Magnitude and biophysical regulators of methane emission and consumption in the Australian agricultural, forest, and submerged landscapes: A review, Plant and Soil*. doi: 10.1007/s11104-007-9446-7.
- Davey, A. and Marchant, H. J. (1983) 'Seasonal variation in nitrogen fixation by Nostoc commune Vaucher at the Vestfold Hills, Antarctica', *Phycologia*, 22(4), pp. 377–385. doi: 10.2216/i0031-8884-22-4-377.1.
- Davidson, E. A. (2009) 'The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide since 1860', *Nature Geoscience*. Nature Publishing Group, 2(9), pp. 659–662. doi: 10.1038/ngeo608.
- Davidson, E. A. and Verchot, L. V. (2000) 'Testing the hole-in-the-pipe model of nitric and nitrous oxide emissions from soils using the TRAGNET database', *Global Biogeochemical Cycles*, 14(4), pp. 1035–1043. doi: 10.1029/1999GB001223.
- Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., Dias, P. L. da Silva, Wofsy, S. C., Zhang, X. (2007) 'Couplings between changes in the climate system and biogeochemistry', in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press. doi: Cited By (since 1996) 525rExport Date 12 August 2012.
- Di, H. J. and Cameron, K. C. (2002) 'Nitrate leaching in temperate agroecosystems: Sources, factors and mitigating strategies', *Nutrient Cycling in Agroecosystems*, 64(3), pp. 237–256. doi: 10.1023/A:1021471531188.
- Duiker, S. W. and Lal, R. (1999) 'Crop residue and tillage effects on carbon sequestration in a Luvisol in central Ohio', *Soil and Tillage Research*, 52(1–2), pp. 73–81. doi: 10.1016/S0167-1987(99)00059-8.
- EC-JRC/PBL (2017) *Emissions Database for Global Atmospheric Research v4.3.2. Joint Research Centre of the European Commission/PBL Netherlands Environmental Assessment Agency*. Available at: <http://edgar.jrc.ec.europa.eu/overview.php?v=432>.

European Commission (2015) *Assessment of separate collection schemes in the 28 capitals of the EU*. Brussels. Available at: https://ec.europa.eu/environment/waste/studies/pdf/Separate_collection_Final_Report.pdf.

EEA (2013) *Managing Municipal Solid Waste: A Review of Achievements in 32 European Countries*, Publications Office of the European Union. doi: 10.2800/71424.

Ermolaev, E. (2015) *Greenhouse Gas Emissions from Food and Garden Waste Composting Effects of Management and Process Conditions*, Dissertation.

Ettwig, K. F., Francoijs, Kees-Jan, Janssen-Megens, Eva M., van Alen, T., Dutilh, B. E., Luesken, F., Stunnenberg, H., Le Paslier, D., Wu, M. L., Pelletier, E., Strous, M., Jetten, M. S. M., de Beer, D., Butler, M. K., Zedelius, J., Wessels, H. J. C. T., Schreiber, F., Weissenbach, J., van de Pas-Schoonen, K. T., Kuypers, M. M. M., Mangenot, S., Op den Camp, Huub J. M., Gloerich, J. (2010) 'Nitrite-driven anaerobic methane oxidation by oxygenic bacteria', *Nature*. Nature Publishing Group, 464(7288), pp. 543–548. doi: 10.1038/nature08883.

Eurostat (2005) *Waste generated and treated in Europe*.

EUROSTAT (2019) *European statistics Municipal waste statistics*. Available at: https://ec.europa.eu/eurostat/statistics-explained/index.php/Municipal_waste_statistics#Municipal_waste_generation.

FAOSTAT (2017) *Food and Agriculture Organization of the United Nations*. Available at: <http://www.fao.org/faostat/en/>.

Fernandes, A. C., Déjean Guerra, M., Ribeiro, R., Rodrigues, S. (2018) '*Relatório do Estado do Ambiente 2018*' [State of the Environment Report 2018], Agência Portuguesa do Ambiente.

Fitamo, T., Boldrin, A., Boe, K., Angelidaki, I., Scheutz, C. (2016) 'Co-digestion of food and garden waste with mixed sludge from wastewater treatment in continuously stirred tank reactors', *Bioresource Technology*, 206(January), pp. 245–254. doi: 10.1016/j.biortech.2016.01.085.

Frenzel, P. (2000) 'Plant-Associated Methane Oxidation in Rice Fields and Wetlands', pp. 85–114. doi: 10.1007/978-1-4615-4187-5_3.

Fruteau de Lacroix, H., Desbois, S. and Saint-Joly, C. (1997) 'Anaerobic Digestion of Municipal Solid Organic Waste: Valorga full-scale plant in Tilburg, the Netherlands', *Water Science and Technology*, 36(6–7), pp. 457–462.

Galloway, J. N., Townsend, Alan R., Erismann, Jan Willem, Bekunda, M., Cai, Z., Freney, John R., Martinelli, Luiz A., Seitzinger, Sybil P., Sutton, Mark A. (2008) 'Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions', *Science*, 320(5878), pp. 889–892. doi: 10.1126/science.1136674.

Gödde, M. and Conrad, R. (2000) 'Influence of soil properties on the turnover of nitric oxide and nitrous oxide by nitrification and denitrification at constant temperature and moisture', *Biology and Fertility of Soils Fertile Soils*, 32(2), pp. 120–128.

