CH$_4$ and N$_2$O from waste composting

A thesis presented for the degree of Doctor of Philosophy

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Abstract

This research programme aimed to investigate methane (CH$_4$) and nitrous oxide (N$_2$O) emissions from large-scale composting facilities, with particular emphasis on advanced and newly emerging composting technologies. The atmospheric concentrations of CH$_4$ and N$_2$O are increasing, and they are respectively the second and third largest contributors to the global greenhouse effect after carbon dioxide. During field trials at large-scale composting facilities and in laboratory studies, the generation of CH$_4$ and N$_2$O was detected from a range of composting processes. Gaseous emissions from composting result from the interaction of a complex combination of controlling factors influencing the microbial production of CH$_4$ and N$_2$O. Waste biodegradability in particular was shown to have significant influence on emission of CH$_4$ and N$_2$O. Compliance with the EU landfill directive will result in the composting of wastes of varying biodegradability, the effect of this compliance on emission of CH$_4$ and N$_2$O from composting requires further investigation. Emissions of CH$_4$ and N$_2$O during composting have not been adequately quantified in the UK. A future projection of the contribution of composting to the UK greenhouse gas inventory was an estimated 24.6 Kt CH$_4$ year$^{-1}$ and 2.5 Kt N$_2$O year$^{-1}$ from open windrows, which currently account for 80% of the composting systems employed. There is urgent need for further study into the emission of CH$_4$ and N$_2$O from the UK composting sector as the Kyoto protocol requires emissions from all sources to be accounted for. While significant emission of CH$_4$ and N$_2$O was recorded for open air mechanically turned windrow systems, the level of emissions from in-vessel composting facilities was more difficult to determine. The combination of in-vessel composting and open air windrow composting would appear to greatly mitigate emissions compared to windrow systems alone, but more research into the environmental benefits of combining composting systems is required.
Acknowledgements

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Special thanks go to Sarah, Sam and Lexie for making everything worthwhile.
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1 Introduction

1.1 General Overview

Methane (CH$_4$) and nitrous oxide (N$_2$O) are, respectively, the second and third largest contributors to Earth's anthropogenically enhanced greenhouse effect after carbon dioxide (CO$_2$). Methane and nitrous oxide have been identified as two of the six greenhouse gases listed in the Kyoto protocol that require emission reduction. Atmospheric concentrations of CH$_4$ and N$_2$O have been increasing during recent history and this is thought to be a reflection of industrial advancement (Watson et al. 2000). The levels of methane and nitrous oxide have increased 151 ±25% (700 to 1750 ppbv), and 17 ±5% (270 to 316 ppbv) respectively during the last 250 years (IPCC 2002). Moreover, these levels are continuing to rise, with CH$_4$ concentrations increasing at around 1.7 ppbv year$^{-1}$ (Dlugokencky et al. 1998)), and N$_2$O rising at around 0.75 ppb year$^{-1}$ (Watson et al. 2000, Dlugokencky et al. 1998).

Waste disposal and waste treatment facilities are known to contribute to anthropogenic sources of greenhouse gases, with emission of methane from landfill being regarded as a major source. Estimates of the contribution of methane from landfill to total global methane emissions range from 6% to 10% (Hein et al. 1997; Fung et al. 1991, IPCC 2001). Importantly, the type of waste treatment facility which is selected to process particular wastes can affect the nature of the greenhouse gases that are emitted and the degree of the resulting environmental impact. Petts & Eduljee (1994) calculated that the methane emissions from landfilling one tonne of household refuse were six times more potent a source of greenhouse gases than were the carbon dioxide emissions from incinerating a similar amount of waste. They further recommended that "a study of comparative greenhouse gas emissions from various alternative disposal techniques can form part of a Best Practicable Environmental Option (BPEO) analysis to aid the selection of a preferred waste disposal solution."
It is important to note that although methane emission is clearly associated with landfill, there are no documented measurements of N$_2$O having been emitted from UK landfills (Baggott et al. 2003). In developing more sustainable waste management practices to replace landfill, it is essential that the new treatment regimes do not substitute one pollutant for another. For example, during vermicomposting of food waste Frederickson & Howell (2002) reported significant emission of N$_2$O which would not have occurred if the waste had been landfilled.

Hence, while methane from landfill remains the largest single source of greenhouse gas emissions, emissions from other waste management options have been identified but have not been adequately quantified in the UK.

A recent review of the environmental and health effects of waste management practices (DEFRA 2004) reported that Municipal Solid Waste processing and disposal accounts for 27% of UK total methane emissions and concluded that this was mainly from landfill. However, they also made a number of high priority recommendations relating to the composting and other waste management sectors. For example, it recommended that a study should be commissioned to "characterise and quantify emissions of particulates, micro-organisms, VOCs and methane from in-vessel and/or windrow composting of Municipal Solid Waste (MSW). This is a significant area of uncertainty at present, and could become more important if composting of MSW becomes more widespread." This recommendation clearly acknowledged the lack of peer-reviewed data on greenhouse emissions from commercial-scale composting systems operating under UK conditions.

Knowledge of the potential of key waste treatment options to emit specific greenhouse gases would appear to be an important element in reducing the overall impact of waste treatment facilities. This is particularly important in the promotion of more sustainable waste management practices and for the adoption of innovative types of waste processing facilities which aim to minimise emission of CH$_4$ and N$_2$O. However, with the exception of
methane from landfill, very little data on the emission of CH$_4$ and N$_2$O from large--scale waste processing technologies, such as composting, is available to aid decision making relating to process selection.

This thesis aims to contribute to knowledge about the environmental impact of large--scale composting systems, particularly relating to emission of CH$_4$ and N$_2$O. An important aspect of the work is the focus on evaluating emissions of CH$_4$ and N$_2$O from advanced composting technologies, such as in--vessel systems and vermicomposting as well as from the newly emerging mechanical and biological treatment (MBT) sector. With an estimated 16 fold expansion in the UK composting capacity needed to meet European landfill diversion targets (Slater & Frederickson, 2001) and with the current interest in installing MBT facilities, it is highly likely that increasing amounts of household waste will be processed using advanced biological treatment systems. It is anticipated that the findings presented in this thesis will significantly contribute to the development of enhanced sustainable waste management practises in the UK, especially in relation to emission of CH$_4$ and N$_2$O.

1.2 Sources of CH$_4$ and N$_2$O

Global sources and sinks of CH$_4$ and N$_2$O are shown in Tables 1.1 and 1.2. Landfilled waste is shown to make a considerable contribution to atmospheric methane. For both gases the sources are greater than the sinks, highlighting the causes of the ongoing increase in the concentration of these gases in the atmosphere.
Table 1.1 Estimated sources and sinks of CH₄ (Tg year⁻¹) (from IPCC 2001)

<table>
<thead>
<tr>
<th>Sources</th>
<th>Tg year⁻¹</th>
<th>Sinks</th>
<th>Tg year⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>165 (92–237)</td>
<td></td>
<td>480 (450–510)</td>
</tr>
<tr>
<td>Other</td>
<td>40 (35–45)</td>
<td>Tropospheric OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stratospheric loss</td>
<td>43 (46–40)</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
<td></td>
<td>Soils</td>
<td>27 (10–44)</td>
</tr>
<tr>
<td>Fossil sources</td>
<td>93 (75–110)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enteric fermentation</td>
<td>98 (80–115)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rice paddies</td>
<td>63 (25–100)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>39 (23–55)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Landfills</td>
<td>54 (35–73)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>18 (15–20)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total source</strong></td>
<td>570 (380–755)</td>
<td></td>
<td>550 (506–594)</td>
</tr>
<tr>
<td><strong>Total sink</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 1.2 Estimated sources and sinks of N\textsubscript{2}O (Tg year\textsuperscript{-1}) (from IPCC 2001)

<table>
<thead>
<tr>
<th>Sources</th>
<th>Tg year\textsuperscript{-1}</th>
<th>Sinks</th>
<th>Tg year\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean</td>
<td>3.6 (2.8–5.7)</td>
<td>Atmosphere</td>
<td></td>
</tr>
<tr>
<td>Atmosphere (NH\textsubscript{3} oxidation)</td>
<td>0.6 (0.3–1.2)</td>
<td>Stratospheric loss</td>
<td>12.5 (9–16)</td>
</tr>
<tr>
<td>Soils</td>
<td>6.6 (3.3–9.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural soils</td>
<td>1.9 (0.7–4.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomass burning</td>
<td>0.5 (0.2–0.8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial sources</td>
<td>0.7 (0.2–1.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cattle and feedlots</td>
<td>1.0 (0.2–2.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total source</td>
<td>14.9 (7.7–24.5)</td>
<td>Total sink</td>
<td>12.5 (9–16)</td>
</tr>
</tbody>
</table>

1.3 Origins of methane and nitrous oxide

1.3.1 Methanogenesis

CH\textsubscript{4} is produced by the strictly anaerobic micro–organisms called methanogens (Hellebrand 1998), performing the final step in the decomposition of organic material, and an integral part of the global carbon cycle (Ferry 2002). Methanogenesis is the lowest energy–yielding step in anaerobic systems forming the terminal step in the degradation of organic carbon and only occurs after other electron acceptors such as NO\textsubscript{3}⁻, Fe\textsuperscript{3+}, and SO\textsubscript{4}\textsuperscript{2–} have been consumed (Atlas & Bartha 1997; Conrad 1989). The production of
methane is a reduction reaction that involves the addition of a hydrogen ion (H\(^+\)), these reactions are termed hydrogenation reactions (Atlas & Bartha 1997). Methanogens cannot degrade ‘raw’ organic matter and can only utilise a limited number of substrates, these by three major pathways being; (1) reduction of CO\(_2\), (2) fermentation of acetate, and (3) the breakdown of methanol or methylamines (Ferry 2002). Biological production of methane is therefore mediated by other micro–organisms that produce substrate suitable for methanogenic reduction (McCormick 2001). The reduction of CO\(_2\) and the fermentation of acetate have been found to be the most likely pathways of CH\(_4\) production accounting for 33% and 66% of methanogenesis respectively in natural systems (Conrad, 1999). Net methanogenesis may occur within the anaerobic zones of an organic matrix (where other electron acceptors such as NO\(_3^-\) are not present), and may result in CH\(_4\) emission (Barber & Ferry 2001). Several species of methanogen have been found to be tolerant of O\(_2\) exposure and may retain their ability to produce CH\(_4\) after exposure to O\(_2\) (Barber & Ferry 2001). Equations 1.1 and 1.2 show the production of CH\(_4\) from CO\(_2\) reduction and fermentation of acetate respectively (Ferry 2002).

**Equation 1.1** \(4H_2 + CO_2 = CH_4 + 2H_2O\)

**Equation 1.2** \(CH_3CO_2^- + H_2O = CH_4 + HCO_3^-\)

**Equation 1.3** CH\(_4\) emission = CH\(_4\) production - CH\(_4\) oxidation - change in stored CH\(_4\)

A similar approach to the measurement of CH\(_4\) emission from peatlands can be applied to composting systems, this is referred to as the methane balance equation and is shown in Equation 1.3 (Segers & Leffelaar 2003).
1.3.2 Nitrous oxide production

$\text{N}_2\text{O}$ emission from composting originates from the microbial transformations of nitrogen (N) as organic material degrades. Fresh organic material at the start of decomposing undergoes ammonification, this is when N locked up in organic macromolecules (such as proteins, nucleic acid, and amino acids) become available to decomposer organisms and breaks down into ammonium (NH$_4^+$) (Katterer 2002). Once N has been mineralised to NH$_4^+$ and it becomes available to organisms that convert the NH$_4^+$ to nitrate (NO$_3^-$) via the intermediaries hydroxylamine (NH$_2$OH) and nitroxy l (NOH) (Katterer 2002, Caton 2002). This, under aerobic conditions, is a two-stage process, firstly ammonia oxidising (nitrite) bacteria catabolise NH$_4^+$ into nitrite (NO$_2^-$), then nitrite oxidising (nitrate) bacteria mineralise nitrite to NO$_3^-$ (Hagopian & Riley 1998). It is during the ammonia oxidising stage of nitrification that N$_2$O is produced when nitrite is used as an artificial electron acceptor under low O$_2$ conditions. It is the low O$_2$ conditions that enhance nitrifier N$_2$O production. (Alleman & Preston 1992). Nitrite oxidising bacteria under anaerobic conditions can reduce nitrite to nitric oxide (NO) but not to nitrous oxide (Hagopian & Riley 1998). The sequence of ammonia oxidation and nitrite oxidation followed by the reductive process ‘nitrate denitrification’ is shown below in Equation 1.4.

Equation 1.4 \[ \text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]

Denitrification, the transformation of NO$_3^-$ to N$_2$, is performed by a wide variety of heterotrophic micro-organisms that can inhabit both aerobic and anaerobic environments (Trogler 1999). Under aerobic conditions denitrifiers metabolise O$_2$, when conditions become anaerobic they switch to using NO$_3^-$ as the terminal electron acceptor. Czepiel et al. (1996) found that ‘microaerobic’ conditions resulted in optimal denitrification $\text{N}_2\text{O}$ production (Gejlsbjerg et al. 1998). NO$_3^-$ reduction to NO is the first step in denitrification followed by further reduction to $\text{N}_2\text{O}$ and finally to $\text{N}_2$ (Katterer 2002). Czepiel et al. (1996) showed that under anaerobic conditions the denitrification of NO$_3^-$ to $\text{N}_2$ is complete, but at
low O₂ conditions N₂O is released due to denitrifiers preferentially using NO₃⁻ as the terminal electron acceptor (De Weaver et al. 2002). Holtan–Hartwig et al. (2002) found that N₂O reduction has a higher activation energy than N₂O production, therefore the ratio of N₂O/N₂ production increases with decreasing temperature. Low temperatures can inhibit nitrification and denitrification rates at a rate of around a 5% reduction in activity for a drop of 1 °C (between 22 – 4 °C) (Pfenning & McMahon 2002, and Dincer & Kargi 2000). Machefert et al. 2002 measured increased levels of nitrous oxide from soil during summer compared to winter and concluded that this was primarily due to the temperature dependence of both nitrification and denitrification. The effect of low temperature inhibition of N₂O reductase would need to be taken into account in a study of N₂O emission from composting. Very large short-lived pulses of N₂O flux have been observed from soils as a response to a change in conditions (e.g. temperature and moisture) (Machefert 2002), a phenomenon that might be repeated in composting. Increased moisture or a sudden increase in temperature can trigger an N₂O flux pulse by either increasing microbial activity or hydraulically forcing gas from the pores spaces in the soil or waste (Mummey et al. 1997, Prieme & Christensen 2001), as can the introduction of NO₃⁻ to a denitrifying community (De Weaver et al. 2002).

1.4 Composting industry trends

Composting is the controlled decomposition of organic materials at both mesophilic (0–40°C) and thermophilic (40°C+) temperatures undertaken by a microbial community that includes aerobic, anaerobic and nitrogen-fixing bacteria, fungi, and actinomycetes and (Bess, 1999). Composting has been in use for centuries as a way of recycling organic wastes back to the soil in the form of plant available nutrients. Large scale municipal composting originated in Holland in the 1920’s during a period of great demand for compost for land reclamation projects (Slater & Frederickson 2001). This study is not only concerned with the use of composting as a way of producing a suitable stabilised agricultural/horticultural product, but also as a means of rendering an active
biodegradable waste biologically inactive prior to landfill using MBT technology. The composting process is typically performed using a variety of methods varying in size, aeration type, and composting material used, as well as employing various processing technologies such as enclosed or open systems, and batch or continuous flow systems. The process of composting and the types of systems used to undertake composting are discussed more fully later in this chapter.

In the UK presently 1.97 million tonnes of organic waste is composted annually at 325 sites, 82% of these operating open air turned windrows (Slater et al. 2005). The UK's population of 60 million people produces around 30 million tonnes of municipal solid waste (MSW) per year. An estimated 68% of MSW is biodegradable (DETR 1999). At present 85% of MSW is landfilled, 7% incinerated, 6% recycled and only around 2% composted (DETR 1999, Slater & Frederickson 2001). Landfill has long been recognised as being a significant methane source (IPCC 2001). Around 0.7 Tg year$^{-1}$ of CH$_4$ are produced by landfill in the UK alone (Salway et al. 2000) and around 54 Tg CH$_4$ year$^{-1}$ globally (IPCC 2001). There are no documented measurements of N$_2$O emitted from landfill.

Composting is seen as a more 'environmentally sound' method of biodegradable waste treatment, it is a growing industry and is acquiring greater significance as a waste management option (DETR 2000). There is a current drive to enhance alternative disposal routes for biological MSW with composting being a significant alternative method, however little is known about the emission of CH$_4$ and N$_2$O from the variety of composting systems and how management practices may effect these emissions. The emission of CH$_4$ and N$_2$O along with other climate–relevant gases from composting has been poorly studied, and there have been no extensive studies on how composting management practices can reduce these emissions, while maintaining composting process and end product quality.
Currently in the UK, approximately 82% of municipal waste is composted using turned windrows in the open-air (Slater et al. 2005). These are elongated trapezoidal piles of organic waste of which most (90%) are used to process garden waste. This waste is commonly referred to as 'green waste'. Other composting methods include in-vessel enclosed systems, static (not actively aerated) piles and vermicomposting. Vermicomposting is the non-thermophilic biodegradation of organic material through interaction between earthworms and micro-organisms (Arancon et al. 2002). Composting and vermicomposting feature throughout this thesis. Since it is important to fully understand the complex reactions taking place during waste stabilisation to enable the relationship between waste characteristics and gaseous emissions to be developed, both processes will be reviewed in some detail in this chapter.

1.4.1 The composting process


The composting process is often considered to comprise three distinct phases, which may be defined by the different temperatures at which each phase takes place:

- An initial phase taking place at temperatures close to ambient (mesophilic, up to 40°C).
- A phase at elevated temperatures, where biological activity causes heating to thermophilic temperatures (40°C or more).
- A maturation phase, following thermophilic activity where more complex substrates are degraded at a slower rate (hence a slower rate of heat generation).
A range of organisms are involved in the complete decomposition of organic matter under controlled conditions such as bacteria, actinomycetes, fungi, protozoa, annelids, arthropods. The controlled composting process *per se* is mediated by a diverse community of micro-organisms, many of which are not individually capable of fully mineralising the biodegradable materials. Decomposition during composting may proceed via a series of intermediate compounds degraded by different sets of organisms. These intermediate compounds may be phytotoxic and/or odorous. These intermediate organic products may either serve as substrates for other micro-organisms or may remain, for a period of time, in the compost residue.

Perhaps the most important phase during composting is the thermophilic phase, which is thought to be dominated by bacteria, actinomycetes, and some fungi (Finstein & Morris 1975). Temperatures as high as 70 °C to 80 °C may be reached if an uncontrolled build-up of heat within the composting material is allowed to continue and much depends on the size of the composting pile. The thermophilic stage occurs due to the rapid and intense decomposition of readily degradable substrates such as proteins, starches, and later cellulose (Biddlestone & Gray 1982, Forsyth & Webley 1948, Jeris & Regan 1973), however, the decomposition is undertaken by a relatively small range of micro-organisms, compared with the much broader range carrying out degradation at mesophilic temperatures (Peters *et al.* 2000, Strom 1985). Some organisms are active at both mesophilic and thermophilic temperatures (Waksman *et al.* 1939).

The thermophilic stage of the composting process ceases as the readily degradable substrates become limiting, and the temperature of the composting material falls to ambient levels. Further composting, (maturation or curing) takes place close to ambient temperatures. As temperatures fall from thermophilic ranges fungal activity resumes (Anid 1986). During this stage the majority of degradation of complex polymers such as lignin, and ligno-cellulose takes place (mainly through the activities of basidiomycete fungi),
phytotoxicity abates and nitrogen in the form of biomass, compost residue and ammonia begins to be oxidised to nitrate (de Bertoldi et al. 1983, Zach et al. 2000).

Many authors consider the thermophilic phase to be the most important stage during the overall composting process, however, there is a considerable amount of evidence suggesting that decomposition rates are highest at processing temperatures within the lower thermophilic/upper mesophilic range (Bardos & Lopez–Real 1989, de Bertoldi et al. 1983, Forsyth & Webley 1948, Gray et al. 1971, Jeris & Regan 1973, Miller et al. 1989, Niese Neumeyer–Seekatz 1979, Smith et al. 1987, Strom 1985, Stutzenberger et al. 1970 and 1971, Suhler & Finstein 1977, Tansey & Brock 1978, Waksman et al. 1939, Webley 1948). While it is extremely difficult to control and reduce processing temperatures to these levels for relatively simple composting technologies such as mechanically turned windrow systems, this is a particular strength of more advanced in–vessel systems which incorporate temperature and oxygen feedback control systems.

While there is a need to reduce processing temperatures to enhance decomposition and increase processing rates during composting, there is also a need to maintain high temperatures to sanitise the waste undergoing composting. However, maintaining a balance between elevated composting rates and maintaining high sanitisation temperatures is difficult to achieve as temperatures above 65°C can only be tolerated by a limited range of micro–organisms.

Finstein et al. (1987) suggested that maintaining a temperature between 55°C and 60 °C for at least three days throughout the entire compost pile is likely to maximise rates of decomposition, while still achieving an acceptable degree of thermal inactivation of pathogens. This suggestion is supported by other research (Biddlestone & Gray 1982). However, some studies suggest that thermal inactivation of pathogens in compost such as Ascaris Lumbricoides require temperatures higher than 60 °C (Andrews et al. 1994, de Bertoldi et al. 1988, Lofgren 1979, Stentiford et al. 1985, US EPA 1971).
Effective control of processing temperature is a particularly important consideration in the UK for the composting of source segregated household waste containing kitchen wastes, which must be processed in accordance with the Animal By–Products Regulations (DEFRA, 2003). Temperature–time relationships, related to the thermal inactivation of specific animal diseases, are at the core of the Animal By–Products Regulations (ABPRs). The scope and implications of the ABPRs are discussed elsewhere in this chapter, as is a brief review of in–vessel composting processes. The use of in–vessel systems is an essential requirement for controlling thermal deactivation of pathogens thereby making these systems a requirement for specific types of high–risk wastes.

Three important terms have been defined, relating to the characteristics of waste at different stages of decomposition during extended composting. These are stability, maturity and phytotoxicity. The first of these is stability, which refers to the degree of biological decomposition of the waste and this is often referred to as biodegradability. Compost respiration rate is the most common approach to compost stability or biodegradability assessment and also for the determination of rates of composting. Biodegradability measurement using respirometry techniques is a key feature of this thesis. Measurements such as these are used to provide an estimate of microbial activity and are typically assessed on the basis of oxygen uptake or carbon dioxide production (Hoitink & Frost 2002, Lasaridi & Stentiford 1999, Pressel & Bidlingmaier 1981, Richard et al. 1993, Swannell et al. 1993, Zimmerman & Richard 1992). The use of respiration testing to assess waste characteristics during composting and as a measure of waste biodegradability is an important aspect of the work presented in this thesis and is explored in detail throughout the thesis.

Secondly, maturity refers to the ability of a compost to support plant growth. During composting, materials with a high level of biodegradability are mineralised or converted into slowly degradable “humified” forms. In young composts intermediate breakdown
products and degradable materials can remain such as fatty acids and ammonia compounds. These compounds are odorous, and may also be inhibitory to plant growth. Also some stages of plant growth can be sensitive to high conductivity, depending on the plant species, and immature composts often have high levels of conductivity. Lastly, phytotoxicity refers to the potential for detrimental effects of compost on plant growth. Composts may have phytotoxic effects because they contain high levels of certain trace elements or organic pollutants. This effect is unrelated to compost stability or maturity. Young composts may contain substances inhibitory to plant growth related to the breakdown and degradation processes still taking place (as described above) or because naturally occurring inhibitory substances such as phenolics from certain woody materials have not yet had time to degrade. Compost stability and maturity assessments include chemical analyses, microbiological assays and higher plant bioassays. Bio-assays based on effects on germination are the most common techniques used for assessing compost maturity and phytotoxicity based on the work of Zucconi et al. (1981), and Grundy et al. (1998).

1.4.2 The vermicomposting process

The natural occurrence of particular species of earthworms at a sewage works led to research into the use of earthworms for the treatment and composting of sewage sludge (Hartenstein 1978). However, much of the research work relating to earthworms and organic matter was focused largely on the production of earthworms rather than on addressing the stabilisation of waste (Tomati & Grappelli 1984, Lofs–Holmin 1985).

Research then shifted to investigate the use of earthworms to treat animal, vegetable and industrial wastes (Edwards & Neuhauser 1988). There was increasing recognition of the economic value of waste treatment and the vermicomposted products (Fieldson 1988). Moreover, the composted products of waste vermicomposting were increasingly investigated for their horticultural value (Edwards & Burrows 1988).
Edwards (1988) investigated the use of specially designed waste processing beds with automated methods of waste application specifically for vermicomposting. He also identified the most appropriate species of earthworm for vermicomposting, as well as each species' nutritional, biological and environmental requirements. Successful vermicomposting, as with traditional composting involves closely controlling a range of key parameters, e.g., temperature, moisture, and nutritional composition of the waste. Also many other physico-chemical and biological factors must be controlled, specific to the growth, survival, and reproduction of earthworms (Hartenstein et al. 1979, Neuhauser et al. 1980, Kaplan et al. 1980, Hartenstein 1982). These factors relate predominantly to the production of earthworms, rather than the decomposition and treatment of wastes (Edwards 1988).

Vermicomposting, unlike traditional composting, operates under lower temperature (20–25°C) and higher moisture (70–80%) regimes. Aeration and mixing is achieved through the burrowing activity of the earthworms, as well as the ingestion and egestion of waste material as casts. Smaller amounts of waste are processed during vermicomposting, in a more continuous process, adding fresh layers of waste once previous applications have been processed (Edwards 1988). Although it is well established that earthworms increase rates of decomposition (e.g. Loehr et al. 1984), the stabilization of waste has not been well studied and many fundamental factors need to be evaluated to assure the technical and economic success of such processes (Edwards & Bohlen 1996).

In terms of comparing traditional composting with vermicomposting, both processes result in organic matter loss via microbial metabolism into CO₂ and H₂O. Traditional composting, an exothermic process, can also result in considerable moisture loss through evaporation (Stentiford 1996). However, lower temperatures associated with vermicomposting operations (20–25°C) result in lower rates of desiccation. Volume reduction may also occur due to structural changes within composting material. During
composting, material is broken down into smaller particles (Gray et al. 1971), and may become more compact. Vermicomposting also results in the reduction of particle size as small amounts of waste are ingested by earthworms before being egested as earthworm faeces (casts) (Mitchell 1978).

Although, it is recognized that traditional composting and vermicomposting methods operate under very different conditions and can produce very different composted products (Dominguez et al. 1997), very few comparative studies of these processes have been conducted. Comparisons between traditional composting and vermicomposting have focused mainly upon the final composted products rather than on process considerations or environmental impact (Haimi & Huhta 1987, Subler et al. 1998). Vincelas–Akpa & Loquet (1997) examined organic matter loss and organic matter transformations during the vermicomposting and composting of maple waste, under small scale laboratory conditions. Gellens & Verstraete (1995) evaluated a large–scale batch vermicomposting system, processing pre–composted VFGP (vegetable food garden paper) waste mixed with non–recyclable paper.

1.4.3 Advanced composting systems

Advanced composting methods take many forms as shown below and much research has investigated particular engineering and practical aspects of these. A number of studies have investigated the process engineering and technical aspects of commercial composting with particular regard to more advanced methods such as static pile and in–vessel systems. Examples are de Bertoldi (1992), Hoitink et al. (1993), Canet & Pomares (1995), Anon (1996b), Balis et al. (1996), Keener et al. (1996), Lopez–Real & Baptista (1996), Lynch & Cherry (1996), Michel & Reddy (1996), Muchel & Reddy (1996), Steuteville (1996b), Sela & Avnimelech (1997). Korner et al. (1997) explored the effect of composting procedures on the quality of the resultant compost. A comparative study of the effects of using different porous textiles during windrow composting was undertaken.

More advanced systems of composting are seen as having many advantages over open air windrow systems. According to Slater et al. (2001) as with all waste processing systems, open windrow composting has the potential to pollute the environment, cause disamenity to the locality or harm to public health if good operating practices are not observed. A more controllable version of windrow composting is the aerated static pile approach, which may be carried out in the open or under cover. Aerated static pile composting is the most common form of open composting system, adopted world-wide, where the composting material is not mixed or turned during composting (Sikora et al. 1981, Roig & Bernal 1996, Williams et al. 1996, Sesay et al. 1997). It is a composting process commonly used in many countries, but not, so far, to any significant extent in the UK. Aerated static pile composting typically takes 8 to 20 weeks depending upon the feedstock used and the expected application of the compost produced. The composting mixture is placed on top of a perforated pipe or pipes, a perforated pavement, or diffusion plates that are linked to a fan. Once formed, the pile is not mixed or turned until composting is complete. The pile is typically covered with a layer of mature compost, about 15 – 30 cm thick, to prevent the outer surface of the pile from drying out, and to limit any release of odour. This layer can also allow even the outside layer of the composting materials to reach the higher temperatures required for composting and pasteurisation. The type of basic forced aeration used for these static aerated systems is often employed in more advanced systems.

In order to minimise the environmental impact of composting and to enhance and control the composting process, highly sophisticated enclosed composting systems have been developed throughout Europe, based on forced aeration technology. These often use computer–controlled systems to manage the aeration rate, moisture content and temperature of the composting materials. They have been termed 'in–vessel' and cover a
wide range of composting systems. The principle behind an in-vessel system is to provide air and moisture at a level that optimises microbial activity as rapidly as possible and then maintains it for the desired period. This is obviously easier than in open composting operations where control over ambient temperatures and the elements is more challenging (The Composting Association, 2004). It is also possible for more difficult feedstocks to be composted using in-vessel systems since they are protected from the wider environment and enclosure helps prevent pathogen vectors such as scavenging birds and vermin from gaining access to the feedstock. In addition, the enclosure of decomposing organic materials allows potentially harmful emissions to be contained and possibly treated prior to release into the environment.

In-vessel systems share the common feature that the material being composted is contained and, usually, enclosed. In most cases, enclosure means that the composting materials are not affected by the external environment (temperature, rainfall, etc.) and the processing conditions can be controlled accurately to make composting more efficient. In addition, emissions from enclosed composting processes, such as bioaerosols, odours and leachate, can be monitored and treated.

In-vessel composting systems have been developed from a wide range of industries. Tunnels have come from the mushroom industry, air handling equipment and computer controls from the development of greenhouses and mixing techniques from sewage processing, This has led to the diversity of in-vessel systems that are now employed for the 'active' thermophilic phase of composting. Although there are many different types of in-vessel system, these processes can be classified into five broad categories (Slater et al. 2001):

- Containers, which consist of relatively small units in which air is forced through perforated floors into the composting materials.
- Tunnels, which are longer and more sophisticated than containers, and are designed to accept larger quantities of waste.
- Agitated bays, which consist of rows of rectangular beds separated by low walls on each side along which turning and shredding machines either straddle the bays or run along a rail at the top of the walls.
- Silos or tower systems, which are vertical units into which feedstocks are loaded into the top of the unit and are composted as they pass down through the unit.
- Enclosed halls, in which the composting materials are laid on the floor of the hall, usually in one long bed, where large bucket wheels are used to turn and move the material through the system.

1.4.4 Mechanical Biological Treatment (MBT)

A number of studies have recently focused on advantages and disadvantages of mechanical biological treatment for processing residual household waste (for example DEFRA 2004, and Baddeley et al. 2005). Mechanical biological treatment is a generic term that encompasses a wide range of technologies that aim to process waste by a mixture of biological treatment and mechanical separation. In MBT the biodegradable fraction is treated post sorting, whilst in BMT the biological treatment or a thermal treatment such as autoclaving or thermal drying of the waste is undertaken prior to the sorting of the waste.

MBT plants are thought to be necessary since the quantity of municipal solid waste is currently increasing and there is a growing problem for local authorities particularly as the available landfill space in the UK is decreasing. In addition, the introduction of the EC landfill directive means that the European Commission has set challenging targets to reduce the amount of biodegradable waste going to landfill. Compliance with the directive
requires an increased deployment of recycling and recovery operations for biodegradable waste.

In MBT mixed waste is firstly sorted via a series of mechanical treatment options that separate out recyclable materials (e.g. metal and glass). All systems have sorting processes that separate various fractions and mechanically degrade the organic fractions through shredding, wetting and tumbling, or through the addition of steam. The main effect is to concentrate these fractions for further processing. The key difference between various systems is the choice adopted for processing the higher calorific value materials. Options include producing a substitute for fossil fuels (refuse derived fuel – RDF), or removing the higher calorific components such as plastics and processing the residue to produce compost. The main biological process can be carried out either aerobically (composting) or anaerobically (anaerobic digestion – AD). Whilst biologically these are different processes the final degraded solid products are similar, with anaerobic digestion having the added benefit of generating a gas with a high methane content that can be used as a fuel.

Bio–mechanical treatment (BMT) is a special case of MBT where the whole of the waste is treated biologically prior to sorting. This biological treatment is principally to dry the waste thus making subsequent mechanical separation more effective. Waste is aerated within composting vessels; as temperature rises so the moisture is driven off. After one to two weeks the waste is dried and undergoes mechanical separation to generate a fuel (RDF) fraction. The fuel is then prepared for market. The reject waste is still high in organics and can undergo further composting to generate a poor quality compost for landfill cover, but typically this fraction is simply landfilled as the most readily degradable materials are lost in the initial composting stage. BMT technology has been used in Germany, Austria, Switzerland and Italy for around a decade. The development of mixed waste digestion in Europe started with the Refcom project in the late 1970s. This and similar projects generally failed due to the inability to produce acceptable quality digestate.
Interest in the treating of mixed waste has increased due to the requirement for pre-treatment of waste for landfilling. A large number of plants have been constructed in recent years as a response to the demands of the Landfill Directive.

1.4.5 Key legislation affecting the composting sector

There are a number of drivers promoting expansion and change within the composting sector. The two most important legislative drivers influencing the sector and which are of most relevance to this thesis are the EC council directive on the landfill of waste (EUDirective 1999) and The Animal By-Products Regulations (DEFRA 2003). The way in which the UK currently deals with MSW is now subject to considerable change due to the legally binding compliance with the EU landfill directive. This directive has the result of diverting an increasing proportion of the biodegradable fraction of MSW to alternative disposal sources other than landfill. Estimates indicate that in order to meet the targets there will be a 16-fold increase in composting activity (DETR 1999, Slater & Frederickson 2001). The targets set by the European Union Landfill directive (EUDirective 1999) are set out as follows:

- By 2010 biodegradable municipal solid waste (BMSW) going to landfills must be reduced to 75% of the total amount (by weight) of BMSW produced in 1995.
- By 2013 BMSW going to landfills must be reduced to 50% of the total amount (by weight) of BMSW produced in 1995.
- By 2020 BMSW going to landfills must be reduced to 35% of the total amount (by weight) of BMSW produced in 1995.
The Animal By-Products Regulations (DEFRA 2003) and the EC Animal By-Products Regulation 1774/2002, which has been amended by Commission Regulation No 808/2003 in combination, regulate the collection, transportation, storage, handling, processing, and disposal of animal by-products not intended for human consumption.

Animal by-products include animal carcases, parts of animal carcases (including blood) or products of animal origin not intended for human consumption. There are three categories of animal by-products. These are:

- **Category 1** – includes bodies of pet, zoo, and circus animals, high risk material such as brains, and any mixture of category 1 material with any other waste. International catering waste from non-EU countries is also included. These wastes cannot be treated by composting.

- **Category 2** – includes products of animal origin containing veterinary residues, slaughtered animals, and parts thereof that are not for human consumption. These may be composted if they have been treated in an approved processing plant using processing method I specified in EU Regulation 1774 i.e. 133°C, 3 bar pressure for 20 minutes (the EU Pressure rendering standard). After this pasteurization the Category 2 waste may be used as feed stock for composting in accordance with the UK standard for meat-included category 3 catering waste. Compost produced using this method is not allowed to be applied to agricultural land.

- **Category 3** – includes animals or parts of animals that are fit for human consumption but are no longer intended for human consumption. This includes catering wastes and food processing industry wastes. The composting of Category 3 animal by-products must follow the EU Regulation to the following standard:

The maximum particle size for the composting material must be 12 mm. A minimum processing temperature of 70°C must be maintained by exothermic reaction from
microbial activity, although external heating to prevent cold spots is allowed. The 70°C temperature must be maintained for a minimum of 60 minutes.

The EU regulation permits member state to introduce national standards for treating meat included and excluded catering wastes.

For meat-excluded Category 3 catering waste composting the UK composting standard offers two treatment options:

- In a closed composting reactor – The waste must achieve a temperature of 70°C for 1 hour for material with a maximum particle size of 6 cm, or 60°C for 2 days for material with a maximum particle size of 40 cm.
- Housed windrow – The waste must achieve a temperature of 60°C for 8 days, for material with a maximum particle size of 40 cm. The pile must be turned at least 3 times, at no less than 2 day intervals. Composted material treated in a housed windrow or closed composting reactor must be stored for 18 days prior to land application. The 18 day storage period does not need to take place in an enclosed system. Vermicomposting is considered a permissible method of storage.

For meat-included Category 3 catering wastes the UK standard requires a two barrier process:

- Barrier I – The waste must be treated initially in accordance with one of the options for meat-excluded category 3 catering waste. After this composting process the waste must be treated in a second barrier.
- Barrier 2 – The requirement is for a repeat of the Barrier I treatment either in a closed composting reactor or housed windrow. This second barrier may also take place in an open windrow, if this method is used the waste must achieve a
minimum temperature of 60°C for 8 days with a maximum particle size of 40 cm. The pile must be turned every 2 days.

- The two composting barriers have to take place in separate and distinct vessels or composting areas. The composting operator needs to demonstrate that the material within such a vessel achieves the temperature requirements for each of the stages separately. The separation of the two barriers is to prevent cross-contamination of wastes between the composting processes.

1.5 Methane and nitrous oxide emission from composting

It has long been considered that the use of composting to stabilise biodegradable municipal solid waste (BMSW) is more favourable than depositing raw BMSW material in landfill. The stability of organic material can be defined as being the level of activity of the microbial biomass (Butler et al. 2001). To stabilise BMSW the available biodegradable organic matter will need to be microbially consumed (Haug 1993). Stabilising organic matter in landfill gives rise to significant CH₄ production because of the anaerobic conditions present (Park 2001). Composting is predominately an aerobic process, however, the rate and composition of gaseous emissions during composting are highly variable from both differing composting processes and pre–composted material (Zeman et al. 2002). A number of studies have been done on emission of CH₄ and N₂O from composting, mainly focussing on livestock manure composting. Studies on the emission of radiatively important gases from cattle manure and sludge composting will not give data comparable to BMSW composting but may help to discern the origin of CH₄ and N₂O from the composting process, and indicate some emission abatement strategies.

Beck–Friis et al. (2000) in their study of CH₄ and N₂O emission from organic household waste composting measured up to 5 g CH₄ m⁻² hr⁻¹ from MSW composting. They also demonstrated that N₂O emissions increased with composting process age. The peak N₂O emission rate measured in this study was 61 mg N₂O m⁻² hr⁻¹ and was attributed to the
composting material being at the optimum temperature for nitrifying bacteria (40°C) combined with the presence of semi aerobic zones within the composting pile. Czepiel et al. (1996) also associated N₂O emissions with restricted O₂ supply, suggesting that the 0.7 g N₂O kg⁻¹ (2.2 g N₂O m⁻² day⁻¹) and 0.5 g N₂O kg⁻¹ (0.5 g N₂O m⁻² day⁻¹) emission rates for sludge and livestock wastes respectively were primarily due to a reduction in O₂ supply to the composting mass. Dairy cow deep litter composting was the focus of a study by Sommer & Dahl (1999), and they detected losses of N during composting as N₂O, although the vast majority of N loss (up to 20% of the initial N content) was emitted as NH₃. Emissions of N₂O detailed in their study were higher than those measured in Beck-Friis et al. (2000) and Czepiel et al. (1996). The peak emission rate of N₂O detected in this study was around 9.6 g N₂O m⁻² hr⁻¹. Mean N₂O emission rate is not given for the deep litter composting process studied in Sommer & Dahl (1999) so comparison with Beck-Friis et al. (2000) and Czepiel et al. (1996) is not possible. Analysis of the C:N ratio of the material studied in all three investigations is also incomplete, as are the temperatures of the composting material during processing. It is likely that these parameters would influence the rate of N₂O emission but such conclusions cannot be drawn due to lack of data.