Granhall, U. (1970) 'Acetylene Reduction by Blue-Green Algae Isolated from Swedish Soils', *Wiley*, 44(1), pp. 17–22.

Gruber, N. and Galloway, J. N. (2008) 'An Earth-system perspective of the global nitrogen cycle', *Nature*, 451(7176), pp. 293–296. doi: 10.1038/nature06592.

Gulledge, J. and Schimel, J. P. (1998) 'Low-Concentration Kinetics of Atmospheric CH₄ Oxidation in Soil and Mechanism of NH₄ Inhibition', *Applied and Environmental Microbiology*, 64(11).

- Gundersen, P., Schmidt, I. K. and Raulund-Rasmussen, K. (2006) 'Leaching of nitrate from temperate forests – effects of air pollution and forest management', *Environmental Reviews*, 14(1), pp. 1–57. doi: 10.1139/a05-015.
- Haynes, R. J. (1986) *Mineral Nitrogen in the plant-soil system*. Physiological ecology.
- Hungria, M. and Vargas, M. A. T. (2000) 'Environmental factors affecting N₂ fixation in grain legumes in the tropics, with an emphasis on Brazil', *Field Crops Research*, 65(2–3), pp. 151–164. doi: 10.1016/S0378-4290(99)00084-2.
- Hutchinson, G. L. and Davidson, E. A. (1993) 'Processes for Production and Consumption of Gaseous Nitrogen Oxides in Soil', *American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America*, (55). doi: 10.2134/asaspecpub55.c5.
- Hutchinson, G. L. and Mosier, A. R. (1981) 'Improved Soil Cover Method for Field Measurement of Nitrous Oxide Fluxes¹', *Soil Science Society of America Journal*, 45(2), p. 311. doi: 10.2136/sssaj1981.03615995004500020017x.
- Hütsch, B. W., Russell, P. and Mengel, K. (1996) 'CH₄ oxidation in two temperate arable soils as affected by nitrate and ammonium application', *Biology and Fertility of Soils*, 23(1), pp. 86–92. doi: 10.1007/s003740050142.
- IPCC (2006a) 'Agriculture, Forestry and Other Land Use', *2006 IPCC Guidelines for National Greenhouse Gas Inventories*, 4, p. 6.1-6.49. doi: 10.1111/j.1749-6632.2009.05320.x.
- IPCC (2006b) 'IPCC Guidelines for National Greenhouse Gas Inventories, Chapter 4: N₂O - DIRECT EMISSIONS FROM AGRICULTURAL SOILS'.
- IPCC (2006c) 'IPCC Guidelines for National Greenhouse Gas Inventories. Chapter 11: N₂O emissions from managed soils, and CO₂ emissions from lime and urea application', p. 11.1-11.54. Available at: http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/4_Volume4/V4_11_Ch11_N2O&CO2.pdf.
- IPMA (2019) *Instituto Português do Mar e da Atmosfera*. Available at: <http://portaldoclima.pt/pt/>.
- Jansson, S. L. and Persson, J. (1982) 'Mineralization and Immobilization of Soil Nitrogen by Microorganisms', *Clark, F. E. And T. Rosswall (Ed.). Ecological Bulletins Nfr (Naturvetenskapliga Forskningsradet) No. 33, PROCEEDING(22)*, pp. P179-195.
- Jardine, C. N., Boardman, B., Osman, A., Vowles, J., Palmer, J. (2004) 'Methane UK Report', *The environmental change institute*, 44(0). Available at: www.eci.ox.ac.uk.
- Jones, D. L., Healey, John R., Willett, Victoria B., Hodge, A., Farrar, John F. (2004) 'Dissolved organic nitrogen uptake by plants—an important N uptake pathway?', *Soil Biology and Biochemistry*, 37(3), pp. 413–423. doi: 10.1016/j.soilbio.2004.08.008.
- Keppeler, F., Hamilton, John T.G., Braß, M., Röckmann, T. (2006) 'Methane emissions from terrestrial plants under aerobic conditions', *Nature*, 439(7073), pp. 187–191. doi: 10.1038/nature04420.
- Kravchenko, I., Boeckx, P., Galchenko, V., Van Cleemput, O. (2002) 'Short- and medium-term effects of NH₄⁺ on CH₄ and N₂O fluxes in arable soils with a different texture', *Soil Biology and Biochemistry*, 34(5), pp. 669–678. doi: 10.1016/S0038-0717(01)00232-2.
- Lai, D. Y. F. (2009) 'Methane Dynamics in Northern Peatlands: A Review', *Pedosphere*. Soil Science Society of China, 19(4), pp. 409–421. doi: 10.1016/S1002-0160(09)00003-4.
- Lassaletta, L., Billen, G., Grizzetti, B., Anglade, J., Garnier, J. (2014) '50 year trends in nitrogen use efficiency of world cropping systems: The relationship between yield and nitrogen input to cropland', *Environmental Research Letters*. IOP Publishing, 9(10). doi: 10.1088/1748-9326/9/10/105011.

- Lowe, D. C. (2006) 'Global change: A green source of surprise.', *Nature*, 439, pp. 148–149.
- Mattos, D., Alva, A. K., Paramasivam, S., Graetz, D. A. (2003) 'Nitrogen volatilization and mineralization in a sandy Entisol of Florida under citrus', *Communications in Soil Science and Plant Analysis*, 34(13–14), pp. 1803–1824. doi: 10.1081/CSS-120023216.
- Mchale, P. J., Mitchell, M. J. and Bowles, F. P. (1998) 'Soil warming in a northern hardwood forest: trace gas fluxes and leaf litter decomposition', *Canadian Journal of Forest Research*, 1372, pp. 1365–1372.
- Meisinger, J. J. (1984) 'Management of Soils and Pests for Nitrogen Utilization', *Agricultural Research Service, USDA*.
- Meisinger, J. J., Schepers, J. S., Calderón, F. J., Raun, W. R., Jenkinson, D. S. (2008) 'Soil Nitrogen Budgets', pp. 505–562. doi: 10.2134/agronmonogr49.c13.
- Le Mer, J. Le and Roger, P. (2007) 'Production, oxidation, emission and consumption of methane by soils: A review', *European Journal of Soil Biology*, 37(1), pp. 25–50. doi: 10.1016/S1164-5563(01)01067-6.
- Messenger, D. J., McLeod, A. R. and Fry, S. C. (2009) 'The role of ultraviolet radiation, photosensitizers, reactive oxygen species and ester groups in mechanisms of methane formation from pectin', *Plant, Cell and Environment*, 32(1), pp. 1–9. doi: 10.1111/j.1365-3040.2008.01892.x.
- Müller, C. and Sherlock, R. R. (2004) 'Nitrous oxide emissions from temperate grassland ecosystems in the Northern and Southern Hemispheres', *Global Biogeochemical Cycles*, 18(1), p. n/a-n/a. doi: 10.1029/2003gb002175.
- Mulumba, L. N. and Lal, R. (2008) 'Mulching effects on selected soil physical properties', *Soil and Tillage Research*, 98(1), pp. 106–111. doi: 10.1016/j.still.2007.10.011.
- Nacry, P., Bouguyon, E. and Gojon, A. (2013) 'Nitrogen acquisition by roots: Physiological and developmental mechanisms ensuring plant adaptation to a fluctuating resource', *Plant and Soil*, 370(1–2), pp. 1–29. doi: 10.1007/s11104-013-1645-9.
- Norton, J. M. and Stark, J. M. (2010) 'Regulation and measurement of nitrification in terrestrial systems', *Methods in Enzymology*, 486(C), pp. 343–368. doi: 10.1016/B978-0-12-381294-0.00015-8.
- OECD (2012) *Greenhouse gas emissions and the potential for mitigation from materials management within OECD countries*.
- Prosser, J. I., Bohannan, Brendan J M, Curtis, Tom P, Ellis, Richard J, Firestone, Mary K, Freckleton, Rob P, Green, Jessica L., Green, Laura E., Killham, Ken, Lennon, Jack J., Osborn, A Mark, Solan, Martin, Gast, Christopher J Van Der, Young, J Peter W (2007) 'The role of ecological theory in microbial ecology', *Nature Publishing Group*, 5(May), pp. 384–392. doi: 10.1038/nrmicro1643.
- Pugesgaard, S., Petersen, Søren O., Chirinda, Ngonidzashe, Olesen, Jørgen E. (2016) 'Crop residues as driver for N₂O emissions from a sandy loam soil', *Agricultural and Forest Meteorology*. Elsevier B.V., 233, pp. 45–54. doi: 10.1016/j.agrformet.2016.11.007.
- Qiu, Q. *et al.* (2015) 'Effects of plant-derived dissolved organic matter (DOM) on soil CO₂ and N₂O emissions and soil carbon and nitrogen sequestrations', *Applied Soil Ecology*. Elsevier B.V., 96, pp. 122–130. doi: 10.1016/j.apsoil.2015.07.016.
- Ramanathan, V. *et al.* (1985) 'Trace gas trends and their potential role in climate change', 90, pp. 5547–5566.