Hao et al. (2001) measured significant emission of CH₄ and N₂O from cattle manure windrow composting accounting for 1.8% and 0.6% of the original C and N of the material respectively prior to composting. They demonstrated that high rates of CH₄ and N₂O emission were always associated with high O₂ consumption, and concluded that a higher rate of microbial activity in the composting pile enhanced CH₄ and N₂O emission. Hao et al (2001) also showed that very high concentrations of CH₄ (20 %) formed within areas of the composting pile where O₂ concentrations were between 0 and 3 %, and that a moisture content of over 60% moisture severely restricted O₂ supply to these anaerobic zones. The small particle size of the cattle manure composting material further inhibited O₂ supply to these zones due to greatly reduced air diffusion rates. A similar description of the origin of CH₄ and N₂O emission from composting was made by Hellebrand & Kalk
in their study of solid manure composting. They suggested that the heterogeneous mixture of straw and manure used in their windrow composting study promoted the development of anaerobic zones thereby enhancing methanogenic CH$_4$ production, and interrupting N transformation leading to elevated N$_2$O production. Hellebrand & Kalk (2001) suggested using a layered system during composting to reduce anaerobic zone development and therefore mitigate CH$_4$ and N$_2$O emissions. They proposed that using this system would result in less compaction and compression of the composting mass, and allow more O$_2$ to diffuse into the material. However, measurement of O$_2$ concentration within the composting mass was not performed to confirm this.

The emission rate pattern of CH$_4$ and N$_2$O was also investigated by Hellmann et al. (1997) in their study of the windrow composting of the organic fraction of source separated municipal solid waste. This study used the measurement of microbial biomass and community structure as an indicator of the presence of methanogen and nitrifier/denitrifier populations. The pattern of microbial biomass accumulation and CH$_4$ and N$_2$O emission indicated a similar emission regime to that proposed by Sommer and Moller (2000) where CH$_4$ emission occurs at the initial and middle (thermophilic) stages of composting, and N$_2$O at the very start of composting and toward the latter stages when high temperatures did not inhibit nitrification/denitrification. It was during the thermophilic stage of composting that considerable methanogenic CH$_4$ production was shown to occur.

A similar pattern of emission has been observed in a number of studies: N$_2$O emission during the initial and latter stages of the composting process where lower temperatures prevailed (<45 °C), and CH$_4$ emission during the middle thermophilic (and low oxygen) stage. Hellebrand (1998) on the study of N$_2$O and other trace gas emission from composting found that 1.8 g CH$_4$ m$^{-2}$ hr$^{-1}$ can be emitted from dung windrows, and that N$_2$O emissions accounted for 0.5% of the initial N content of the waste. They also demonstrated a change in the nature of N emission during composting with NH$_3$ being emitted in the early stages of composting, and latter stages being dominated by N$_2$O.
emissions, and that emission of N\textsubscript{2}O increased as the oxygen concentration within the composting pile decreased. Morand \textit{et al} (2005) also concluded that 0.5\% of the initial N in mixed poplar bark and poultry manure composting was released as N\textsubscript{2}O, and that the emission rate increased significantly in the latter stages of composting (after 2 months). They found a relationship between C:N ratio and emission of N where ammonia volatilisation and emission of nitrogen oxides increased more than proportionally with the initial N content of the composting material.

Jackel \textit{et al} (2004) proposed that highly adapted methanogens inhabiting anoxic zones are tolerant to the high temperature in the composting pile. They concluded that the thermophilic conditions during this stage of composting enhanced anaerobic zone development. This was due to the lower O\textsubscript{2} solubility in water at these temperatures (only 51 \% of the solubility at 20 °C), therefore maximising CH\textsubscript{4} production within these zones. In contrast to Jackel \textit{et al} (2004), Pier and Kelly (1997) identified the upper mesophilic temperature range (35 – 40°C) as optimum for CH\textsubscript{4} production. Their results showed a 50\% decrease in CH\textsubscript{4} productivity at either 30 or 50°C. Comparing the composting processes detailed in Jackel \textit{et al} (2004) and Pier and Kelly (1997) shows differences in waste type (biowaste compared to sawdust respectively), and operational temperature (thermophilic compared to mesophilic respectively). Compost pile size cannot be compared as this information was not provided by Pier and Kelly (1997), C:N ratios of the wastes were not given, and importantly, O\textsubscript{2} concentrations within the composting mass were not measured for either study. The data supplied in these two contrasting studies highlight the difficulty in comparing CH\textsubscript{4} and N\textsubscript{2}O emission results from different composting processes.

The relationship between forms of C and N present in a composting waste and the potential for emission of CH\textsubscript{4} and N\textsubscript{2}O was the focus of a study by Jokela \textit{et al}. (2002). The main conclusions of this investigation were that the potential for a waste to produce CH\textsubscript{4} and N\textsubscript{2}O was greatly reduced after composting. The study demonstrates that the
more putrescible, and therefore biodegradable, a waste is, the greater potential it has for CH₄ and N₂O generation when composted. This notion of the CH₄ and N₂O emission potential of a composting process being related to the availability of C and N in the material was also suggested by Majumdar et al. (2005).

Various drivers for the production and emission of CH₄ and N₂O during composting have been identified. Effects of pile size, and therefore composting material compaction, were investigated by Fukumoto et al. (2003) found CH₄ and N₂O emission rates were related to pile size. They demonstrated that an increase in pile size gave rise to composting material compaction leading to enhanced CH₄ and N₂O generation and emission. In the case of swine composting without forced aeration, they found this lead to the volume of anaerobic zones within the pile increasing logarithmically against the volume of aerobic zones as the size of the pile increased. This correlation between the density of the composting mass and emission of CH₄ and N₂O was also made by Sommer & Moller (2000). Kuroda et al (1996) also identified that CH₄ and N₂O production and emission during composting can be enhanced by a combination of an increase in pile size and insufficient aeration.

The involvement of anoxic zones within the composting pile in the generation and emission of CH₄ and N₂O was investigated by He et al. (2000). This study on the composting of food waste concluded that these anaerobic sites were present even when active aeration was employed during composting. They contended that these anoxic micro-sites could be present in well aerated compost piles, and may occupy single waste particles ranging from several micrometres to 4-5 mm in diameter. The relationship between the composting aeration method and the emission of N₂O was investigated by Beline & Martinez (2002). They concluded that reducing aeration can reduce the emission of N₂O during pig slurry composting. Reduction of active aeration during this composting process allowed anoxic zones to become established, therefore providing conditions suitable to complete anaerobic denitrification to N₂. In this study composting using either continuous or intermittent aeration gave rise to the highest N₂O fluxes, and
was attributed to the interruption of denitrification caused by fluctuating O₂ levels resulting in enhanced N₂O production.

Emission of CH₄ and N₂O from vermicomposting has been little studied. Frederickson & Howell (2002) assessed the potential for a large scale vermicomposting process to produce CH₄ and N₂O emissions. They found that composting pulped potato waste using this method resulted in potentially significant N₂O emission from the surface of the vermicomposting material, and that emission of N₂O was positively correlated to earthworm stocking density. Patni et al. (2000) also concluded that N₂O was released during vermicomposting, although at a considerably lower rate. They measured an emission rate of 4.38 kg N₂O-N ha⁻¹ yr⁻¹ from hog manure slurries compared to the flux rate of 275 kg N₂O-N ha⁻¹ yr⁻¹ reported in Frederickson & Howell (2002). Patni et al. (2000) does not however provide details regarding earthworm stocking density, the physico-chemical characteristics of the liquid hog manure, the rate of waste application, and the temperature of the vermicomposting system. Therefore, the reasons for the difference in flux rates between the two processes cannot be determined due to a lack of comparative data.

Earthworms in the natural environment have been identified as being the source of N₂O emission. Karsten & Darke (1997) Measured N₂O emissions from earthworms concluding that they contribute around 16 % of the total N₂O released from forest soils. The study identified the mechanism for N₂O emission from earthworms. This involved the denitrification of NO₃ within the earthworm gut which, they contended, was a semi-aerobic micro-site populated by high levels of denitrifying bacteria. Analysis of the gut contents of the earthworm Lumbricus rubellus confirmed the presence of this bacterial population and found it to be present in a higher proportion to that found in the surrounding soil. A following study by Matthies et al. (1999) also arrived at these conclusions by stimulating N₂O production via the application of a NO₃ solution to the earthworm skin. The application of NH₄ did not stimulate N₂O production. Therefore this identified denitrification
as being the route via which N$_2$O was produced. A major conclusion to this study was that earthworms potentially contribute 33% of the total emission of N$_2$O from garden soils. Vermicomposting has been shown to provide conditions ideal for nitrification and accumulation of NO$_3$ (Short et al 1999). Therefore, as NO$_3$ has been found to stimulate N$_2$O emission from earthworms, vermicomposting may have the potential to be a significant source of N$_2$O emission.

The rate of emission of CH$_4$ and N$_2$O from composting is likely to be governed by the interactions between a number of operational parameters and material characteristics. These parameters include composting process method, scale, temperature, particle size, aeration regime, and the physico-chemical characteristics of the waste. All present literature on the emission of CH$_4$ and N$_2$O from composting deals with differing pre-composting material, from the above-mentioned cattle manure to fresh cuttings of mixed herbage from fallow land. With the predicted expansion in the number of open air and enclosed composting facilities, it is essential to better understand the effect of each composting process on waste characteristics and on the resulting environmental impact. In terms of environmental impact of composting systems, while much emphasis in the UK in recent years has focused on bioaerosol emissions there has been little research into other emissions to air. A recent review of the environmental and health effects of waste management practices (DEFRA 2004) made a number of high priority recommendations relating to the composting sector. In particular it recommended that a study should be commissioned to "characterise and quantify emissions of particulates, micro-organisms, volatile organic compounds, and methane from in-vessel and/or windrow composting of MSW". This is a significant area of uncertainty at present, and could become more important if composting of MSW becomes more widespread. The recommendation clearly acknowledged the lack of peer-reviewed data on greenhouse emissions from commercial-scale composting systems operating under UK conditions.
1.6 Thesis aims and layout

The emission of CH\textsubscript{4} and N\textsubscript{2}O from composting has not been well researched and standard protocols for the measurement of emission from the many differing composting methods have not been universally adopted. Knowledge of the extent of CH\textsubscript{4} and N\textsubscript{2}O emission from the various composting methods, verification of the emission monitoring protocols and practical emission abatement methods are set to become essential elements in the development of more sustainable methods of waste composting. The imminent changes that the waste industry will be going through in order to comply with the EU landfill directive are likely to promote a significant increase in the use of composting as a waste management option.

The main aim of this research programme was to explore the emission of CH\textsubscript{4} and N\textsubscript{2}O from a range of composting processing. The objectives of the research programme were to:

i) Assess the nature and level of CH\textsubscript{4} and N\textsubscript{2}O emissions from selected composting processes.

ii) Develop appropriate sampling protocols and methods for the measurement of these emissions.

iii) Develop a respirometry method for effectively measuring the biodegradability of waste at key stages during composting.

iv) Investigate the mechanisms of CH\textsubscript{4} and N\textsubscript{2}O production during composting with particular regard to the role of waste biodegradability.

v) Undertake a preliminary assessment relating to the total emissions of CH\textsubscript{4} and N\textsubscript{2}O from the UK windrow composting sector.

vi) Suggest a limited range of technical and process-based options for the mitigation of emission.
It was considered that emphasis should be placed on the study of full size composting activities as the issues raised during this study closely relate to actual field emission of CH\textsubscript{4} and N\textsubscript{2}O. Main methods of analysis used to address the thesis aims are shown in the Methods Chapter, other methods, more specific to individual chapters are detailed within those chapters.

Chapter 3 details a preliminary comparison of the emission of CH\textsubscript{4} and N\textsubscript{2}O from 3 different composting methods; windrow composting, covered static forced aeration composting, and in–vessel composting. These methods were used to process the same waste type (source segregated household waste). Gas sampling protocols were investigated during this study, and potential mechanisms for the production and emission of CH\textsubscript{4} and N\textsubscript{2}O were identified.

In Chapter 4 a comparison of the processing of two different waste types (residual household waste and source segregated household waste) using the same in–vessel composting system (an agricultural clamp) was made. No published data exists on the production and emission of CH\textsubscript{4} and N\textsubscript{2}O from these in–vessel composting systems.

Work detailed in Chapter 5 was presented at the 1\textsuperscript{st} UK international biodegradable waste conference (Nottingham) and details the emission of CH\textsubscript{4} and N\textsubscript{2}O from vermicomposting. The application of vermicomposting techniques to waste processing is on the increase globally and the study presented in Chapter 5 builds on previous research carried out by the Open University, work that identified vermicomposting as being a significant point source of N\textsubscript{2}O emission (Frederickson & Howell 2002). The effect of process temperature on the emission of N\textsubscript{2}O from vermicomposting is the focus of study in this chapter.

Chapter 6 is based on a journal article published by Waste Management (Hobson et al. 2005). The comparison of the mechanisms of production, and nature of CH\textsubscript{4} and N\textsubscript{2}O emission from windrow and vermicomposting after in–vessel pre–treatment are detailed.
This study highlights the way the two composting processes differ operationally in the degradation of organic wastes, and differ in their CH$_4$ and N$_2$O emission pathways.

Identified during the preceding chapters is the effect of waste biodegradability on CH$_4$ and N$_2$O emission. Chapter 7 presents the laboratory scale study of CH$_4$ and N$_2$O production within wastes of differing biodegradability under varying aeration regimes. Two artificial wastes of differing biodegradability are synthesized based on the relative contents of organic compounds (such as cellulose and lignin). Details of a test, developed in conjunction with WRc PLC (on behalf of the Environment Agency), to measure the biodegradability of wastes are included in this chapter and applied to the wastes under investigation. The two synthesized wastes are composted in the laboratory under both sufficient and insufficient aeration regimes and production of CH$_4$ and N$_2$O is recorded.

Chapter 8 is a general discussion of the findings detailed in the various investigations. Included in this chapter are data relating to the comparison of the CH$_4$ and N$_2$O emission data presented in Chapters 3 to 7 with that of other studies. An attempt is also made to provide projections of future CH$_4$ and N$_2$O emission based on the proposed increase in composting activity due to compliance with the landfill directive. The development of a respirometry system can be followed through the previous chapters. During the respirometry research programme detailed in this thesis the DR4 respiration test was developed. This was jointly developed with WRc PLC and was adopted by the Environment Agency as one or two essential tests to be used for assessment of waste biodegradability associated with MBT processing. Details of this work are also shown in Chapter 6, including how respirometry can be used to assess the CH$_4$ and N$_2$O emission potential.
2 Methods

2.1 N₂O and CH₄ sample collection: the static chamber method

The static chamber method involves calculation of a flux by periodically taking samples from within a defined chamber ‘head space’ and then measuring the change in gas concentration during the period of linear concentration change. The static chamber method is commonly used to measure trace gas emissions from a surface and has been validated in comparison to micrometeorological methods (Laville et al. 1999). Static chambers have been extensively employed to measure methane emission from rice paddies (Agnihotri 1999; Adhya et al. 2000) and composting (Hellman et al. 1997; Hellebrand 1998; Beck-Friis 2000). For this study cylinders of 0.0707m² cross sectional area and height of around 0.3m were pressed into the compost material to a depth of around 0.05m, after allowing time for gas evolved due to disturbance of the material to disperse, the cylinders were topped and sealed. The open base of the chambers featured sharpened edges to minimise disturbance of the compost when locating them on the surface of the composting material. The closed chamber (0.25m x 0.0707m² in volume) now captured any gas flux from the bed. Samples of around 60ml were taken at t=0 (when the cylinders were topped) then at regular intervals thereafter. Once a sample was removed (via syringe) it was immediately injected into an evacuated glass vial and labelled. CH₄ and N₂O fluxes were calculated using equation 2.1.

Equation 2.1 Calculation of CH₄ or N₂O flux rate

\[
\text{Flux CH}_4 \text{ or N}_2\text{O mg m}^{-2} \text{ hr}^{-1} = \frac{\Delta C \times F \times V}{a \times t}
\]

Where \( \Delta C \) is the change in CH₄ or N₂O concentration (ppm), \( F \) is a concentration to mass conversion function (derived from equation 2.2), \( V \) is the volume of the headspace (m³), \( a \) is the soil area as defined by the chamber (m²) and \( t \) is the enclosure time (hours).
Equation 2.2 Calculation of the concentration to mass conversion function used in equation 2.1

Concentration to mass conversion function

\[ F = \frac{m}{R \times (273 + T)} \]

Where \( m \) is the molecular weight of the either CH\(_4\) or N\(_2\)O (g mol\(^{-1}\)), \( R \) is a constant (8.206 x 10\(^{-5}\) atm K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the air temperature at the time of sampling (°C).

Figure 2.1 Static chamber test set-up

To verify the static chamber's integrity the following tests were carried out. An open chamber bottom was immersed in water to make a seal, and contained a small box of vermicomposting worms and bedding material (25 x 15 x 7 cm, Figure 2.1). The lid was fitted and samples taken at 15 minute intervals (0-120 minutes then two additional samples taken at 270 and 295 minutes). Samples were taken from the top of the chamber (through a septum) and from the bottom of the chamber through a tube. N\(_2\)O concentration rise during the 120 minutes was linear and continued to be so for the later 270 and 295 minutes samples; the R\(^2\) values for the trends were 0.9986 and 0.9967 for the bottom and top respectively (Figure 2.1). It can therefore be concluded on the basis of these data that N\(_2\)O neither leaked nor settled into a stratified pattern within the chambers.
Should any loss of sample occur in the field when using these chambers it is highly likely it can be attributed to leakage from the open base of the cylinders.

A similar pattern of good linearity and agreement between top and bottom sample points within the chamber was observed in a subsequent test. Two sample runs similar to those above were performed which lasted 60 minutes at 15 minute sampling intervals. ($R^2 = 0.98$ and 0.99 for top and bottom sampling points respectively). These data lead to the conclusion that static chamber sampling duration could be reduced to 30 minutes while still resulting in a true flux. Gas sample loss through the base may be due to the venturi effect of external air current drawing out sample combined with microbial N$_2$O reduction.

Figure 2.2 N$_2$O Concentration within flux chamber at bottom and top sampling points.

The chambers used in this study had two different types of lids interchangeable between cylinders. Chamber lids were attached to the cylinders with metal clips, one type with spacers under the clips lifting them approximately 1 mm and one type with the clips located directly onto the surface of the lids. To test the integrity of the chambers when used with both lids, two test runs were undertaken using the same test method as described previously for testing stratification of gases within the chamber. Table 2.1
shows results of this test show that $\text{N}_2\text{O}$ concentration within the chambers was linear in both tests and that the chambers were equally leak proof ($R^2 = 0.99$ in both cases).