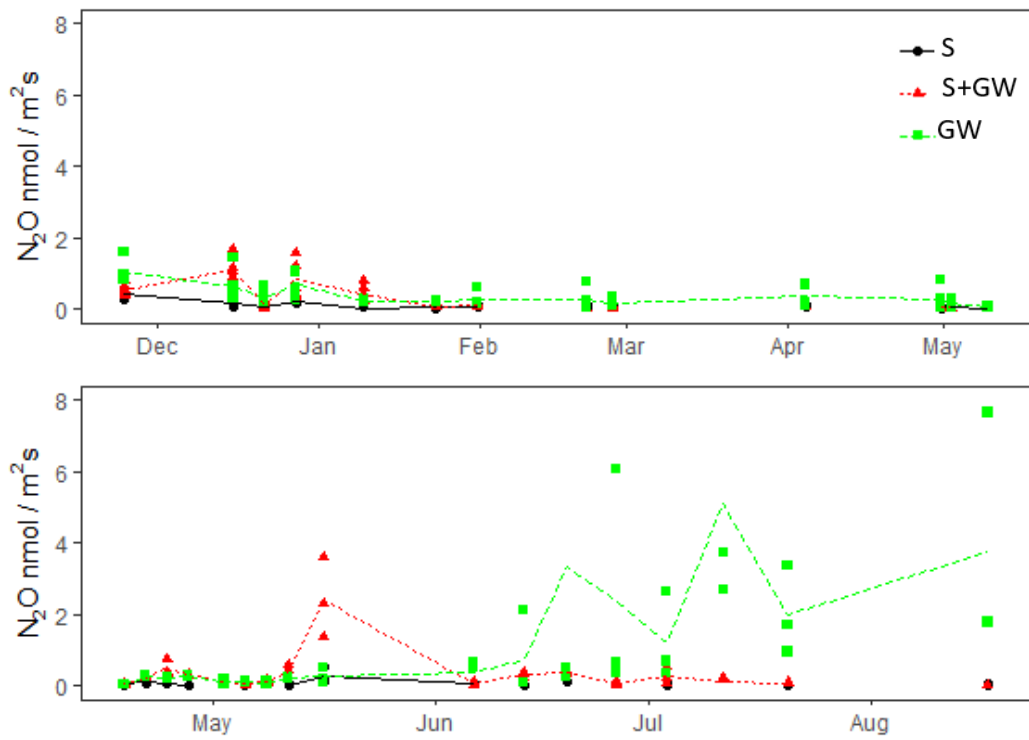
- Rathore, A. L., Pal, A. R. and Sahu, K. K. (1998) 'Tillage and mulching effects on water use, root growth and yield of rainfed mustard and chickpea grown after lowland rice', *Journal of the Science of Food and Agriculture*, 78(2), pp. 149–161. doi: 10.1002/(SICI)1097-0010(199810)78:2<149::AID-JSFA94>3.0.CO;2-U.
- Reay, D. S. *et al.* (2018) 'Methane and Global Environmental Change', *Annual Review of Environment and Resources*, 43(1), pp. 165–192. doi: 10.1146/annurev-environ-102017-030154.
- Reeburgh, W. . (2003) 'Global Methane Biogeochemistry', *Treatise on Geochemistry*, (1901), pp. 1–32. doi: <http://dx.doi.org/10.1016/B0-08-043751-6/04036-6>.
- Répubblica Portuguesa (2014) *Green Growth Commitment*. doi: 10.1016/s1520-765x(01)90111-7.
- Rodrigues, M. Â. and Coutinho, J. F. (2000) *Eficiência de utilização do azoto pelas plantas*, *Edição do Instituto Politécnico de Bragança*. Available at: <https://bibliotecadigital.ipb.pt/bitstream/10198/205/1/47> - Eficiência de utilização de azoto pelas plantas.pdf.
- Russell, C. A. *et al.* (2007) 'Effect of temperature and nitrogen source on nitrification in a sandy soil', *Communications in Soil Science and Plant Analysis*, 33(11–12), pp. 1975–1989. doi: 10.1081/CSS-120004836.
- Scotland Government (2010) *Scotland's Zero Waste Plan*, *The Scottish Government*. Available at: <http://www.gov.scot/Resource/0045/00458945.pdf>.
- Scottish Government (2018) 'Climate Change Plan: The Third Report on Proposals and Policies 2018-2032', *Scottish Government report*, (February), p. 222. doi: 9781788516518.
- SICN (2019) *Municípios vão passar a recolher de forma seletiva os resíduos orgânicos*. Available at: <https://sicnoticias.pt/pais/2019-08-12-Municipios-vao-passar-a-recolher-de-forma-seletiva-os-residuos-organicos?fbclid=IwAR2xB1UIDzepoNB68ogGikXmROPZqX4fMPv9gdITOPHP-Qzau9Mr8F0xOIU>.
- Skiba, U., Jones, S. K., Dragosits, U., Drewer, J., Fowler, D., Rees, R. M., Pappa, V. A., Cardenas, L., Chadwick, D., Yamulki, S., Manning, A. J. (2012) 'UK emissions of the greenhouse gas nitrous oxide', *Philosophical Transactions of the Royal Society B: Biological Sciences*, 367(1593), pp. 1175–1185. doi: 10.1098/rstb.2011.0356.
- Smith, A. *et al.* (2001) *Waste management options and climate change: Final report to the European Commission*.
- Smith, K. A. *et al.* (2003) 'Exchange of green house gases between soil and atmosphere: interactions of soil physical factors and biological processes', (December), pp. 779–791. doi: 10.1046/j.1365-2389.2003.00567.x.
- Smith, K. A. *et al.* (2012) 'The role of N₂O derived from crop-based biofuels, and from agriculture in general, in Earth's climate', *Philosophical Transactions of the Royal Society B: Biological Sciences*, 367(1593), pp. 1169–1174. doi: 10.1098/rstb.2011.0313.
- Smith, V. H. and Schindler, D. W. (2009) 'Eutrophication science: where do we go from here?', *Trends in Ecology and Evolution*, 24(4), pp. 201–207. doi: 10.1016/j.tree.2008.11.009.
- Solomon, S. *et al.* (2007) *Climate Change 2007: The Physical Science Basis, Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. doi: 10.1017/CBO9781107415324.004.
- Sommer, S. G., Schjoerring, J. K. and Denmead, O. T. (2004) 'Ammonia Emission from Mineral Fertilizers and Fertilized Crops', 2113(December 2004), pp. 557–622. doi: 10.1016/s0065-2113(03)82008-4.
- Strous, M. *et al.* (1998) 'The sequencing batch reactor as a powerful tool for the study.pdf', *Applied Microbiology and Biotechnology*, 50, pp. 589–596. doi: 10.1007/s002530051340.