Table 2.1 $\text{N}_2\text{O}$ concentration rise within two chambers of differing lid types over 60 minutes.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>$\text{N}_2\text{O}$ (ppm) using lid with no spacers (needle - top)</th>
<th>$\text{N}_2\text{O}$ (ppm) using lid with no spacers (tube - bottom)</th>
<th>$\text{N}_2\text{O}$ (ppm) using lid with spacers (needle - top)</th>
<th>$\text{N}_2\text{O}$ (ppm) using lid with spacers (tube - bottom)</th>
</tr>
</thead>
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<tr>
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<td>0.24</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>15</td>
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<td>0.44</td>
<td>0.42</td>
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<td>0.66</td>
<td>0.65</td>
<td>0.64</td>
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<tr>
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<td>0.86</td>
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<td>60</td>
<td>1.06</td>
<td>1.07</td>
<td>1.04</td>
<td>1.05</td>
</tr>
</tbody>
</table>

2.2 Gas chromatography

Gases sampled in the field from static chambers were either stored in the syringes they were collected in or transferred to glass Evacutainer vials prior to transportation to the laboratory for gas chromatograph (GC) analysis. The GC used throughout this study was an Al Cambridge GC 94 m fitted with a 2 m Poropack Q column, a flame ionization detector (FID) for methane measurement and an electron capture detector (ECD), both connected to a Varian data interface. Gas chromatography relies on a porous column (stationary phase) to partition different compounds that may be introduced to a carrier gas (mobile phase) which is passing through the column. Individual components within the column are retarded for different lengths of time depending on the extent of interaction between the component and the column with components emerging in order of increasing interaction with the column.
Methane detection (FID)

When methane emerges from the column it is detected by a flame ionization detector (FID), where, after first being pyrolysed in a H₂/air flame, resulting ions and electrons allow a current to flow between an electrode and an ion collector. The current is then measured, converted to a digital signal which passes via the data interface unit to the Varian software which calculates the area beneath the curve produced by variations in current with time.

Nitrous oxide detection (ECD)

When N₂O emerges from the column it is detected on an electron capture detector (ECD). The radioactive element inside the detector emits electrons (beta particles) which collide with and ionize some of the carrier gas. This reaction forms a stable cloud of free electrons in the ECD detector cell. The ECD electronics work to maintain a constant current equal to the standing current through the electron cloud by applying a periodic pulse to the anode and cathode. If the current drops below the set standing current value, the number of pulses per second increases to maintain the standing current. When electronegative compounds enter the ECD cell from the column, they immediately combine with some of the free electrons, temporarily reducing the number remaining in the electron cloud. When the electron population is decreased, the pulse rate is increased to maintain a constant current equal to the standing current. The pulse rate is converted to an analogue output which passes to the data interface unit and Varian software on a separate channel to the FID signal.

Specifications for the gas chromatograph are as follows

GC type – Al Cambridge GC 94 m
Column – 2 m Poropak Q
Detector types – Flame ionisation and electron capture
Oven temperature – 60°C
Valve temperature – 50°C
Detector temperature – 320°C
Carrier gas – nitrogen
Detection limit for CH₄ – 0.1 ppm (FID)*
Detection limit for N₂O – 0.05 ppm (PID)*

* Determined by multiplying the standard deviation of 10 background air measurements by 3 (Willard et al 1988).

2.3 Concentration to mass conversion factor for respiration rate calculation

The equations used to calculate compost respiration rates require conversion of gas concentration units to mass units. In conversion of these units the temperature and pressure of the gas at the time of sampling have to be taken into account. The equation used to calculate the concentration to mass conversion function is known as the combined gas law (equation 2.3).

Equation 2.3 Combined gas law

\[
\left( \frac{P_1 \times V_1}{T_1} \right) = \left( \frac{P_2 \times V_2}{T_2} \right)
\]

Where \( P_1, V_1 \) and \( T_1 \) are standard pressure, temperature and molar volume (1 atm, 273°K, and 22.4 l mol⁻¹ respectively), and \( P_2, V_2, \) and \( T_2 \) are the atmospheric pressure, temperature, and molar volume at the time of gas measurement.

\( V_2 \) is the value used in equations 3.1 and 4.1 as a concentration to mass conversion function. All gas measurements in this study were undertaken at atmospheric pressure therefore \( P_2 \) is regarded as being 1 atm. \( P_1 \) is also 1 atm so both \( P_1 \) and \( P_2 \) cancel out
and are no longer needed in the equation. The equation is re-arranged to calculate $V_2$ as shown in equation 2.4.

Equation 2.4 Calculation of concentration to mass conversion function $V_2$

$\left( \frac{V_1 \times T_2}{T_1} \right) = V_2$

The calculation of the amount (weight) of CH$_4$ and N$_2$O produced from a composting process is done using equation 2.5. This equation allows the conversion of a volume (litres) of CH$_4$ and N$_2$O to a mass (g).

Equation 2.5 Conversion of CH$_4$ and N$_2$O volume to mass

$\text{CH}_4 \text{ or N}_2\text{O g} = m \times \left( \frac{PV}{RT} \right)$

Where $m$ is the molecular weight of either CH$_4$ or N$_2$O, $P$ is the pressure at the time of measurement (1 atm), $V$ is the volume of gas (litres), $R$ is a constant (0.08206 L atm K$^{-1}$ mol$^{-1}$), and $T$ is the temperature at the time of measurement (K).

2.4 Principle of respirometry

What follows is a brief description in the use of respirometry for waste analysis including the methods used in this study for respiration rate determination. Respirometry was used in Chapters 3, 4, 5, and 7 of this study, with a discussion on the different methods used in other studies included in Chapter 6. Respirometry provides a measure of the uptake of O$_2$ or production of CO$_2$ being performed by an organism or group of organisms. Measurement of O$_2$ or CO$_2$ can be made by either titration, gas chromatograph or, as in the case of the apparatus used in this study, on-line analyser. Respirometry has been
used for some time to give a good estimate of stability (degree to which readily degradable organic matter has decomposed) or biodegradability of a waste through measurement of microbial activity (Haug 1993).


Various methods have been employed to prepare samples, perform respirometry (e.g. flow rates, temperature), and report results. Some methods measure a static respiration index (uptake of O₂ or production of CO₂ without aeration), others, including the method used in this study, measure a dynamic respiration. This dynamic approach is also used in standard test methods for waste stability in the USA (ASTM D5975-96) and Germany (AT4), and involves the passing air through the waste and determining O₂ and CO₂ concentration in the air stream before and after the waste sample. Expression of results can be made as either a mean of 24 hours of highest O₂ uptake rate or CO₂ consumption, or the 4 day cumulative O₂ uptake rate or CO₂ consumption.

Listed below are the parameters used in the methods of dynamic respiration rate determination used in each Chapter in this study.

Chapter 3

- Sample not amended (no shredding or nutrient supplements)
- Sample size 5 kg
- Flow rate through sample 5 L minute⁻¹
• Moisture content 50%

• Temperature 35°C

• Data expressed as a mean of 24 hours of highest CO₂ consumption

Chapters 3 and 5 used the same operating parameters as above but results were expressed as the 4 day cumulative O₂ uptake rate.

Chapter 6

The "draft standard method" used in this chapter is described below, variations of this method were tested in the development of the DR4 standard for organic household waste stability analysis. Details of the development of this standard are in Chapter 6.

• Sample shredded to 20 mm

• Sample size 100 g dry matter waste, 100 g dry matter mature compost inoculum

• Flow rate through sample 500 ml minute⁻¹

• Moisture content 50%

• Temperature 35°C

• Data expressed as the 4 day cumulative O₂ uptake rate

2.5 Methods used in the physico-chemical characterisation of waste

2.5.1 Total Kjeldahl N, P and K determination

This Kjeldahl digestion was the British Standard method BS EN 13654-1. The digestion for nitrogen (ammonium N and most organic N) was modified to include nitrate and nitrite N by reduction to ammonium. The method was modified by adding 1.25g of sodium
thiosulphate to each digestion to chemically reduce any nitrates present to ammonium. This was followed by distillation of ammonia and titration with standard acid.

2.5.2 Total organic carbon determination

Loss on ignition was used as the test for organic carbon content, and the resulting change in weight allows for a calculation of organic content and was undertaken as follows:

1. Crucibles were pre-ignited to 450°C to ensure they were clean, and then placed in a desiccator till use.
2. Samples were weighed into crucibles with a 4 decimal scale (approximately 3 g)
3. Samples were dried overnight at 103°C
4. reweigh samples and record
5. After re-weighing and recording, samples were put in a furnace overnight at 550°C after which samples weighed and loss on ignition determined using equation 2.6

Equation 2.6 formula for the calculation of the loss on ignition content of a waste sample

\[
\text{Loss on ignition} \% = \frac{(O_w - I_w) \times 100}{(O_w - C_w)}
\]

Where \( C_w \) is weight of crucible, \( O_w \) is weight of oven dried sample and crucible, and \( I_w \) is weight of ignited sample and crucible.

The loss on ignition content of compost was used to provide an estimate of the total organic carbon (TOC) content. It is generally accepted that a good estimate of the TOC compost can be arrived at by dividing the loss on ignition figure by 1.8 (Wu et al. 2000, Richard 1996, and Abu Qdais & Hamoda 2004).
2.5.3 Extraction of water soluble nutrients from compost and bedding materials and measurement of pH and conductivity

This procedure was derived from Draft BS: EN 13652, EN 13037 & EN 13038. Fresh compost samples were manually homogenised and 30 g were transferred to a 1 L bottle. Samples were shaken with 300ml water for 1 hour (120 rpm) at room temperature. Samples were then filtered through filter paper (Whatman 42), (discarding the first 10ml), pH and conductivity were determined (Labodtest analyser) and samples were collected in cap-able plastic vials for ion chromatograph analysis.

Water soluble nutrient analysis using Ion Chromatography

The soluble nutrient (Na, NH₄, K, Mg, Ca, F, Cl, NO₃, PO₄, and SO₄) were determined using a Dionex DX-100 ion chromatograph. The sample to be analysed (the analyte) is applied to a stationary fixed material (the adsorbent) in the column and then a second material (the eluent) is passed through the stationary phase. The compounds contained within the analyte are then partitioned between the stationary adsorbent and the moving eluent. As the eluent moves through the column the components of the eluent will move down the column at different speeds separating from one another, arriving at the conductivity detector at different times, generating peaks on a chromatogram. Calibration of the chromatogram with known standards is required prior to the analysis of unknowns.

Specifications for the Ion chromatograph are as follows.

Ion Chromatograph - Dionex DX-100
Guard Column - Dionex Ionpac CG2, 4 mm x 50 mm
Analytical Column - Dionex Ionpac 4 mm x 250 mm
Suppressor - Dionex Cation Micromembrane Suppressor
Integrator - SP-4400
Detection - Conductivity, 30 μs full scale

Injection - 50 μl, via injection loop

Eluent - 16 mM – 40 mM HCL/methansulphonic acid (cations), and 2.7 mM NaCO3/0.3 mM NaHCO3 (anions)

Regenerant - 0.070 M tetramethylammonium hydroxide at 4 ml min⁻¹

2.5.4 Acid and Neutral detergent fibre analysis

Acid detergent fibre (ADF) was determined using Gerhardt fibre bag apparatus using the Gerhardt method AN-04-206. Neutral detergent fibre was determined using Gerhardt fibre bag apparatus using the Gerhardt method AN-04-204.
3 Effect of process type on waste stabilisation rates and emission of CH$_4$ and N$_2$O

3.1 Introduction

As discussed in Chapter 1, many studies have indicated that the type of composting process employed can greatly affect the rate that organic matter is decomposed (stabilized) during composting and this will contribute significantly to the environmental impact of each system. The nature of the composting process can also determine the time taken to produce a mature compost product as well as influencing the physico-chemical characteristics of the final product. The production and emission of CH$_4$ and N$_2$O are microbially mediated, and the rates of these (mostly anaerobic) microbial processes are related to temperature, O$_2$ levels (moisture) and the availability of labile carbon (changes in the physico-chemical characteristics of the waste). Hence, it is important to be able to monitor the changes in waste characteristics taking place during composting to enable predictions to made about gaseous and liquid emissions for particular composting methods and to control the operational aspects of each process.

Curtis et al. (2005) composted animal waste and straw using three composting methods (turned windrow and covered/uncovered passively aerated piles) and concluded that the different methods "produced materials with significant differences in several physical and chemical properties, both spatially within and between treatments". A particular feature of the study was the use of respirometry to assess the degree to which labile carbon was decreased by each process and as an indicator of waste stabilization and maturity. Although all the treatments had relatively stable respiration rates by day 176, it was clear that the respiration profiles during the composting process were very different depending on process characteristics. A respirometer was used to determine the microbiological activity (an indicator of compost stability) of partially composted material. Stability is
defined as the degree of decomposition or maturity of the composting material (Brewer & Sullivan 2003). Respirometry was found to be a useful technique for monitoring levels of biodegradable carbon and for characterising the performance of competing processes especially during the early stages of composting when the gaseous emissions were likely to be highest.

As highlighted in Chapter 1, the use and selection of respirometry techniques to determine waste stability has been the focus of much debate in recent years and this topic will be explored in detail in Chapter 6. Respirometry has been used in many forms to assess waste stability but until recently it has not been used extensively for research purposes (Lasaridi & Stentiford, 1998).

While respirometry is a rapidly developing technique for determining waste stability and for evaluating the potential environmental impact of biodegradable waste, many studies have employed other appropriate physico-chemical parameters. Typically, authors have used the carbon content and the volatile solids content of waste to assess stability changes. Frederickson (1999) measured losses in waste volatile solids (VS) content and changes in C:N ratio to assess the effect of process conditions (i.e. turning frequency) on stabilisation rates for a mechanically turned windrow system. The relative rates of decomposition for the first 4 weeks of composting were calculated for a frequently turned (3 times per week) and a less frequently turned (1 time per week) windrow. It was concluded that the rate of decrease in the VS content for the frequently turned windrow was approximately 20% greater than for the less frequently turned windrow. By week 12, however, there was no statistically significant difference in the volatile solids content for the two treatments suggesting that processing conditions can affect waste stability and hence environmental impact more profoundly during the early stages of composting. Cooper and Golueke (1982) also showed that enhancing the composting process also affected waste stabilisation rate differentially during composting. For a sewage sludge mix, they found that turning the pile 3 times per week destroyed 38% of the VS content in
the first 35 days compared to 26% for once per week. By day 52, the frequently-turned regime had destroyed only 44% VS in total whereas turning once per week had destroyed 48%.

The state of decomposition of the waste during different stages of the composting process is clearly an important consideration in terms of its environmental impact and capacity to pollute through liquid and gaseous emissions. For example, Biasioli et al. (2004) successfully linked waste characteristics to environmental impact in terms of odour levels which were found to be positively correlated with waste biodegradability, as determined by respirometry testing. They characterised the 80-day composting process into 4 phases according to the Respirometric Index (RI) of the waste. The odour concentration decreased after the active phase (first 5 days) but they reported that the rate of odour decease was slower than would be expected given the relatively low biological activity as shown by the RI.

Morand et al. (2005) investigated the gaseous emissions including ammonia and greenhouse gases from composting various mixes of bark and manure, and characterised according to high and low C:N. They detected N₂O in a limited number of samples and for these treatments their findings agreed with Hellebrand (1998), concluding that 0.5% of initial nitrogen was lost as N₂O. Importantly, for nitrogen emissions to air they concluded that the first phase of composting emitted primarily ammonia while the latter stages resulted mainly in N₂O emissions. While CH₄ was emitted from all treatments, no pattern of emission could be discerned during the experiment.

Respirometry has much to offer in helping to characterise the waste's capacity to emit particular gaseous compounds at different times during the composting process. Hence, a particular feature of the research programme presented here will be the use, development and evaluation of respirometry techniques to help better understand the relationship between the state of waste biodegradability and the potential to generate CH₄ and N₂O.
The experiment detailed in this chapter sought to investigate the extent to which different composting methods, reflecting differing processing conditions, affected the stabilisation rate of source segregated household waste and to explore the potential of each method to emit CH\textsubscript{4} and N\textsubscript{2}O.

The three methods of composting studied were:

1. Mechanically turned windrow composting (WC).
2. Covered static forced aeration composting (CSFAC).
3. In-vessel composting (IVC).

The experiment was conducted at full-scale and formed part of a wider series of collaborative initiatives between the Open University, Cleanaway Ltd, Enviros Ltd and London ReMaDe. The project was funded in part by The Norlands Foundation. The experiment was undertaken at Rainham Marshes landfill site, Essex, UK using source segregated household waste from a separate waste collection trial in Bexley, Kent. The project commenced in July 2002 with the operational duties being performed by Cleanaway Ltd staff. The Open University contributed to the overall experimental design and was responsible for devising and delivering the performance monitoring regime for each composting method and for evaluating the environmental impact of each, with particular regard to greenhouse gas emissions.

The composting methods utilised for the trial were selected to represent the typical systems currently in operation (WC) as well as potentially important enclosed systems capable of processing kitchen waste (CSFAC, IVC), which were seen as compliant with the Animal By-Product regulations (DEFRA 2003). Slater & Frederickson (2001) predicted that a 16 fold increase in windrow composting is required in order to comply with the European Landfill Directive (as detailed in Chapter 1), suggesting that mechanically-turned windrow systems processing green waste are likely to greatly increase in number.
in the future. Moreover, the predicted continuing dominance of open-air windrow systems utilising green wastes and the future potential of enclosed systems was echoed by Slater et al. (2005). They reported that “to date the industry has been able to sustain growth with a reliance on green waste, which accounted for 95% of municipal wastes composted, and virtually all household wastes composted”.

Despite considerable and sustained growth, only approximately one-fifth of the estimated 7 Mt of household garden waste arisings in the UK in 2003/04 were composted by the industry, whilst the estimated 6 Mt of kitchen wastes remained a largely untapped resource. Using data from the 2003-04 Composting Association survey, they confirmed that open-air windrow technology was used at 278 of the 325 sites reported in the survey, accounting for 82% of wastes composted in 2003/04. However, there was some evidence to show that the enclosed composting sector was starting to develop, with the number of sites employing in-vessel technologies increasing from 12 in 2001/02 to 18 in 2003/04.

Many well-documented studies have identified WC as a potential source of CH₄ and N₂O emissions (reviewed in Chapter 1). However, while it is accepted that windrow systems can give rise to greenhouse gas emissions due to poor aeration and the presence of anaerobic zones, the potential of forced-air composting systems to generate and emit similar gases has not been adequately explored.

Covered static forced aeration composting is widely employed in continental Europe for the treatment of a variety of organic wastes. The general formation of a pile is similar to windrow composting, with waste typically piled over perforated pipes allowing air to be blown into the composting material. This eliminates the need to turn the pile (either mechanically or manually) as in traditional WC. Forced aeration composting has been shown to provide greater air supply to composting material, generating higher O₂ levels within the pile (Zhu et al. 2004).
In-vessel composting has become a widely-used method of processing organic waste prior to re-use or landfill. Because of the legislative requirements of the EC Landfill Directive (EC 1999) and recent Animal by-product regulations (DEFRA 2003), there is an increased requirement to process waste that might potentially contain kitchen waste in enclosed composting systems. As mentioned above, data on emissions of CH$_4$ and N$_2$O from these types of systems are very limited.

Project Aim

To undertake a series of parallel composting trials using three composting methods and one waste type, to assess the effect of each method on the waste stabilisation rate and on its capacity to emit CH$_4$ and N$_2$O.

Project Objectives

1. To design and develop a respirometry system with the capability of measuring large and small changes in stability (biodegradability) for a wide range of waste types.

2. To identify appropriate methods, equipment and protocols for accurately measuring CH$_4$ and N$_2$O emissions from a wide range of full-scale composting systems.

3. To develop a waste sampling regime for each composting system which would allow stability changes to be determined during the course of the experiment.

4. To identify one representative time or stage during the composting process to undertake monitoring of CH$_4$ and N$_2$O emissions to enable comparison of emissions from each system to be made.

5. To undertake all waste sampling and emissions monitoring procedures and respirometry studies to enable the effectiveness of each composting system to be assessed along with its capacity to produce CH$_4$ and N$_2$O.

6. To contribute to the design of a full-scale experiment which would evaluate the effect of three different composting methods on respective waste stabilisation rates and emission of CH$_4$ and N$_2$O.
3.2 Materials and Methods

3.2.1 Waste characteristics

The waste material selected for composting by each method was source segregated household waste derived from a separate collection trial in Bexley, Kent. The physico-chemical characteristics of the waste were determined prior to composting (Table 3.1). The composition of the waste was predominantly green waste with some non-meat kitchen waste and inert material (glass, plastics, and metals). The waste prior to composting was shredded on-site and samples for analyses were derived from 5 separate sub-samples (10 kg each) taken directly from the output conveyor of the composting site shredder. The physical characteristics of the waste were determined by manually sorting the whole sample (5 x 10 kg).

Respiration rate was determined using an apparatus specifically designed and developed at the Open University to test composts (described in section 3.2.5). The fundamental principles of respirometry are detailed in the Methods Chapter (section 2.5). Volatile solids and total nitrogen content were determined using methods described in Chapter 2 (section 2.6), as were all volatile solids and total N determinations relating to this chapter.

Table 3.1 Mean physical and chemical characteristics of the initial (fresh) composting material subjected to full-scale windrow, covered static forced aeration and in-vessel (system 1) composting. Range of results shown in brackets

<table>
<thead>
<tr>
<th>Green waste (%)</th>
<th>Non-meat kitchen waste (%)</th>
<th>Glass (%)</th>
<th>Metals (%)</th>
<th>Plastics (%)</th>
<th>Respiration rate mg CO2 hr⁻¹ kgVS⁻¹</th>
<th>Volatile solids (%)</th>
<th>Total N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 (73 – 87)</td>
<td>10 (8 – 13)</td>
<td>2 (1 – 3)</td>
<td>1 (0 – 2)</td>
<td>7 (3 – 13)</td>
<td>904 (601 – 1545)</td>
<td>64.9 (53.7 – 72.7)</td>
<td>1.45 (1.01 – 1.97)</td>
</tr>
</tbody>
</table>
3.2.2 Windrow composting (WC)

Shredded source segregated household waste was formed into a windrow with the approximate dimensions 3 m high x 3 m wide x 20 m long (Figure 3.1). As with all treatments examined in this study, the duration of composting was 86 days. The windrow turning regime was established prior to commencement of composting with mechanical turning being scheduled to take place approximately every two weeks.

Samples of partially composted material (3 x 10 kg) were collected from the windrow every 7 days for respirometry analysis. The schedule for monitoring trace gas emissions to air from the windrow was determined to be just prior to the first mechanical turning of the windrow. This was to assess if the initial active phase of composting as determined by respirometry had led to the development of anaerobic zones within the composting material, and therefore CH$_4$ and N$_2$O emission (He et al. 2000). Monitoring for CH$_4$ and N$_2$O emissions was undertaken after 15 days from commencement of composting and before the pile was turned for the first time.

Static flux chamber CH$_4$ and N$_2$O sampling

It has been recognised that the pattern of airflow in windrow composting is a 'chimney effect' (Haug 1986) (Figure 2.1). As the temperature of the composting material rises, convection draws in fresh air from the sides of the windrow exiting at the peak of the pile (Lynch & Cherry 1996). The method most widely employed for sampling windrow emissions take advantage of this airflow pattern with static flux chambers situated on the peak of the pile (Sommer & Moller 2000, Czepiel et al. 1996, Hao et al. 2001, Hellebrand & Kalk 2001, Fukumoto et al. 2003). Verification of the integrity of the gas flux chambers used in this chapter is detailed in Methods 2.1. This method was used 15 days after composting started. The static chambers were placed simultaneously at equal distance apart (2 m) along the peak of the windrow (n = 6). They were then pressed into the
composting material (to a depth of 5 cm) ensuring no gaps were left between the base of the cylinders and the composting material. Some manipulation of the material around the base of the chamber was necessary to provide a sufficient seal. After allowing 2 hours for any gas released due to compression and disturbance of the composting material to disperse, the chambers were sealed and initial samples were taken. Samples were then taken at 10, 20 and 30 minutes. Samples were taken from the septum located in the chamber lid using a 60 ml Braun Omnifix syringe fitted with a luer 3-way tap and luer needle and were injected into 10 ml glass vials (Evacutainer). The labelled vials were transported to the lab for gas chromatograph (GC) analysis of CH$_4$ and N$_2$O within 24 hours, details of the GC analysis of CH$_4$ and N$_2$O are included in the Methods Chapter (section 2.2).

Figure 3.1 Windrow pile format and 'chimney effect' air flow pattern, CH$_4$ and N$_2$O flux was sampled on the peak of the windrow as indicated
3.2.3 Covered static pile forced aeration composting (CSFAC)

As with the WC treatment, the shredded source segregated household waste was formed into a windrow with the approximate dimensions 3 m high x 3 m wide x 20 m long (Figures 3.2 and 3.3). The material used to cover the pile was a breathable fabric (Gortex) designed to allow gas exchange but retain moisture in the composting pile. The system was operated as directed by the manufacturers and more detailed information about this system can be found at http://www.gore.com/en_xx/products/fabrics/swt/.

Samples of partially composted material were collected from the forced aeration windrow according to the same schedule as the mechanically turned windrow and these were also subjected to respirometry analysis.

Trace gas fluxes were measured 15 days after composting started to coincide with flux sampling from the full-scale windrow and allow a comparison of $\text{CH}_4$ and $\text{N}_2\text{O}$ from the two systems to be made. As with the WC method, static flux chambers were used to sample emissions. Because the flux chambers could not be pressed into the composting material, the chambers were placed on the surface of the cover and weighed down with engineering bricks to provide a seal against the cover material. After weighing the chambers down they were left for 2 hours before being sealed so that any gases released due to this compression would not affect the flux reading. Samples were taken when the chambers were sealed, then at 10, 20 and 30 minutes. The flux chambers ($n = 6$) were placed simultaneously, located along the peak of the CSFAC pile with around 2 m separating each chamber. Samples were then collected as previously described.
Figure 3.2 Configuration of the covered forced aeration compost pile

Figure 3.3 Source segregated household waste being piled onto aeration pipes
3.2.4 In-vessel composting systems

The enclosed container in-vessel composting system is shown in schematic form in Figure 3.2. It was provided with air and leachate re-circulation. Source segregated household waste (approximately 7 tonnes) was loaded into the container through a hinged roof. When loaded, the hinged lid was closed and an electric fan drew air from the headspace of the container and channelled down to the perforated floor and back into the composting mass. The air then passed through the composting material and back into the headspace where it was drawn off again for recirculation. Temperature probes located in the sides of the container allowed continuous monitoring of the heat generated by the composting mass which is a requirement of the Animal by-products regulations (DEFRA 2003).

The system was designed to react to high temperatures within the container, which may inhibit composting (temperatures greater than 68°C are known to cause inhibition in similar systems (Haug 1993)). If temperature increased, a louvered door was automatically opened to allow the fan to draw cool ambient air into the air circulation stream. Leachate collecting at the base of the container was also re-circulated and applied to the surface of the composting material.
Figure 3.4 Dimensions, operation and sampling locations for the In-Vessel Composting system (IVC)

Figure 3.5 In-Vessel composting container with side loading door open
Sampling CH₄ and N₂O from the in-vessel composting system

Due to the complexity of the system configuration and operation, three methods were used to assess the greenhouse gas production potential of the IVC system: (1) sampling direct from the material to measure CH₄ and N₂O production, (2) sampling from the headspace of the IVC system while the process was running, and (3) sampling from the headspace of the system after the air circulation fans were switched off and the headspace air allowed to equilibrate with ambient air for around 3 hours.

Sampling the gas within the composting material from the surface of the IVC system was not possible due to safety issues regarding the hinged metal roof of the system. To allow gas samples to be taken from the composting mass, a 2 m hollow spike probe was fully inserted into the composting material through sampling ports located on the side of the container (used for temperature probe insertion). Sampling was done after 7 days of continuous in-vessel composting. A 60 ml syringe was used to draw first the volume of the spike probe (200 ml), then the sample (60 ml). Two samples were taken from the material and were injected into 10 ml ‘Evacutainers’ for transport to the laboratory for GC analysis (within 24 hours).

For headspace sampling, flexible tubes (Tygon1/4"ID) were installed into IVC system and fastened to the roof prior to loading. The headspace sampling tubes were attached to the water re-circulation bar that runs along the inside of the IV system roof, care was taken to ensure the tubes could move freely, did not become blocked or impede any moving parts of the IVC system. Samples (60 ml) were taken after first drawing off the volume of the tube (400 ml) by syringe. Samples were injected into ‘Evacutainers’ and transported to the laboratory for GC analysis (within 24 hours). Sampling of the headspace gas of the IVC system was done at 15 days from the start of composting (n = 4).
To gain insight into the mechanisms of production of CH$_4$ and N$_2$O within IVC material a measure of the passive build-up of CH$_4$ and N$_2$O into the headspace of IVC system without aeration was made. To measure this passive release of CH$_4$ and N$_2$O, firstly the aeration fan was turned off. The roof of the system was then opened and the headspace gas allowed to equilibrate with outside air (for around 3 hours). The roof was then closed and samples of the headspace gas taken using the installed tubes and sampling method employed for headspace gas sampling while the system was running. Samples were taken (in duplicate) from the time the roof was closed then every 5 minutes for 30 minutes (n = 14). To identify any temporal change in the production of CH$_4$ and N$_2$O this sampling was performed at the start of IV composting and again after 7 days.

3.2.5 Respiration rate determination

A respirometry facility was developed to provide a measure of the microbial activity taking place within compost samples. Levels of microbial activity provide good estimates of the stability or biodegradability of the waste under study (Haug 1993). The respirometry system comprised three 20 L cylindrical (PVC 30 cm diameter, 45 cm high) chambers designed for the analysis of unconditioned samples, i.e., those not specifically amended by shredding or adding nutrients prior to respiration rate determination. The moisture content of samples was amended to 50%. Figure 3.6 shows the configuration of the chambers indicating the temperature control method. Copper pipe (coated with radiator enamel) was installed in the chambers through which heated water was pumped (Grant GR04) providing heat to the waste samples. The shape of the pipe was designed as to allow them to be pressed into the compost sample under analysis when loading the chambers. Temperature in the copper pipe was controlled at 35°C providing conditions favourable for most of the microbial population (Clark et al. 1978).

In this system, production of CO$_2$ (a measure of microbial activity and potentially the degree of biodegradability) and aeration flow rate were continually logged. The
respirometer design was adapted from the basic system recommended by the manufacturer (Sable Systems, Connecticut, USA). The system employed the ‘flow through’ dynamic method that produced respirometric values that reflected the aerobic process (Adani et al. 2001).

Figure 3.6 Configuration of the respirometer chambers with airflow and copper pipe heating method indicated.

Figure 3.7 shows the layout of the complete respirometry system developed to measure microbial activity in compost samples. CO$_2$ production was determined by subsampling the output stream using a multiplexing unit (Sable MUX) to alternate between subsample lines. Fresh outside air was pumped through the chambers at ~5 L minute$^{-1}$ via flow metres (Sierra Top Trak). The chambers were loaded with 4 kg of unconditioned sample adjusted to 50% H$_2$O content.

The output air from the chambers was sub-sampled (at approximately 200 ml minute$^{-1}$) and passed into a multiplexing unit. From here the sub-sample passed first through a
drying column (Drierite), and CO₂ was measured (Sable CA-02). Data from the CO₂ analyser and the flow metres was channelled via a data interface unit (Sable UI2) to a PC for respiration rate calculation. The respirometer software (Sable DAC) controlled the selection of alternate sub-sampling lines via the data interface and multiplexing units. Each time the multiplexer switched to a new chamber sub-sample the concentration of CO₂ in the sample slowly changed (over ~2 minutes) after which a steady concentration was recorded. It is this steady state concentration that represents the CO₂ in the output from the chamber. The multiplexer switched to a different chamber every 20 minutes. When the cycle of 3 chambers was complete, outside air was sampled to provide a baseline CO₂ level (required for respiration rate calculation). Respiration rate was calculated using equation 3.1.

Equation 3.1

\[
\text{Respiration rate (mg CO}_2\text{ hr}^{-1}\text{ kg VS}^{-1}) = \frac{((M - A) \times (F \times 1.2) \times (m + f)) \times D}{VS}
\]

Where \( A \) is ambient CO₂ (%), \( M \) is measured chamber CO₂ (%) (averaged over 10 minutes of stable data), \( F \) is flow rate through the chamber (ml minute⁻¹), \( m \) is the molecular weight of CO₂ (g mol⁻¹) \( f \) is a concentration to mass conversion function (l mol⁻¹) ('V2' as calculated in the Methods Chapter Equation 2.4), \( D \) is the proportion of dry matter in the sample (% dry matter +100), and \( VS \) is the proportion of volatile solids in the sample (% volatile solids +100).
Figure 3.7 Respirometer system developed to measure microbial activity in compost samples. Data, air flow and sample flow path are indicated.

3.3 Results

Waste stabilisation

Figure 3.8 shows the effect of each of the three composting processes on the rate of waste stabilisation during the full 86 day composting duration. Respiration rates for waste from the three treatments declined steeply during the first 7 days, and thereafter were slowly reduced. All three methods were equally effective in stabilising the waste by week 6, with no statistically significant difference between respiration rates being observed at any time.
Figure 3.8 Effect of process type on the rate of waste stabilisation by measurement of respiration rate for the in-vessel composting (IVC), covered static forced aeration composting, and windrow composting (WC) systems

3.3.1 Windrow and covered forced aeration composting emissions

Table 3.2 shows CH$_4$ and N$_2$O fluxes, and composting material characteristics of WC and CSFAC systems at day 15 of composting. CH$_4$ fluxes from WC ranged from 1.1 mgCH$_4$ m$^{-2}$ hr$^{-1}$ to 66.2 mgCH$_4$ m$^{-2}$ hr$^{-1}$. CH$_4$ fluxes from the CSFAC system ranged from 10.6 mgCH$_4$ m$^{-2}$ hr$^{-1}$ to 22.9 mgCH$_4$ m$^{-2}$ hr$^{-1}$. A much larger variability of readings was observed with WC (n = 6).
Table 3.2 CH₄ and N₂O flux and composting material characteristics of windrow, covered forced aeration composting and in-vessel systems at day 15 of composting. Range of results shown in brackets

<table>
<thead>
<tr>
<th>System</th>
<th>Mean CH₄ flux mg m⁻² hr⁻¹ ±SD</th>
<th>Mean N₂O flux mg m⁻³ hr⁻¹ ±SD</th>
<th>Moisture content % H₂O ±SD</th>
<th>Volatile Solids %VS</th>
<th>Respiration rate mg CO₂ hr⁻¹ kgVS⁻¹</th>
<th>Kjeldahl N% ±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windrow composting</td>
<td>20.1 (1.1 - 62.2)</td>
<td>9.3 (6.9 - 9.8)</td>
<td>35.2 (29.2 - 38.1)</td>
<td>47.7 (45.3 - 49.4)</td>
<td>446 (429 - 473)</td>
<td>1.4 (1.3 - 1.5)</td>
</tr>
<tr>
<td>Covered forced aeration pile</td>
<td>15.6 (10.6 - 22.9)</td>
<td>1.8 (0.2 - 3.8)</td>
<td>45.4 (41.7 - 47.8)</td>
<td>48.1 (45.0 - 52.2)</td>
<td>456 (329 - 548)</td>
<td>1.4 (1.2 - 1.6)</td>
</tr>
<tr>
<td>In-vessel composting system</td>
<td>-</td>
<td>-</td>
<td>53.2 (49.3 - 58.2)</td>
<td>48.2 (46.3 - 50.0)</td>
<td>368 (260 - 453)</td>
<td>1.12 (0.8 - 1.3)</td>
</tr>
</tbody>
</table>

3.3.2 In-vessel composting analysis results

Table 3.3 shows passive build up of CH₄, N₂O and CO₂ in the headspace of the in-vessel composting system at the start of composting (day 0) and after 7 days composting. The headspace volume of IV system 1 at day 0 of composting was 3.5 m³. The total amount of N₂O passively released into the headspace of the system at the start of composting after 30 minutes was approximately 0.24 g. The headspace volume of the IVC system after 7 days composting had increased to 7.6 m³ due to compression and slumping of the composting mass. The amount of CH₄ passively released into the headspace of the IVC system was 2.6 g. The weight of CH₄ and N₂O passively released into the headspace of the in-vessel system was calculated using equation 2.5 in the Methods Chapter. Selected characteristics for the material composted in the IVC system at the time of gas sampling are shown in Table 3.2, where CH₄ and N₂O concentrations within the composting material were 240.7 and 8.9 ppm respectively (n = 2), and CH₄ and N₂O concentrations within the IVC headspace were 38.9 and 0.9 ppm respectively (n = 2).
Table 3.3 Mean CH$_4$, N$_2$O and CO$_2$ concentration passively released into the headspace of in-vessel composting system 1 at the start of composting (day 0) and after 7 days composting (0–30 minutes). Individual repetitions are shown in table A.I.1

<table>
<thead>
<tr>
<th>Sample time (minutes)</th>
<th>Day 0 N$_2$O (ppm)</th>
<th>Day 0 CH$_4$ (ppm)</th>
<th>Day 0 CO$_2$ (%)</th>
<th>Day 7 N$_2$O (ppm)</th>
<th>Day 7 CH$_4$ (ppm)</th>
<th>Day 7 CO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.3</td>
<td>2.1</td>
<td>0.03</td>
<td>0.2</td>
<td>5</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>2.3</td>
<td>0.5</td>
<td>0.3</td>
<td>49</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>10.7</td>
<td>2.4</td>
<td>0.6</td>
<td>0.5</td>
<td>116</td>
<td>0.3</td>
</tr>
<tr>
<td>15</td>
<td>16.6</td>
<td>2.5</td>
<td>0.8</td>
<td>0.6</td>
<td>204</td>
<td>0.4</td>
</tr>
<tr>
<td>20</td>
<td>22.8</td>
<td>2.9</td>
<td>1.0</td>
<td>0.7</td>
<td>354</td>
<td>0.5</td>
</tr>
<tr>
<td>25</td>
<td>30.5</td>
<td>3.0</td>
<td>1.2</td>
<td>0.8</td>
<td>393</td>
<td>0.8</td>
</tr>
<tr>
<td>30</td>
<td>35.7</td>
<td>3.3</td>
<td>1.3</td>
<td>0.9</td>
<td>517</td>
<td>0.8</td>
</tr>
</tbody>
</table>

3.4 Discussion

From the respiration studies that were undertaken on the partially composted and stabilised wastes from each treatment, it would appear that all three composting methods were equally effective in stabilising the source segregated household waste. Respiration rates for all materials after 7, 42 and 86 days were similar, indicating that the mechanically turned windrow method was equally effective at stabilising the organic matter compared with the more advanced actively aerated methods.

From studies by other authors comparing the effects of composting processes on stabilisation rates, it is typically the case that differences in short term levels of stability can be negated after extended composting times. That is to say, research suggests that
effective composting processes can achieve stabilisation of waste much more quickly than less effective processes but during the extended duration of composting that is required to produce marketable compost, the levels of waste stability produced by different processes tend to equalise.

In this study respiration rates were assessed every week. However, the rapid decline in respiration rate in one week (Figure 3.8) suggests that it is necessary to sample and test much more frequently during the first two weeks of active composting to develop more useful stability profiles and to clearly delineate between the effectiveness of composting processes with very different operational characteristics. This is especially important during the active initial stages of composting when each process may be expected to have elevated environmental impacts such as greenhouse gas and other emissions.

3.4.1 Windrow and forced aeration composting

Emission data from the study of windrow and forced aeration composting has shown release of CH$_4$ and N$_2$O from all three composting methods. Emission of CH$_4$ and N$_2$O has been attributed to the development of anaerobic zones within the composting material. He et al. (2000) described anoxic microsite formation as being the main driver for greenhouse gas generation. If significant anaerobic zones are allowed to develop within the composting pile (and other electron acceptors such as NO$_3^-$ are not present), net methanogenesis may occur, resulting in CH$_4$ emission (Barber & Ferry 2001). The microbial production of N$_2$O is primarily determined by the availability of NO$_3^-$ and O$_2$. The two pathways for production of N$_2$O during composting are nitrification (an aerobic process) and denitrification (an anaerobic process) at low O$_2$ conditions (Czepiel et al. 1996).