- Strous, M., Gijss Kuenen, J. and Jetten, M. S. M. (1999) 'Key Physiology of Anaerobic Ammonium Oxidation Downloaded from', *Applied and Environmental Microbiology*, 65(7), pp. 3248–3250. doi: papers2://publication/uuid/E9A1573A-6D62-420E-94D0-CA7C84D0FEB9.
- Strynchuk, J., Royal, J. and England, G. (1999) 'Grass and leaf decomposition and nutrient release study under wet conditions', in *6th Biennial Stormwater Research and Watershed Management Conference*, p. 96.
- Tang, C. and Rengel, Z. (2003) 'Role of Plant Cation/Anion Uptake Ratio in Soil Acidification', in *Handbook of Soil Acidity*, pp. 263–284. doi: 10.1201/9781315152325-9.
- Themelis, N. J. and Ulloa, P. A. (2007) 'Methane generation in landfills', *Renewable Energy*, 32(7), pp. 1243–1257. doi: 10.1016/j.renene.2006.04.020.
- Thomson, A. J. *et al.* (2012) 'Biological sources and sinks of nitrous oxide and strategies to mitigate emissions', *Philosophical Transactions of the Royal Society B: Biological Sciences*, 367(1593), pp. 1157–1168. doi: 10.1098/rstb.2011.0415.
- Tian, D. and Niu, S. (2015) 'A global analysis of soil acidification caused by nitrogen addition', *Environmental Research Letters*. IOP Publishing, 10(2). doi: 10.1088/1748-9326/10/2/024019.
- Tisdale, S. L. and Nelson, W. L. (1985) 'Soil Fertility and Fertilizers', 56–8585(ii).
- UK Government, D. for E. F. & R. A. (2013) *Mechanical Biological Treatment of Municipal Solid Waste, London, UK*.
- Vallejo, A. *et al.* (2004) 'Comparison of N losses (NO₃⁻, N₂O, NO) from surface applied, injected or amended (DCD) pig slurry of an irrigated soil in a Mediterranean climate', *Plant and Soil*, 272(1–2), pp. 313–325. doi: 10.1007/s11104-004-5754-3.
- Varenes, A. de (2003) *Produtividade dos solos e ambiente*. 1st edn. Escolar Editora.
- Verdi, L. *et al.* (2018) 'Greenhouse gas and ammonia emissions from soil: the effect of organic matter and fertilisation method', *Italian Journal of Agronomy*, 11. doi: 10.4081/ija.2018.1124.
- Wang, X. *et al.* (2019) *The Effects of Mulch and Nitrogen Fertilizer on the Soil Environment of Crop Plants*. 1st edn, *Advances in Agronomy*. 1st edn. Elsevier Inc. doi: 10.1016/bs.agron.2018.08.003.
- Watanabe, T., Kimura, M. and Asakawa, S. (2007) 'Dynamics of methanogenic archaeal communities based on rRNA analysis and their relation to methanogenic activity in Japanese paddy field soils', *Soil Biology and Biochemistry*, 39(11), pp. 2877–2887. doi: 10.1016/j.soilbio.2007.05.030.
- Weil, R. R. and Brady, N. C. (2016) *The Nature and Properties of Soils. 15th edition*.
- Whitehead, D. C. (2000) *Nutrient Elements in Grassland: Soil-plant-animal Relationships*. Edited by CAB International. CABI Publishing.
- Zero Waste Scotland (2019) *Scotland's Food Waste Reduction Action Plan*. Available at: <https://www.zerowastescotland.org.uk/food-waste/reduction-action-plan>.