The mechanically turned windrow treatment had higher CH$_4$ and N$_2$O fluxes than the CSFAC pile (Table 3.2), although this difference was only significant for the N$_2$O ($p = 0.03$
compared to p = 0.3 for the CH₄ (t-test for dependent samples, Statistica)). From the CH₄ and N₂O flux data it may be concluded that the windrow harboured more developed anaerobic or semi-aerobic zones than the CSFAC pile. There are a number of ways composting operating parameters can influence greenhouse gas emission. The nature of the material being composted has been shown to have an influence on anaerobic zone development. Hellebrand & Kalk (2001) describe the effect of having a heterogeneous mix of material in windrow composting encouraging compression and anoxic zone development. Particle size also has a direct influence on the permeability of the composting material by inhibiting air diffusion rates (Hao et al. 2001). The composting material for the WC and CSFAC processes was however the same, with therefore no differences in particle size and heterogeneity, and no differential influence on CH₄ and N₂O emission. Sommer & Dahl (1999) identified the influence of temperature on CH₄ and N₂O emission, they found an inhibitory effect of higher temperatures on N₂O emission during composting. N₂O released during the thermophilic stage of composting probably originates from the cool surface layers of the pile. Microbial CH₄ production and oxidation can take place within thermophilic zones during composting, and is undertaken by a group of micro-organisms similar to those inhabiting hot springs (Jackel et al. 2004). Flux data for the windrows and forced aeration system were gathered at the same thermophilic period of composting, therefore the effect of differing temperature can be ruled out as a cause of the variation in CH₄ and N₂O flux. Another influence on the potential of a composting process to emit CH₄ and N₂O is the availability of C in the material (Majumdar et al. 2005). A measure of the available C, and therefore biodegradability, in an organic material can be made by using respirometry. For this study the mean respiration rates of the WC and CSFAC piles were 446 mgCO₂ hr⁻¹ kgVS⁻¹ and 456 mgCO₂ hr⁻¹ kgVS⁻¹ respectively (at the time of flux sampling) were not significantly different. A difference in the biodegradability of the material subjected to WC and CSFAC cannot therefore be regarded as causing the difference in emission of CH₄ and N₂O. One of the factors most affecting the development of anaerobic zones with a pile is pile size. Fukmoto et al. (2003) found that an increase in pile size led to material compaction and anoxic zone formation,
however the size of the WC and CSFAC piles was the same and would have had equal influence on anaerobic zone development.

The composting material for the WC and CSFAC was the same, as was the pile size, respiration rates, and time of flux sampling of the two processes. The WC and CSFAC pile differed in the way the composting material was aerated, it is therefore this operating parameter that was considered as being the major influence on differing CH$_4$ and N$_2$O fluxes from the two systems. The windrow relied on the chimney effect for fresh air input whereas the CSFAC pile had active continuous aeration. The continuous aeration of the CSFAC pile appeared to provide less opportunity for anaerobic zone development than the WC pile, resulting in lower CH$_4$ and N$_2$O production and emission.

It is clear from the results of this initial study of windrow and CSFAC composting processes that CH$_4$ and N$_2$O can be potentially problematic by-products of the composting process.

3.4.2 In-vessel composting

Measurements taken at the start (day 0) of in-vessel composting showed a passive build up of 0.24 g N$_2$O after 30 minutes. With N$_2$O being formed most favourably under low O$_2$ conditions (Czepiel et al. 1996), this indicates that even at the start of the IV composting process there is insufficient aeration within some areas of the composting mass. The sampling procedure was repeated after 7 days in-vessel treatment and a build up of 2.6 g CH$_4$ after 30 minutes was detected (amounts of CH$_4$ and N$_2$O were calculated using equation 2.5). CH$_4$ producing bacteria only operate under anaerobic conditions, thus potentially highlighting the poor aeration efficiency of this in-vessel system.

It appears that the IVC process studied during this trial promoted the formation of methanogenic zones within the composting material by providing insufficient aeration. The
passive build up of CO\textsubscript{2} initially and after 7 days in-vessel composting in system 1 indicates aerobic respiration was occurring alongside anaerobic methanogenesis. The reduction of CO\textsubscript{2} production after 7 days could be as a result of the inhibition of aerobic composting due to anaerobic zone development, or due to a reduction in labile substrate as a result of enhanced thermophilic composting over the 7 days. Gas sampling of the interior of the waste being processed in the IVC system showed significant concentrations of CH\textsubscript{4} and N\textsubscript{2}O, a reflection of anoxic zone development.

The total N content of the material subjected to in-vessel composting was around 20\% lower than that of the WC and CSFAC piles. This enhanced loss of N is likely to be due to volatilisation of NH\textsubscript{3} combined with production and emission of N\textsubscript{2}O in a depleted oxygen environment. The material processed in the IVC system also differed from the WC and CSFAC material in that it displayed less microbial activity when respirometrically tested. This could have been the result of the more enhanced thermophilic operation of the IVC system degrading the organic C compounds at a higher rate, or could have been due to the loss of N-inhibiting microbial activity. Further studies need to be undertaken on the effect of material biodegradability on respiration rates, and CH\textsubscript{4} and N\textsubscript{2}O emission.

Due to the differences in the technologies associated with each of the three composting methods it was not possible in this study to calculate and compare the amount of CH\textsubscript{4} and N\textsubscript{2}O released to air from these systems. The IVC system studied had an aeration method that circulated air in a closed system. However, water vapour was observed to be released from the lid seal of the container at the time of sampling suggesting that some of the CH\textsubscript{4} and N\textsubscript{2}O produced had the potential to be emitted. Greenhouse gas emissions from in-vessel composting systems have not been widely studied and very few studies have been published. There may be some commercial sensitivity surrounding this issue but it may be concluded from data reported here that these systems can display the same potential to form anaerobic zones and to produce CH\textsubscript{4} and N\textsubscript{2}O as traditional composting methods. The release of CH\textsubscript{4} and N\textsubscript{2}O to air from IVC systems is currently unknown and
needs urgent further investigation as use of IV composting in the UK rose 6% (to 0.24 Mt) between 2002 and 2004, accounting for 20% of the overall rise in composting (Slater et al. 2005).

3.5 Summary and conclusions

A series of parallel composting trials using windrow, covered forced aeration and in-vessel composting methods was undertaken to assess the effect of each method on the stabilisation rate of source segregated household waste and on its capacity to emit CH$_4$ and N$_2$O. The respirometry system and waste sampling regime designed to measure changes in stability (biodegradability) showed each process was equally effective at stabilising SSHW.

The methods, equipment and protocols used to measure CH$_4$ and N$_2$O emissions from the 3 systems showed WC and CSFAC systems had broadly similar emissions at comparable stages of composting. Evidence of CH$_4$ and N$_2$O production was observed in the IVC system, although quantifying emissions to air were not possible due to the closed air-recirculation operation of the process.
4 Emissions to air from in-vessel composting: effect of waste characteristics

4.1 Introduction

Chapter 3 addressed the effect that different types of composting process could have on the emission of greenhouse gases (GHG) from one particularly important waste type; source segregated household waste. Source segregated household waste is an important waste in the sense that increasing emphasis is being placed on its collection and composting as a means of meeting European Community landfill diversion targets. Given the predicted large increase in the amount of this waste that must be biologically treated to meet the targets (Slater and Frederickson, 2001), it is vitally important to better understand the environmental impacts associated with composting this material. As discussed in Chapter 1, it is likely that the future composition of source segregated household waste will contain increasing amounts of highly putrescible kitchen waste which will necessitate the increased utilisation of sophisticated in-vessel composting systems to process the material. Hence, this chapter is devoted to monitoring and evaluating CH\textsubscript{4} and N\textsubscript{2}O generation from a well established type of in-vessel composting system and source segregated household waste will be one of two waste types investigated.

Importantly, the chapter covers not only the composting of source segregated household waste but also includes composting of "residual waste" or "rest waste" which is the household waste remaining after source segregation and kerbside collection of the recyclable fraction of Municipal Solid Waste. Despite removal of a proportion of the biodegradable waste by separate collection, residual waste is known to contain a high proportion of biodegradable material, such as botanical and kitchen organic wastes as well as paper, card and some textiles. Hence, there is now much debate about the need to reduce its level of biodegradability prior to landfill in order to contribute to landfill diversion targets. Consequently, as noted in Chapter 1, Mechanical and Biological
Treatment (MBT) of residual waste is now being seriously considered as a viable waste management option in the UK for the pre-treatment of residual waste prior to landfill. Reducing the biodegradability of this waste stream through biological processing, as part of an MBT facility, may be achieved either aerobically by composting or anaerobically by anaerobic digestion. Therefore in addition to addressing the composting of source segregated household waste, this chapter will also consider the biodegradation of and gaseous emissions from residual waste during biostabilisation in an in-vessel composting system.

The study outlined in this chapter contained a number of important features. The main aim of this study was to explore the effect of waste characteristics on the nature and the concentration of emissions to air, with particular emphasis on emission of CH₄ and N₂O. It also utilised two waste types that have not been well researched in the UK. The waste types used for the study, source segregated household waste and residual, were selected to represent probable future models for sustainable biological treatment of biodegradable waste in the UK. Perhaps the most topical feature of the study was the preliminary investigation into the composting of household residual waste as part of a Mechanical and Biological Treatment (MBT) system and an assessment of its potential to emit a wide range of gaseous and particulate compounds associated with health effects and environmental pollution. It is the author's belief that this was one of the first studies of this type to be undertaken in the UK.

In terms of detecting and measuring greenhouse gas emissions from source segregated household waste it was noted from Chapter 3 that composting systems that employed either static or turned windrows were particularly amenable to the use of the static flux chamber technique for CH₄ and N₂O emissions. However, accurately monitoring GHG emissions from in-vessel composting plants required more sophisticated techniques to fully appreciate the mechanisms underlying potential emissions. In the study presented in Chapter 3, these sampling techniques and the use of respirometry to characterise waste
biodegradability during composting were further developed and applied to a well established type of in-vessel composting plant.

The author gratefully acknowledges the help, support and encouragement given to this project by Donarbon Ltd and for providing the necessary composting facilities and operational support.

In-vessel composting (IVC) is set to become a very widely used method for processing highly biodegradable waste into marketable compost or as part of a pre-treatment system prior to landfill disposal. Features such as an accelerated composting rate, a smaller footprint, and compliance with Animal by-product regulations (DEFRA 2003), have led to increased interest in the use of in-vessel composting systems compared with open air windrow systems (Brown 2001). IVC systems of the type studied in this chapter offer the advantage of internal recirculation of air, thereby re-using spent air and not emitting an exhaust. Bari & Koenig (2001) found that IVC systems of this type appeared to achieve a more uniform temperature distribution and therefore accelerated degradation of organic matter. Stelmachowski et al. (2003) describe this type of enclosed composting as having high temperatures and high rates of oxygen uptake and biodegradation. Along with these advantages, enclosed composting systems are considered to be more reliable and controllable (Stockinger & Doedens 2003). Fundamental features of the composting process are the consumption of \( O_2 \) and generation of heat (Haug 1993).

Bari & Koenig (2001) identified a variety of different IVC systems ranging from small composting bins or containers to large-scale rotating drums and bioreactors. Advantages claimed for the IVC processes include accelerating the speed of composting (e.g. twofold increase in waste stabilisation rates compared with windrow systems), odour control, and a smaller footprint required when compared to windrow composting (Stelmachowski et al. 2003).
Because of the legislative impact of the EC Landfill Directive (EC 1999) and recent Animal by-product regulations (DEFRA 2003), the need to process waste in enclosed systems has increased. Household wastes, especially residual waste may potentially contain kitchen wastes, meat, and human or plant pathogens. DeVleeschauwer et al. (1981) found that household refuse also has a phytotoxic effect attributed to large amounts of acetic (and other organic) acids that required 4 months windrow composting to reduce to safe levels for agriculture.

The aerobic treatment of household wastes prior to landfill has been in use for some time in Germany where it is seen as a viable alternative to incineration (Slater & Frederickson 2001). In continental Europe there has been a steady increase in the use of IVC as a way of mechanically and biologically treating (MBT) waste prior to landfill. In Germany and Austria there are around 50 MBT plants, all incorporating enclosed household waste IVC systems and processing around 2.2 million tonnes of waste per year (Stockinger & Doedens 2003). At present in the UK only 6 sites process residual waste in this way, a total of 71,000 tonnes per year. This figure is expected to rise considerably to enable compliance with the landfill directive (Slater et al. 2005). Stockinger & Doedens (2003) give details of the emission standards that are applied to this type of MBT processing in Germany and Austria (including emission limits for N₂O, NH₃ and total organic carbon). No such standards exist for residual waste and SSHW materials using the IVC system under investigation in this study, or for any enclosed composting systems in the UK.

This chapter details the study of the treatment of two waste types using the same in-vessel composting (IVC) system. The two wastes under investigation were source segregated household waste (SSHW) and residual household waste (RW). To assess the effect that in-vessel composting of different wastes had on CH₄ and N₂O production and emission each waste was characterised during composting using respirometry. The respiration rate of a sample of waste is the consumption of O₂ by the microorganisms within the sample, and is regarded as essential for the characterisation of initial waste and
the measurement of biodegradation during the composting process (Scaglia et al. 2000). Using this method the rates of biodegradation of SSHW and RW were measured throughout IVC providing data that reflected the aerobic microbial consumption of labile substrates within the wastes.

The degree to which the waste has degraded is commonly referred to as the stability of the waste and Adani et al. (2001) refer to respirometry as 'biological stability determination'. Lasaridi and Stentiford (1998) used respirometry to determine the extent to which readily degradable organic substrates within waste had decomposed. The amount of readily available organic matter within the composting mass provides the raw materials for microbial CH₄ and N₂O production. This was observed by Hao et al. (2001) in their study of greenhouse gas emissions from cattle manure composting, who found that the decrease in surface emissions of CH₄ and N₂O occurred in conjunction with a reduction in microbial activity within the composting mass. This finding was reflected by Jokela et al. (2002) who studied municipal solid waste emission potential and reported a reduction of greenhouse gas emission potential being linked with increased compost stability. In a similar study Barrington et al. (2002) found losses of C and N from composting correlated to C availability and the extent of composting, although neither the CH₄ content of C or the N₂O content of N were stated.

There is currently little information on the production or emission of CH₄ and N₂O from IVC systems. The main purpose of this study was to assess how the composting of different waste types affect CH₄ and N₂O production within this type of system, and to explore potential methods of estimating CH₄ and N₂O emission to air. The respirometric analysis of the waste throughout the composting process was used as a method of assessing the amount of readily available substrate within the composting material, therefore providing an indicator of the CH₄ and N₂O emission potential of the waste.
Project Aim

To determine the effect of waste type on the performance of an in-vessel composting system and on gaseous emissions with particular regard to emission of CH₄ and N₂O

Project Objectives

1. To further develop an appropriate respirometry system for accurately determining waste biodegradability.
2. To further develop appropriate methods, equipment and protocols for accurately measuring CH₄ and N₂O emissions from in-vessel composting systems.
3. To design a full-scale experiment that would evaluate the effect of waste type on composting performance and gaseous emissions from in-vessel composting (with particular regard to CH₄ and N₂O).
4. To include in the experiment the operation of an appropriate biological processing method relevant to MBT systems.
5. To monitor the operation of the biological processing plant for emission of NH₃ and total organic carbon in addition to CH₄ and N₂O, to enable a comparison to be made with emission standards in other countries.

4.2 Materials and methods

Composting facility

The in-vessel composting (IVC) system studied in this chapter was a commercial system based on agricultural clamps and a retractable roof fitted with a forced air re-circulation facility and controlled by oxygen and temperature probes. The plant was manufactured by Copperfield Engineering Ltd. and operated by Donarbon Ltd. Cambridge, UK. Details of the system can be found at http://www.wasteology.com/system.php. Figure 4.1 shows the
dimensions, aeration flow path and sampling locations of the IVC system. Figure 4.2 shows the partially filled IVC system with the clamp roof in place. The roof of the clamp was constructed of several parallel struts lying across the top of the side walls of the enclosure. Attached to the roof struts was a non-porous plastic cover. The roof opened by use of pulley system retracting in a concertina fashion and ingress of fresh air was possible at the front and rear of the roof. One end of the enclosure was a removable door to allow machinery access for loading/unloading (maximum capacity approximately 100 tonnes). The aeration system drew air from the headspace and from ingress of fresh air at the rear of the composting unit using an electric fan and channelled it into 3 perforated, protected pipes embedded into the floor of the enclosure. The air then provided aeration to the pile by moving vertically up through the composting mass returning back to the headspace for re-circulation.

For the two experiments detailed in this study, it should be noted that no additional moisture was added to the two waste materials during composting. It was considered that the characteristics of the source segregated household waste were suitable for the waste to undergo the 15-day composting process without low moisture levels causing inhibition of decomposition. However, for the residual waste composting experiment, an essential element in the research design was to evaluate the effect of an extended period of composting on waste moisture level, composting performance and environmental impact. Chapter 1 briefly reviewed MBT processes including operating the biological treatment plant in "drying mode" to produce a relatively dry Solid Recovered Fuel (SRF) fraction while achieving some degree of biodegradable solids reduction. One important aim of the residual waste composting trial was to evaluate the extent to which reduced moisture levels during composting was compatible with reduction in the biodegradable content of the waste.
Figure 4.1 Dimensions, operation and sampling locations for the clamp in-vessel composting system

Figure 4.2 The partially filled clamp in-vessel composting system with retractable roof in place
Characteristics of wastes composted

Two waste types were composted during this study: source segregated household waste (SSHW), and residual waste (RW). Both waste types originated from Cambridgeshire and the composition and characteristics of each were determined by the kerbside collection scheme operated by Cambridgeshire County Council. In terms of collecting compostable or biodegradable materials, the kerbside collection scheme aimed primarily to provide householders with a recycling facility for green and non-meat kitchen waste as well as paper and card.

The kerbside scheme was estimated in October 2005 to collect approximately 40,000 tonnes of source segregated household biodegradable waste per year (personal communication Paton & Associates Ltd). This SSHW is currently composted at the Donarbon composting facility and waste of this type was used in the first of the composting trials described in this chapter. Collecting and composting SSHW clearly removes this significant biodegradable fraction from the residual waste stream which is normally landfilled. Table 4.1 shows the effect of the source segregation scheme on the composition of residual waste in 2005 compared with the composition of residual waste in 2003, before the introduction of the kerbside collection scheme.

It can be seen in Table 4.1 that the typical content of biodegradable waste (organic and paper and card) in residual waste was 67% in 2003 while the biodegradable content in 2005 had decreased to approximately 56%. While the removal of 40,000 tonnes of biodegradable waste from the residual waste clearly represents a significant diversion from landfill, Table 4.1 indicates that the residual waste in Cambridgeshire still contains a very high proportion of biodegradable waste which could be reduced prior to landfill. Moreover, as discussed in Chapter 1, further reduction in the biodegradable content of the residual waste would contribute to meeting the Cambridgeshire Landfill Allowance target as set by the Environment Agency.
Table 4.1 The composition of residual waste for Cambridgeshire in 2003 and 2005 before and after the introduction of the kerbside collection scheme (source Paton & Associates Ltd)

<table>
<thead>
<tr>
<th>Classification</th>
<th>Mean 2003 composition (%)</th>
<th>Mean 2005 composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic (green and kitchen)</td>
<td>45.1</td>
<td>38.5</td>
</tr>
<tr>
<td>Paper and Cardboard</td>
<td>21.8</td>
<td>17.8</td>
</tr>
<tr>
<td>Glass</td>
<td>6.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Heavy Plastics</td>
<td>8.7</td>
<td>4.1</td>
</tr>
<tr>
<td>Light Plastics</td>
<td>6.3</td>
<td>18.9</td>
</tr>
<tr>
<td>Ferrous</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td>Non-ferrous</td>
<td>1.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Textiles</td>
<td>3.1</td>
<td>5.7</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>5.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The use of Mechanical and Biological Treatment plant (MBT) to sort, select and biologically treat the biodegradable fraction of residual waste is now considered to be a viable waste management option. Evaluation of the treatment and environmental impact of composting the biodegradable fraction of residual waste in order to stabilise the waste and to reduce the total biodegradable content is an important element in this chapter.

The first waste type that was composted during this study was source segregated household waste (SSHW) from the on-going kerbside collection system in Cambridgeshire. The date of sampling and the commencement of composting was 9/8/04 (Day 0). The waste material as received was sampled and fractionated in the laboratory after on-site shredding to determine its physico-chemical characteristics. Samples (n = 10) of the SSHW material to be composted in the IVC clamp (each 5 kg) were taken as the material was being loaded into the clamp from different random locations. Tables 4.2 and 4.3 show the physico-chemical profile of the waste used during the study. A particular feature of the waste was the high content of paper (almost 22% by mass) which resulted
in a composting mix with a high carbon content and low total nitrogen content (C:N ratio 39:1, C and N measurement detailed in the Methods Chapter, section 2.6). The composting duration was 15 days with composting being undertaken in two consecutive clamps (approximately 7 days in each) to comply with the Animal by-products regulations (DEFRA 2003).

Further samples of SSHW (n = 10, each 5 kg) were removed from random locations within the interior of the composting mass (with the aid of the composting site operator) on days 4, 8, and 15 of composting. Samples obtained from each sampling visit were analysed for volatile solids, dry matter and total Kjeldahl nitrogen content as before (described in the Methods Chapter, section 2.6). For all sampling periods, an aggregated sample was formed from the 10 sub-samples and subjected to respirometric analysis as described in 4.2.2.

Table 4.2 Composition (mass) of the initial (fresh) source segregated household waste (SSHW) subjected in-vessel clamp composting. The range of results are shown in brackets

<table>
<thead>
<tr>
<th>Green waste and other organics (%)</th>
<th>Paper (%)</th>
<th>Inert contaminants (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>77.5 (70.8 – 83.2)</td>
<td>21.6 (16.7 – 29.1)</td>
<td>1.1 (0.1 – 4.6)</td>
</tr>
</tbody>
</table>

Table 4.3 Selected chemical characteristics of the initial (fresh) source segregated household waste (SSHW) subjected to in-vessel clamp composting. The range of results are shown in brackets

<table>
<thead>
<tr>
<th>Dry solids (%)</th>
<th>Volatile solids (%)</th>
<th>Total N (%)</th>
<th>Respiration rate mgO₂ hr⁻¹ kgVS⁻¹</th>
<th>C:N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.8 (40.1 – 48.5)</td>
<td>68.9 (64.9 – 70.9)</td>
<td>0.98 (0.87 – 1.09)</td>
<td>1282 (931 – 1916)</td>
<td>39:1 (35.4 – 45.2)</td>
</tr>
</tbody>
</table>
The second waste type processed in the IVC system (commencing November 2004) was residual waste (RW) which was the household waste residue remaining after removal of biodegradable waste as part of the kerbside collection scheme and is derived from manually sorting and sub-sampling 10 x 5 kg samples taken from different random locations while the in-vessel clamp was being loaded. The composition and characteristics of the initial (fresh) residual waste are shown in Table 4.4 and Table 4.5.

The IVC clamp was used to biologically pre-treat RW, a process that was designed to render the waste biologically less active and less polluting for landfill disposal. When the IVC clamp was in operation samples of RW could only be retrieved from the surface of the composting material at the time of sampling (due to issues regarding access safety). The duration of composting was 28 days and composting was undertaken in two clamps to comply with the Animal by-products regulations (DEFRA 2003). Each barrier was used for approximately 7 and 21 days. Barrier one was loaded on 18/11/04 and unloaded on 27/11/04. Figure 4.3 shows barrier 1 being unloaded. Barrier two was loaded on 27/11/04 and unloaded on 20/12/04. Since the bulk density of the RW was found to be low compared to the SSHW, due to the high proportion of plastics and other non-biodegradable material, a maximum of 77800 kg of RW could be loaded into the clamp initially.

The RW material was sampled (10 x 5 kg) on days 4, 8, and 14, and when the IV system was emptied (day 28 of IVC) when access to material within the interior of the composting mass could be achieved. As with the SSHW, sub-samples from each of the 10 repeat samples obtained for each sampling visit were analysed for volatile solids, dry matter and total Kjeldahl nitrogen content as described in section 2.6 of the Methods Chapter. An aggregated sample comprising remaining material from the 10 individual replicates and the 3 sub-samples was removed for respirometric analysis as described in 4.2.2.
Figure 4.3 Clamp in-vessel barrier one with roof retracted being unloaded prior to loading of barrier two

Table 4.4 Composition (mass) of the Residual waste (RW) subjected in-vessel clamp composting. The range of results are shown in brackets

<table>
<thead>
<tr>
<th>Metals (%)</th>
<th>Plastics (%)</th>
<th>Glass (%)</th>
<th>Non-combustibles (%)</th>
<th>Organics (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 (0.2 – 8.1)</td>
<td>26.2 (13.1 – 37.7)</td>
<td>1.8 (0.7 – 4.6)</td>
<td>1.2 (0.0 – 4.5)</td>
<td>67.3 (58.4 – 85.1)</td>
</tr>
</tbody>
</table>
Table 4.5 Selected chemical characteristics of the Residual waste (RW) subjected in-vessel clamp composting. The range of results is shown in brackets

<table>
<thead>
<tr>
<th>Dry matter (%)</th>
<th>Volatile solids (%)</th>
<th>Total N (%)</th>
<th>Respiration rate mgO₂ hr⁻¹ kgVS⁻¹</th>
<th>C:N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.8</td>
<td>68.5</td>
<td>0.8</td>
<td>1726</td>
<td>47.6</td>
</tr>
<tr>
<td>(44.3 - 54.2)</td>
<td>(67.4 - 69.7)</td>
<td>(0.75 - 0.86)</td>
<td>(978 - 2234)</td>
<td>(44.3 - 51.6)</td>
</tr>
</tbody>
</table>

4.2.1 Sampling CH₄ and N₂O from in-vessel composting systems

The 3 methods used to assess greenhouse gas production within the IVC system in Chapter 3 were used in this chapter. These 3 methods were: 1 sampling CH₄ and N₂O direct from the material to measure gas production. 2 sampling from the headspace of the IVC system while the process was running. 3 sampling from the headspace of the system to measure passive build up of CH₄ and N₂O (after the air circulation fans were switched off and the headspace air allowed to equilibrate with ambient air for around 3 hours).

4.2.1.1 CH₄ and N₂O sampling from within the composting material

When sampling gas directly from the SSHW being processed, a 2-metre hollow spike probe was used. Sampling was carried out on day 4 of IVC, at a time when access to the surface of the composting material was allowed. Samples were taken vertically at depths of 10, 20, 40, 60, 80, 100 and 150 cm (2 samples for each depth at separate random locations (n = 14)) to test the correlation of CH₄ and N₂O concentration against the depth within the composting mass. Samples for emission of ammonia (NH₃) (Drager Multiwarn) and total volatile organic compounds (VOCs) (Foxboro TVA1000 fitted with photo ionisation and flame ionisation detectors) were taken from 5 and 15 cm below the surface.
of the composting material (n = 3 for both depths). NH₃ volatilisation was identified as a potential reason for enhanced N loss from the IVC system studied in Chapter 3.

Sampling the gas within the RW composting material was undertaken on day 14 of composting (when access to the system was permitted). Gas samples (n = 6) were taken from the interior of the RW material being processed using tubes installed into the interior of the RW by the composting site operator for gas sampling. These ports allowed samples to be taken from around 150 cm below the surface of the composting mass. These tubes were also used to take readings of NH₃, O₂, and CO₂ (Drager Multiwarn) and total volatile organic compounds (VOCs) (Foxboro TVA1000). Figure 4.4 shows total VOC sampling using the portable VOC analyser.

Figure 4.4 VOC sampling using the portable Foxboro TVA100B total VOC analyser
4.2.1.2 Headspace CH₄ and N₂O sampling

For headspace sampling, a flexible tube (Tygon 1/4"ID) was installed into the IVC clamp and fastened to the roof prior to loading. The tube was attached to the struts making up the concertina roof. Care was taken to ensure the tubes could move freely, did not become blocked or impede any moving parts of the IVC system. Samples (60 ml) were taken after first drawing off the volume of the tube (400 ml) by syringe. Samples were injected into 'Evacutainers' and transported to the laboratory for gas chromatograph (GC) analysis (within 24 hours).

Gas sampling when the IVC system was processing SSHW was carried out (using 60 ml brufix syringes) from both the headspace and the recirculation pipe (after the aeration fan and prior to returning to the composting mass) on days 0 (start of composting), 1, 2, 3, 6, 7, 8, 9, 10, 13, 14 of composting with the assistance of the composting site operator. Samples were shipped to the laboratory for GC analysis within 24 hours. Gases were taken in this manner to detect any drop in CH₄ or N₂O concentration between the headspace of the IVC system and the recirculation pipe work. A drop in concentration would identify a leak in the roof of the system, indicating emission to the outside. The composting site operator also provided data on the temperature and oxygen concentration within the composting mass for these sampling days.

Sampling of the headspace gas of the IVC system while it was processing RW was performed 14 days from the start of composting. Samples were taken for CH₄ and N₂O concentration (n = 4 using 60 ml Brufix syringes) and were transported to the laboratory for GC analysis within 24 hours. Readings of NH₃ and total VOCs were also taken from the headspace of the IVC system at this time (n = 3). Samples of the air 1 m outside the roof cover of the IVC were also taken at this time (n = 3). 60 ml Brufix syringe samples were taken for GC analysis (n = 2), and NH₃ and total VOC readings were taken (n = 3).
was assumed that detection of any gases above the ambient would represent emission to the outside.

Total VOCs (using Tenax sorption tubes), and bio-aerosols (using OEM filter cassettes) were also collected. These samples were taken from both the headspace and the sampling zone located 1 m outside the roof of the IVC system. Tenax sorption tubes were analysed by BRE Environment Ltd (using a Perkin Elmer Mass spectrometer) and bio-aerosols were analysed within the Open University Department of Environmental and Mechanical Engineering. Both the VOC tubes and OEM filters were connected to a Gilian LFS personal sampling pump drawing 100 ml min$^{-1}$ for 10 minutes using 1/8” internal diameter Tygon tubing. The VOC and bio-aerosol data were taken to potentially offer supporting evidence of emission from the IVC system.

4.2.1.3 Passive CH$_4$ and N$_2$O into the headspace

The production and passive release of CH$_4$ and N$_2$O from the IVC material without aeration was measured. To collect samples of passive release of CH$_4$ and N$_2$O, firstly the aeration fan was turned off. The roof of the system was then opened and the headspace gas allowed to equilibrate with outside air for around 3 hours. The roof was then closed and samples of the headspace gas taken using the installed tube and sampling method employed for headspace gas sampling while the system was in operation. Samples were taken in duplicate using 60 ml Brufix syringes from the time the roof was closed, then every 0, 5, 30, and 60 minutes, and subjected to GC analysis within 24 hours. Sampling was performed 4 days after the start of composting for the SSHW. Residual waste IVC could not be studied in this way because the composting site operator required the aeration fan to be operational at all times.
4.2.2 Respiration rate determination

The respirometer apparatus was adapted from that detailed in Chapter 3. New additions to this system were three 40 L trapezoidal (PVC 45 cm long, 25 cm wide, 35 cm deep) chambers designed for the analysis of unconditioned samples. The design of the chambers is shown in Figure 4.5. Unconditioned samples were not amended by shredding or adding nutrients prior to respiration rate determination. Temperature control within the chambers was achieved by situating them in a large (200 L) water bath that was equipped with a heater circulator unit (Grant GR08). Temperature within the samples when being analysed were logged using a PICO TC08 datalogger fitted with type K thermocouples (temperature sensors were situated in the centre of the composting material ensuring the effectiveness of the water bath heating system). As with the system described in Chapter 3, temperature was maintained at 35°C and moisture content was amended to 50% thereby providing conditions favourable for most of the microbe population (Clark et al. 1978).
In this system, consumption of O$_2$, (a measure of microbial activity and potentially the degree of biodegradability) and aeration flow rate were continually logged. The respirometer design was adapted from the basic system recommended by the manufacturer (Sable Systems, Connecticut, USA). The system employed the ‘flow through’ dynamic method that produced respirometric values that reflected the aerobic process (Adani et al. 2001).

Figure 4.6 shows the layout of the respirometer system used to analyse the waste in this chapter. The system operated on the same principal as that used in Chapter 3. The
addition of an oxygen analyser was made to this system to allow data to be expressed as oxygen uptake as is used in the American standard test methods dynamic respiration standard D5975-96 (ASTM 1996), and to allow comparison with other respirometric methods such as Lasaridi & Stentiford’s (1998) specific oxygen uptake rate test. For this study the highest mean oxygen uptake rate over 24 hours is used to compare the two waste samples. This method of respirometric analysis was as described in Adani et al. (2001) and is termed the dynamic respiration index. The formula for calculating respiration rate is shown in Equation 4.1.

Equation 4.1

\[
\text{Respiration rate (mg O}_2\text{ hr}^{-1}\text{ kg VS}^{-1}) = \frac{((A - M) \times (F \times 1.2) \times (m + f)) + D}{VS}
\]

Where \(A\) is ambient \(O_2\) (%), \(M\) is measured chamber \(O_2\) (%) (averaged over 10 minutes of stable data), \(F\) is flow rate through the chamber (ml minute\(^{-1}\)), \(m\) is the molecular weight of \(CO_2\) (g mol\(^{-1}\)) \(f\) is a concentration to mass conversion function (l mol\(^{-1}\)) ('V2' as calculated in the Methods Chapter Equation 2.4), \(D\) is the proportion of dry matter in the sample (% dry matter \(\div\)100), and \(VS\) is the proportion of volatile solids in the sample (% volatile solids \(\div\)100).
Figure 4.6 Diagram of the respirometer system developed to measure microbial activity in compost samples. Data, air flow and sample flow path are indicated.

4.3 Results

Temperature profiles during composting

Table 4.6 and Table 4.7 show the temperature profiles for the SSHW composting trial and for the residual waste (RW) trial respectively. While the pile temperature for the SSHW composting trial achieved a mean of 65°C over the 15 day period, the pile temperatures for the residual waste trial were relatively low, especially during composting in the second barrier.
Table 4.6 Temperature profiles and temperature means at various locations in the clamp for the source segregated household waste (SSHW) composting trial

<table>
<thead>
<tr>
<th>Time</th>
<th>Temp Left (°C)</th>
<th>Temp Middle (°C)</th>
<th>Temp Right (°C)</th>
<th>Temp Mean (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Barrier 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 0</td>
<td>71</td>
<td>73</td>
<td>70</td>
<td>71.3</td>
</tr>
<tr>
<td>Day 1</td>
<td>74</td>
<td>75</td>
<td>77</td>
<td>75.3</td>
</tr>
<tr>
<td>Day 2</td>
<td>73</td>
<td>76</td>
<td>73</td>
<td>74.0</td>
</tr>
<tr>
<td>Day 3</td>
<td>69</td>
<td>71</td>
<td>67</td>
<td>69.0</td>
</tr>
<tr>
<td>Day 7</td>
<td>60</td>
<td>nd</td>
<td>64</td>
<td>62.0</td>
</tr>
<tr>
<td>Day 8</td>
<td>63</td>
<td>nd</td>
<td>56</td>
<td>59.5</td>
</tr>
<tr>
<td><strong>Barrier 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Day 9</td>
<td>78</td>
<td>84</td>
<td>82</td>
<td>81.3</td>
</tr>
<tr>
<td>Day 10</td>
<td>nd</td>
<td>82</td>
<td>79</td>
<td>80.5</td>
</tr>
<tr>
<td>Day 11</td>
<td>55</td>
<td>51</td>
<td>44</td>
<td>50.0</td>
</tr>
<tr>
<td>Day 14</td>
<td>52</td>
<td>49</td>
<td>43</td>
<td>48.0</td>
</tr>
<tr>
<td>Day 15</td>
<td>50</td>
<td>47</td>
<td>42</td>
<td>46.3</td>
</tr>
<tr>
<td><strong>Overall mean temperature</strong></td>
<td></td>
<td></td>
<td></td>
<td>65.2</td>
</tr>
</tbody>
</table>
Table 4.7 Temperature profile for the residual waste (RW) composting trial

<table>
<thead>
<tr>
<th>Time</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Barrier One</strong></td>
<td></td>
</tr>
<tr>
<td>Day 0</td>
<td>37.5</td>
</tr>
<tr>
<td>Day 1</td>
<td>58.5</td>
</tr>
<tr>
<td>Day 2</td>
<td>62.5</td>
</tr>
<tr>
<td>Day 3</td>
<td>62.8</td>
</tr>
<tr>
<td>Day 4</td>
<td>60.4</td>
</tr>
<tr>
<td>Day 5</td>
<td>57.5</td>
</tr>
<tr>
<td>Day 6</td>
<td>52.8</td>
</tr>
<tr>
<td><strong>Barrier one mean temp</strong></td>
<td>56.0</td>
</tr>
<tr>
<td><strong>Barrier Two</strong></td>
<td></td>
</tr>
<tr>
<td>Day 9</td>
<td>42.5</td>
</tr>
<tr>
<td>Day 13</td>
<td>49.3</td>
</tr>
<tr>
<td>Day 14</td>
<td>48.8</td>
</tr>
<tr>
<td>Day 15</td>
<td>45.3</td>
</tr>
<tr>
<td>Day 16</td>
<td>38.3</td>
</tr>
<tr>
<td>Day 18</td>
<td>39.3</td>
</tr>
<tr>
<td>Day 19</td>
<td>39.8</td>
</tr>
<tr>
<td>Day 20</td>
<td>37.5</td>
</tr>
<tr>
<td>Day 23</td>
<td>34.3</td>
</tr>
<tr>
<td>Day 24</td>
<td>28.3</td>
</tr>
<tr>
<td>Day 25</td>
<td>27.8</td>
</tr>
<tr>
<td>Day 26</td>
<td>29.5</td>
</tr>
<tr>
<td><strong>Barrier two mean temp</strong></td>
<td>38.4</td>
</tr>
<tr>
<td><strong>Overall mean temp</strong></td>
<td>47.2</td>
</tr>
</tbody>
</table>

Table 4.8 shows passive build up of CH₄ and N₂O in the headspace IVC on day 4 of composting with the aeration system turned off as described in section 4.2.2.3. This sampling was performed on day 4 of composting at which time the headspace volume was approximately 100 m³. Passive release of CH₄ and N₂O into the headspace over 60 minutes is estimated at 40 g and 2 g, respectively (calculated using equation 2.5 in the Methods Chapter). CH₄ and N₂O concentrations in the headspace and recirculation pipe of the IVC system while the system was processing SSHW (as described in section 4.2.2.2) are shown in Table 4.9. Also shown in Table 4.9 is the O₂ concentration within the composting material (data supplied by the composting site operator).
Table 4.8 Passive build up of CH$_4$ and N$_2$O in the headspace of the in-vessel composting system (with aeration system off) at day 4 of source segregated household waste composting. Mean measurements are shown with individual results in brackets.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>CH$_4$ (ppm)</th>
<th>N$_2$O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2 (1.8, 2.4)</td>
<td>0.4 (0.3, 0.4)</td>
</tr>
<tr>
<td>5</td>
<td>21 (19, 23)</td>
<td>2.1 (2.1, 2.0)</td>
</tr>
<tr>
<td>30</td>
<td>275 (287, 273)</td>
<td>5.7 (6.2, 5.2)</td>
</tr>
<tr>
<td>60</td>
<td>577 (570, 584)</td>
<td>10.0 (8.9, 11.1)</td>
</tr>
</tbody>
</table>

Table 4.9 CH$_4$ and N$_2$O concentration in the headspace and recirculation pipe and oxygen concentration within the composting material for the in-vessel composting system during source segregated household waste treatment.