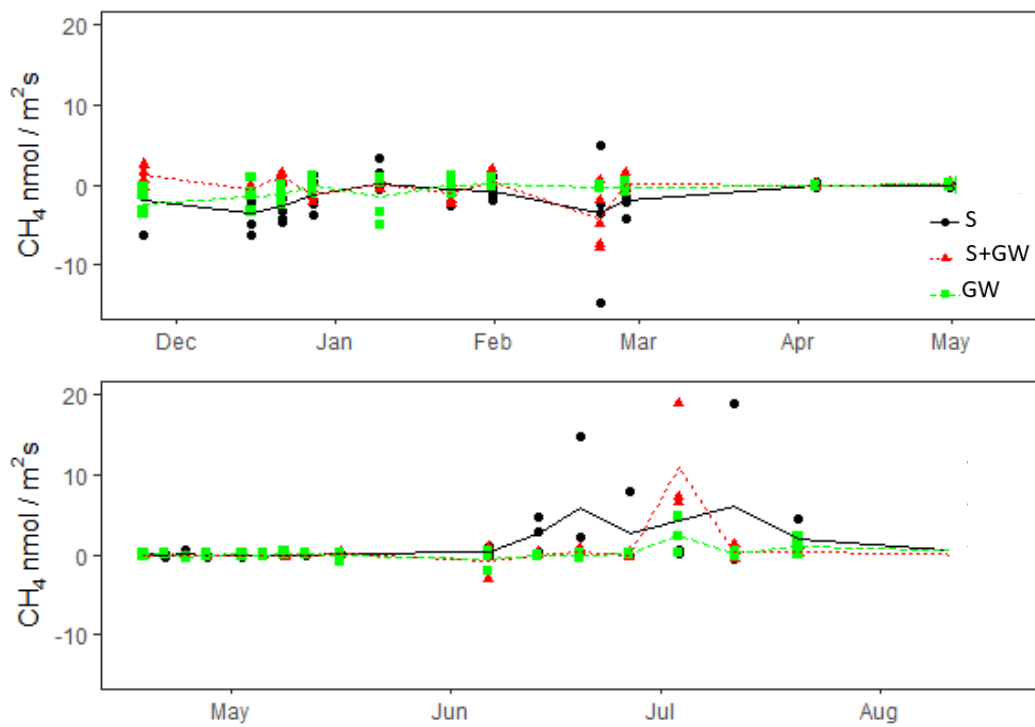
Appendix

Appendix A

1. N₂O emissions from Portugal (above) and Scotland (below) with same scale

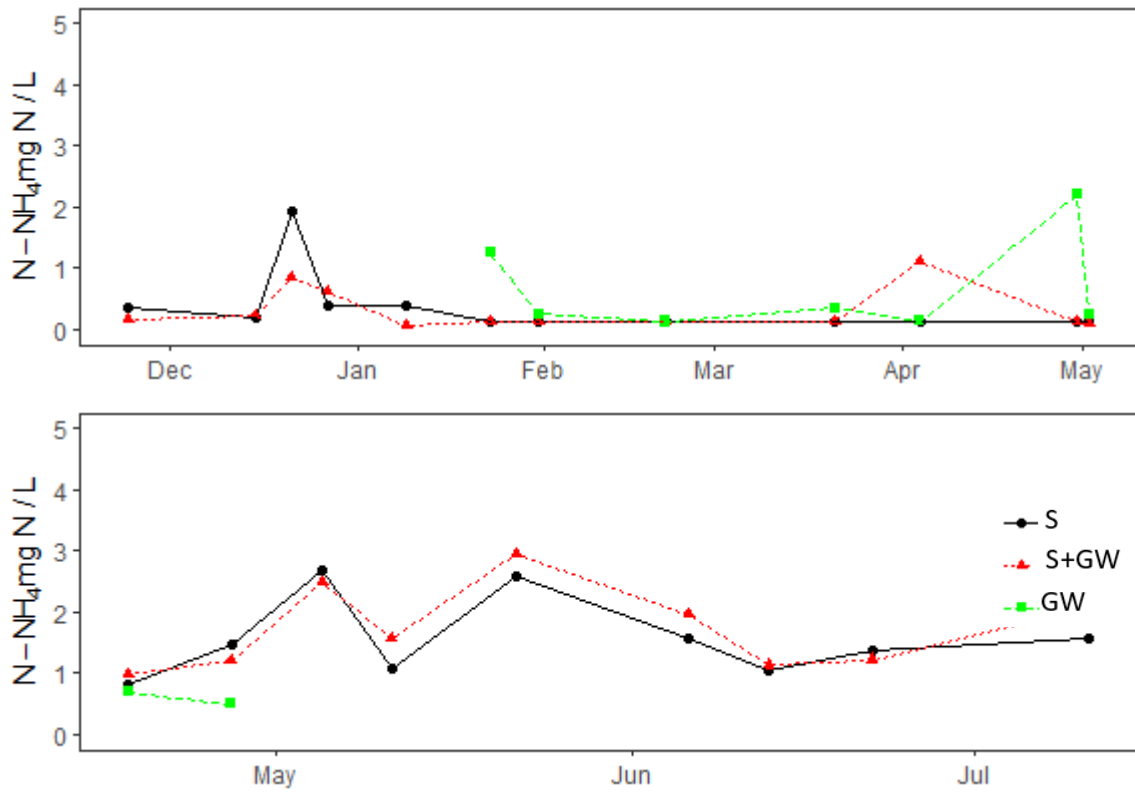


2. CH₄ emissions from Portugal (above) and Scotland (below) with same scale

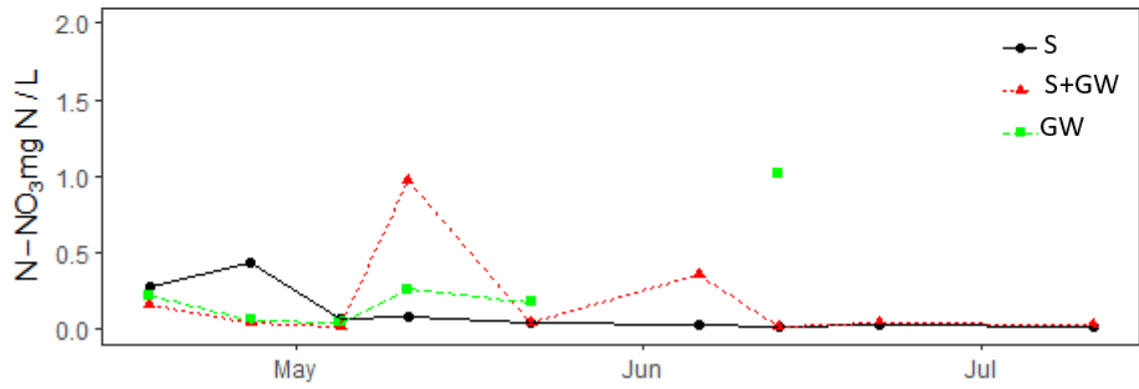
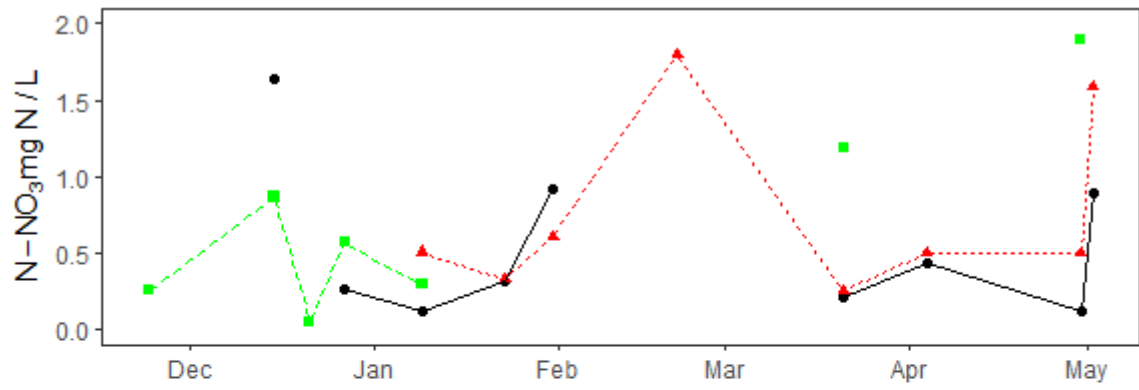


Appendix B

1. Zoom in of N-NH₄⁺ leachings from Portugal and Scotland

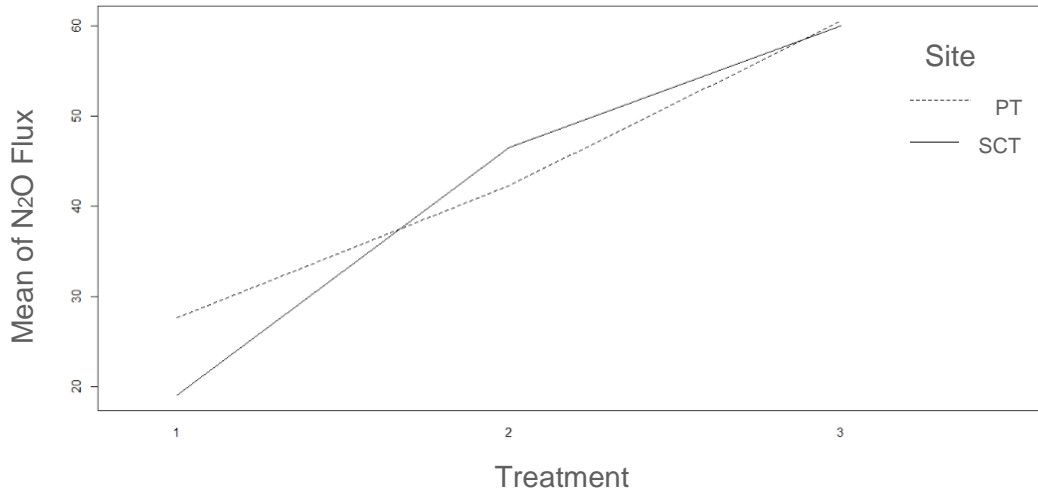


2. Zoom in N-NO₃⁻ leachings Portugal (above) Scotland (below)

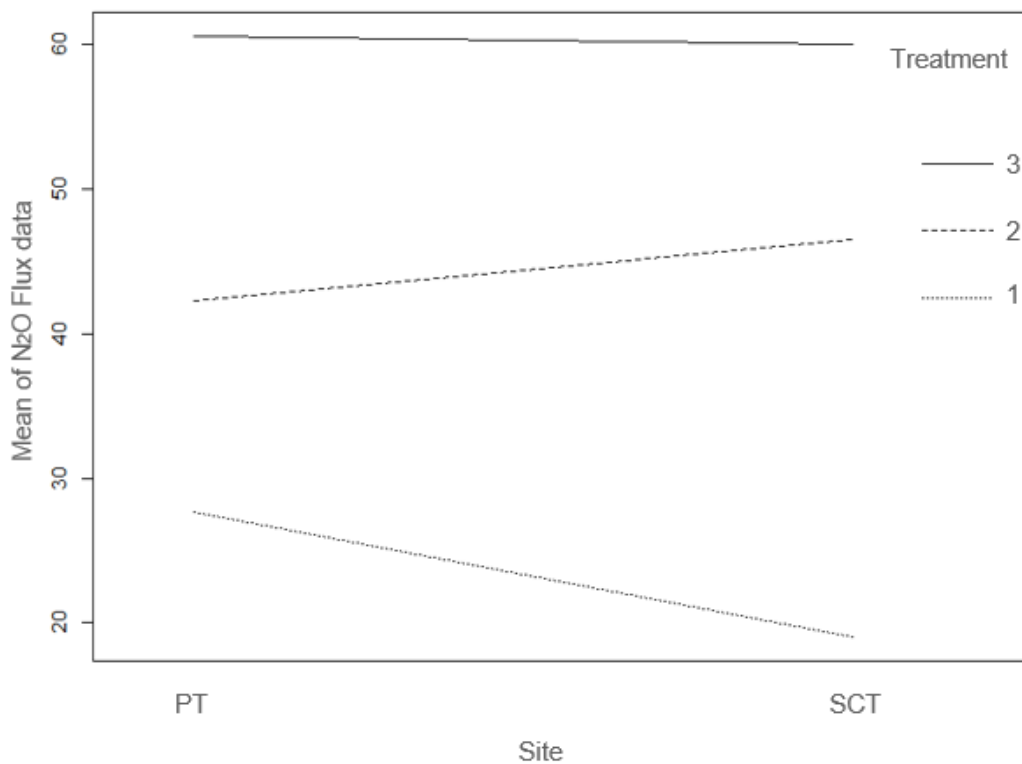


Appendix C

1. Interaction between treatments and N₂O flux means for each site (1– S, 2 – S+GW, 3 – GW)

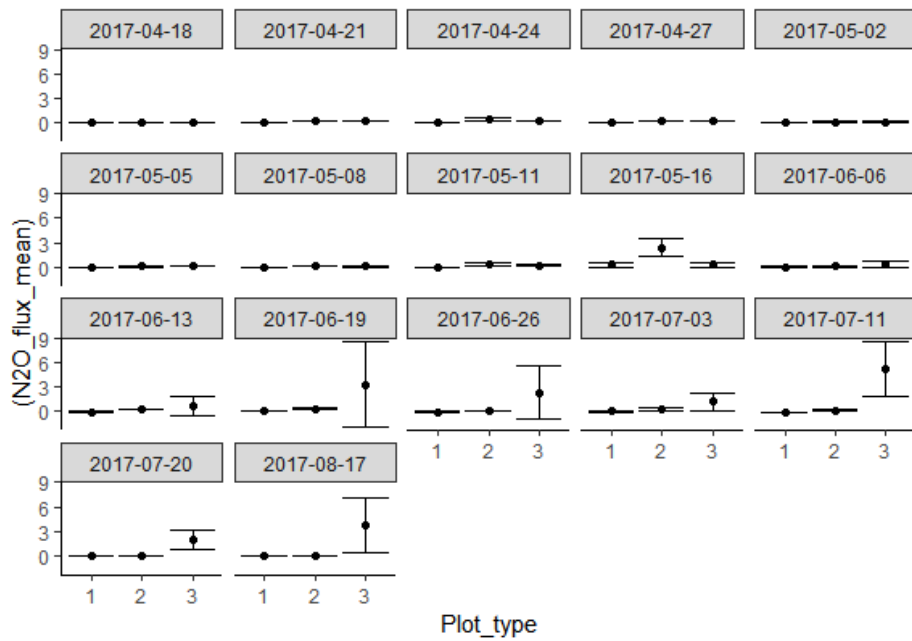
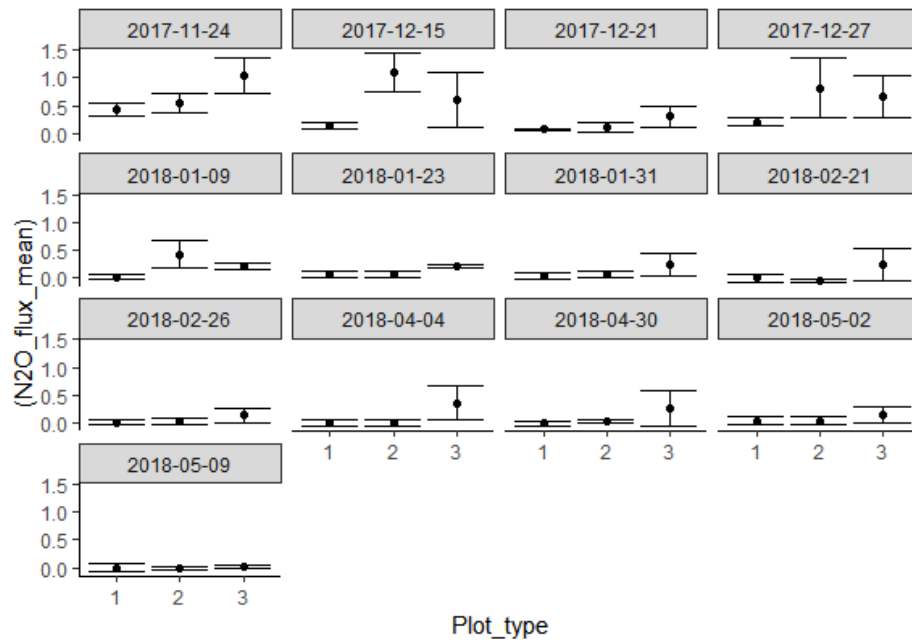


2. Interaction between sites and N₂O flux mean for each treatment (1– S, 2 – S+GW, 3 – GW)



Appendix D

- Standard deviation for N₂O emissions for Portugal (above) and Scotland (below) measurements per treatment (1 – S, 2 – S+GW, 3 – GW)



2. Standard deviation for CH₄ emissions for Portugal (above) and Scotland (below) measurements per treatment (1 – S, 2 – S+GW, 3 – GW)