<table>
<thead>
<tr>
<th>Day of in-vessel composting</th>
<th>Headspace CH$_4$ (ppm)</th>
<th>Pipe CH$_4$ (ppm)</th>
<th>Headspace N$_2$O (ppm)</th>
<th>Pipe N$_2$O (ppm)</th>
<th>Oxygen in composting material (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.2</td>
<td>10.3</td>
<td>7.2</td>
<td>2.6</td>
<td>16.7</td>
</tr>
<tr>
<td>2</td>
<td>33.3</td>
<td>37.7</td>
<td>3.2</td>
<td>2.3</td>
<td>11.6</td>
</tr>
<tr>
<td>3</td>
<td>28.5</td>
<td>3.8</td>
<td>2.6</td>
<td>1.4</td>
<td>15.1</td>
</tr>
<tr>
<td>6</td>
<td>31.7</td>
<td>36.7</td>
<td>3.4</td>
<td>2.6</td>
<td>15.1</td>
</tr>
<tr>
<td>7</td>
<td>79.9</td>
<td>91.6</td>
<td>4.2</td>
<td>3.3</td>
<td>18.5</td>
</tr>
<tr>
<td>8</td>
<td>82.6</td>
<td>74.7</td>
<td>2.2</td>
<td>2.1</td>
<td>17.5</td>
</tr>
<tr>
<td>9</td>
<td>36.6</td>
<td>32.7</td>
<td>4.1</td>
<td>3.7</td>
<td>14.0</td>
</tr>
<tr>
<td>10</td>
<td>64.6</td>
<td>61.9</td>
<td>6.9</td>
<td>3.8</td>
<td>15.3</td>
</tr>
<tr>
<td>11</td>
<td>17.6</td>
<td>36.9</td>
<td>4.5</td>
<td>9.8</td>
<td>19.3</td>
</tr>
<tr>
<td>13</td>
<td>76.7</td>
<td>75.7</td>
<td>3.5</td>
<td>3.9</td>
<td>18.3</td>
</tr>
<tr>
<td>14</td>
<td>101.5</td>
<td>104.8</td>
<td>7.3</td>
<td>6.9</td>
<td>17.7</td>
</tr>
<tr>
<td>Mean</td>
<td>50.4</td>
<td>51.5</td>
<td>4.4</td>
<td>3.8</td>
<td>16.1</td>
</tr>
</tbody>
</table>
Table 4.10 shows CH\(_4\) and N\(_2\)O concentration at various depths within the composting material (SSHW) sampled with the 2 metre spike probe according to the method described in section 4.2.1.1. CH\(_4\) concentration correlated well with sampling depth (R\(^2\) = 0.91) but this was not the case for N\(_2\)O (R\(^2\) = 0.25). Table 4.11 shows concentrations of total VOCs, CO\(_2\), O\(_2\), and NH\(_3\) measured within the source segregated household waste composting material on day 4 of composting at depths 5 and 15 cm. These additional gas samples were taken from the SSWH as described in section 4.2.1.1. Table 4.12 presents results of gas sampling of RW treatment on day 14 of composting. Gases measured were NH\(_3\), CO\(_2\), O\(_2\), CH\(_4\), Total VOCs, and N\(_2\)O from the headspace of the IVC system, 150 cm below the surface of the composting material, 1 m outside the roof of the IVC system, and ambient air.

Table 4.10 CH\(_4\) and N\(_2\)O concentration at various depths within the source segregated household waste sampled vertically from random locations with the 2 metre spike probe on day 4 of composting. Mean measurements are shown with individual results in brackets

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>CH(_4) (ppm)</th>
<th>N(_2)O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>305 (341, 269)</td>
<td>1.9 (1.6, 2.2)</td>
</tr>
<tr>
<td>20</td>
<td>435 (277, 593)</td>
<td>3.7 (4.6, 2.8)</td>
</tr>
<tr>
<td>40</td>
<td>175 (128, 223)</td>
<td>1.3 (0.7, 1.9)</td>
</tr>
<tr>
<td>60</td>
<td>779 (527, 1031)</td>
<td>11.0 (5.7, 16.3)</td>
</tr>
<tr>
<td>80</td>
<td>1860 (2001, 1719)</td>
<td>4.7 (7.1, 2.4)</td>
</tr>
<tr>
<td>100</td>
<td>2063 (793, 3332)</td>
<td>4.4 (4.6, 4.3)</td>
</tr>
<tr>
<td>150</td>
<td>4214 (6911, 1517)</td>
<td>7.9 (11.1, 4.7)</td>
</tr>
</tbody>
</table>
Table 4.11 Concentrations of total volatile organic compounds, carbon dioxide, oxygen, and ammonia measured within the source segregated household waste composting material on day 4 of composting at depths 5 and 15 cm. The range of results is shown in brackets

<table>
<thead>
<tr>
<th>Depth in compost (cm)</th>
<th>Total VOC (ppm)</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
<th>NH₃ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>59 (15.5 – 130)</td>
<td>1.2</td>
<td>19.6</td>
<td>6.0</td>
</tr>
<tr>
<td>15</td>
<td>1442 (774 – 2876)</td>
<td>7.1</td>
<td>13.4</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Table 4.12 Gases measured during residual waste treatment on day 14 of composting. Gases displayed are measurements of ammonia (NH₃), carbon dioxide (CO₂), oxygen (O₂), methane, nitrous oxide, and total volatile organic compounds (Total VOC) concentrations from the headspace of the IVC system, 150 cm below the surface of the composting material, 1 m outside the roof of the IVC system, and ambient air. The range of results is shown in brackets

<table>
<thead>
<tr>
<th>Sample location</th>
<th>NH₃* (ppm)</th>
<th>CO₂* (%)</th>
<th>O₂* (%)</th>
<th>Total VOC^ (ppm)</th>
<th>CH₄ (ppm)</th>
<th>N₂O (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Headspace</td>
<td>10.6</td>
<td>0.7</td>
<td>19.9</td>
<td>27.2</td>
<td>26.1</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>(8.0 – 13.0)</td>
<td>(0.71 – 0.75)</td>
<td>(19.9 – 19.9)</td>
<td>(24.9 – 30.8)</td>
<td>(22.1 – 30.1)</td>
<td>(0.8 – 1.0)</td>
</tr>
<tr>
<td>1 m outside</td>
<td>1.3</td>
<td>0.7</td>
<td>20.6</td>
<td>7.1</td>
<td>6.6</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>(0.0 – 2.0)</td>
<td>(0.71 – 0.75)</td>
<td>(20.6 – 20.6)</td>
<td>(6.5 – 7.8)</td>
<td>(5.1 – 8.0)</td>
<td>(0.6 – 0.8)</td>
</tr>
<tr>
<td>In material</td>
<td>9.7</td>
<td>1.0</td>
<td>19.4</td>
<td>25.1</td>
<td>23.9</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>(6 – 22)</td>
<td>(0.74 – 1.74)</td>
<td>(18.9 – 19.8)</td>
<td>(10.9 – 37.5)</td>
<td>(18.5 – 29.3)</td>
<td>(0.5 – 1.1)</td>
</tr>
<tr>
<td>Ambient air</td>
<td>0.0</td>
<td>0.03</td>
<td>20.7</td>
<td>2.8</td>
<td>2.3</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>(0.0 – 0.0)</td>
<td>(0.03 – 0.03)</td>
<td>(20.7 – 20.7)</td>
<td>(2.7 – 2.9)</td>
<td>(2.1 – 2.5)</td>
<td>(0.5 – 0.6)</td>
</tr>
</tbody>
</table>

*Analysed on Drager multiwarn multigas monitor with an accuracy of ±10%.
^Analysed on a Foxboro TVA 1000B total VOC analyser with an accuracy of ±5%.
Table 4.13 Dynamic respiration index, volatile solids, total Kjeldahl nitrogen and dry solids content of both the source segregated household waste and residual waste throughout the in-vessel composting process. The range of results are shown in table A.1.2

<table>
<thead>
<tr>
<th>Day of SSHW composting</th>
<th>Dynamic respiration index mgO₂ hr⁻¹ kgVS⁻¹</th>
<th>Volatile solids (%)</th>
<th>Total Kjeldahl N (%)</th>
<th>Dry solids (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>1282</td>
<td>68.9</td>
<td>0.9</td>
<td>44.8</td>
</tr>
<tr>
<td>Day 4</td>
<td>1081</td>
<td>68.9</td>
<td>1.1</td>
<td>38.2</td>
</tr>
<tr>
<td>Day 8</td>
<td>978</td>
<td>68.2</td>
<td>1.1</td>
<td>51.8</td>
</tr>
<tr>
<td>Day 14</td>
<td>887</td>
<td>66.2</td>
<td>1.0</td>
<td>54.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Day of RW composting</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>1726</td>
<td>68.6</td>
<td>0.8</td>
<td>48.9</td>
</tr>
<tr>
<td>Day 4</td>
<td>993</td>
<td>77.9</td>
<td>0.8</td>
<td>31.2</td>
</tr>
<tr>
<td>Day 8</td>
<td>935</td>
<td>75.9</td>
<td>0.9</td>
<td>31.1</td>
</tr>
<tr>
<td>Day 14</td>
<td>866</td>
<td>80.9</td>
<td>0.9</td>
<td>29.6</td>
</tr>
<tr>
<td>Day 28</td>
<td>1688</td>
<td>68.8</td>
<td>0.9</td>
<td>82.5</td>
</tr>
</tbody>
</table>

Table 4.13 shows Dynamic respiration index, volatile solids, total Kjeldahl nitrogen and dry solids content of both the source segregated household waste and residual waste throughout the in-vessel composting process. For the residual waste composting trial, the final mass of composted RW material extracted from the clamp was 62160 kg, which represented a loss in mass due to composting of 20.1%. Samples were collected and analysed as described in section 4.2. Table 4.15 gives mass spectrometer analysis of samples collected in Tenax volatile organic compound sampling tubes collected from both the headspace and 1 m outside the roof of the in-vessel composting system on day 14 of composting, sampling was done as is described in section 4.2.1.2. Table 4.14 gives bio-aerosol data showing bacterial and fungal colony forming units (cfu) in samples taken from the headspace and 1 m outside the roof of the in-vessel, sampling was done as is described in section 4.2.1.2.
Table 4.14 Bacterial and fungal colony forming units (cfu) in samples taken from the headspace and 1 metre outside the roof of the in-vessel

<table>
<thead>
<tr>
<th></th>
<th>bacteria cfu/m³</th>
<th>fungi cfu/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-vessel headspace</td>
<td>35417</td>
<td>2917</td>
</tr>
<tr>
<td>1 m outside roof</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.15 Mass spectrometer analysis of samples collected in Tenax volatile organic compound sampling tubes from both the headspace and 1 metre outside the roof of the in-vessel composting system on day 14 of composting

<table>
<thead>
<tr>
<th></th>
<th>1 m outside roof (µg m⁻³)</th>
<th>Headspace (µg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4 aliphatic hydrocarbon</td>
<td>30</td>
<td>373</td>
</tr>
<tr>
<td>C5 aliphatic hydrocarbon</td>
<td>19</td>
<td>165</td>
</tr>
<tr>
<td>n-heptane</td>
<td>17</td>
<td>142</td>
</tr>
<tr>
<td>n-octane</td>
<td>26</td>
<td>39</td>
</tr>
<tr>
<td>Hexamethylocyclotrisiloxane</td>
<td>13</td>
<td>462</td>
</tr>
<tr>
<td>Hexanal</td>
<td>ND</td>
<td>219</td>
</tr>
<tr>
<td>n-nonane</td>
<td>15</td>
<td>55</td>
</tr>
<tr>
<td>Alpha-pinene</td>
<td>25</td>
<td>49</td>
</tr>
<tr>
<td>n-heptanal</td>
<td>ND</td>
<td>111</td>
</tr>
<tr>
<td>Octamethylocyclotetrasiloxane</td>
<td>3</td>
<td>242</td>
</tr>
<tr>
<td>n-decane</td>
<td>17</td>
<td>48</td>
</tr>
<tr>
<td>3-carene</td>
<td>16</td>
<td>31</td>
</tr>
<tr>
<td>Limonene</td>
<td>65</td>
<td>99</td>
</tr>
<tr>
<td>n-octanal</td>
<td>ND</td>
<td>298</td>
</tr>
<tr>
<td>n-undecane</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>2-ethylhexan-1-ol</td>
<td>19</td>
<td>47</td>
</tr>
<tr>
<td>Hexanoic acid</td>
<td>ND</td>
<td>255</td>
</tr>
<tr>
<td>n-nonanal</td>
<td>7</td>
<td>118</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>5</td>
<td>59</td>
</tr>
<tr>
<td>Octanoic acid</td>
<td>ND</td>
<td>249</td>
</tr>
<tr>
<td>n-tetradecane</td>
<td>3</td>
<td>103</td>
</tr>
<tr>
<td>A carboxylic acid</td>
<td>ND</td>
<td>85</td>
</tr>
<tr>
<td>An oxygenate (RT 49.6 min)</td>
<td>ND</td>
<td>287</td>
</tr>
<tr>
<td>An aromatic hydrocarbon (C18H20)</td>
<td>ND</td>
<td>150</td>
</tr>
<tr>
<td>Dibutyl phthalate</td>
<td>ND</td>
<td>131</td>
</tr>
<tr>
<td>Total VOCs</td>
<td>334</td>
<td>4290</td>
</tr>
</tbody>
</table>

(ND = not detected)
4.4 Discussion

Both wastes under study in this chapter, source segregated household waste (SSHW) and residual waste (RW), were subjected to respirometry testing as received and during key stages during composting. The biodegradable material in the fresh residual waste (1726 mg O₂ hr⁻¹ kgVS⁻¹) as received was more biologically active than the SSHW (1282 mg O₂ hr⁻¹ kg VS⁻¹). During the 14 day period over which the activity of the SSHW was assessed, the respiration rate for this material decreased to 887 mg O₂ hr⁻¹ kg VS⁻¹, indicating that the composting process was stabilising the material as might be expected. For the residual waste, the respiration rate also appeared to decrease appreciably for the first 14 days composting. However, the mean temperature recorded for the SSHW composting during the first week in Barrier one was 69°C while for the apparently more biologically active residual waste the Barrier one mean temperature was only 56°C. Moreover, over 14 days composting the mean pile temperatures were found to be SSHW (65°C) and RW (50°C), suggesting that the residual waste was not biodegrading as rapidly as the respiration rates were indicating.

Further analysis of the dry solids contents for both wastes being composted confirmed that the SSHW material was losing some moisture due to the intense composting reaction and this would be expected. However the material sampled from the residual waste composting pile was found to have very high moisture contents which increased during the first 14 days. Due to operational and safety reasons it was only possible to extract waste samples from the outer top layer of the residual waste pile. It was evident from the moisture content data that the composting activity was driving moisture from the bulk of the pile upwards into the upper layer thereby drying most of the waste in the lower pile levels.

The severe drying action taking place in the RW pile was probably due to the high plastics content acting as a bulking agent providing channelling for air to move freely through the waste carrying away moisture and promoting rapid drying. It is likely that the bulk of the
RW pile would have had low moisture contents rather than the high moisture content observed for the waste samples from the upper pile layer. The overall low moisture level for the RW pile would have inhibited biodegradation, accounting for the relatively low temperatures recorded during composting. This assessment was confirmed when the final waste samples were extracted from the bulk of the RW pile after 28 days and subjected to respirometry analysis. The mean dry solids content of the RW was found to be approximately 83% and the Respiration Index for the composted waste (1688 mg O₂ hr⁻¹ Kg VS⁻¹) was only slightly reduced compared with the fresh material (1726 mg O₂ hr⁻¹ Kg VS⁻¹). When the final RW samples (day 28 of composting) were amended to 60% moisture content prior to respirometric analysis this caused a resumption of biological activity (Adani 2001) that had ceased in the dry interior of the RW composting mass.

Richard et al. (2002) demonstrated the effect of moisture on composting, referring to it as the key environmental factor. This view is also put forward by Mario & Carvalho (1999) in the study of moisture control, stating that moisture control in MSW composting governs other control parameters. Clearly, while the waste in the upper layer of the RW pile had been biodegrading, composting in most of the waste had been inhibited due to very low moisture levels. This drying effect was not found for the more dense SSHW and this material appeared to stabilise very successfully during the two week composting period, as demonstrated by the high reaction temperatures and acceptable reduction in waste respiration index.

In addition to temperature differences for the two wastes under investigation there was a detectable difference in O₂ concentrations associated with the two piles. Comparison between SSHW and RW processing using the IVC system can be made for O₂ concentrations within the composting mass. Oxygen concentrations within the composting mass for SSHW (17.7%) was lower than concentrations found for RW processing (19.4%), adding further support to the assertion that the RW was biodegrading at a much slower rate than the SSHW. The difference in temperature and within-material O₂
concentration for the two wastes studied could have been due to lower amounts of microbe-available substrate within the RW compared to the SSHW. Haug (1993) points out that microbiological activity produces heat, and a measure of microbiological activity within compost can be made by respirometric analysis (Lasaridi & Stentiford 1998).

Comparison of CH$_4$ and N$_2$O concentrations within the headspace of the IVC on day 14 for the SSHW and RW processing shows a similar pattern to that of temperature and O$_2$ concentration within the composting material. Concentrations of CH$_4$ and N$_2$O in the headspace of the IVC system were considerably higher for SSHW than for RW (101.5 and 7.3 ppm, and 26.1 and 0.9 ppm respectively on day 14 of composting). The production of CH$_4$ and N$_2$O during composting can be mainly attributed to anaerobic zone development within the composting mass (Beck-Friis et al. 2000). He et al. (2000) suggested anaerobic microsites within composting particles provide a generation pathway to CH$_4$ and N$_2$O production.

The cause of anaerobic zone development was investigated by Kuroda et al (1996) in the study of emissions from swine manure composting, who found that CH$_4$ was easy to generate in large windrows with insufficient aeration. It is likely that more enhanced anaerobic zone development occurred within the SSHW during composting, although as the aeration system used on both waste types was identical this most likely was not the cause of differential CH$_4$ and N$_2$O production.

Another factor controlling production of CH$_4$ and N$_2$O is temperature, a parameter investigated by Sommer & Moller (2000) in the study of greenhouse gas emissions from deep litter, showing enhanced CH$_4$ production during the thermophilic stage of composting, and N$_2$O production in the mesophilic. This pattern was also noted by Beck-Friis et al. (2001) investigating emission dynamics from household organics and more recently Jackel et al. (2004) in the study of thermophilic CH$_4$ production during composting. In contrast, Pier and Kelly (1997) identified the upper mesophilic temperature
range (35 – 40°C) as optimum for CH₄ production, with a 50% decrease in productivity at either 30 or 50°C.

A factor directly controlling the development of anaerobic zones and composting aeration is material compaction which is in turn linked to composting pile size. Fukumoto et al. (2003) demonstrated the effect of composting pile size on CH₄ and N₂O emissions and regarded pile size a major factor in anaerobic development. This finding follows Hellebrand & Kalk (2001) on the study of dung windrow compression and subsequent anoxic zone formation; a solution suggested was composting using a layer-system. A correlation between composting material density and greenhouse gas emission was also made by Sommer & Moller (2000); the highest emission rates in this study showed CH₄ contributing as much global warming potential as CO₂, and N₂O contributing twice as much. However, due to the difficulty in accurately measuring the bulk density of RW and SSHW on a large scale, no rigorous determination of bulk densities were made. Consequently the relationship between higher densities and enhanced anaerobic zone development in the IVC of SSHW cannot be ascertained.

It is evident from the dry mass analysis throughout RW processing that high moisture contents (around 70%) were present prior to the final sample. If this continued down through the profile of the composting material it would have led to significant anaerobic zone formation and CH₄ and N₂O production and emission when gases were sampled on day 14 of composting. Hao et al. (2001) observed this effect of moisture content on CH₄ and N₂O production, suggesting that > 60% moisture severely restricted O₂ supply and led to greenhouse gas formation. The considerably higher dry matter content of the final sample (82.5%) indicates that the drying process had been in progress for some time and is likely to be the cause of lower emissions of CH₄ and N₂O from RW compared to SSHW.

It is clear from O₂ consumption and temperature data that the SSHW IVC composting process was not affected by the problem of drying that was observed in the RW. The
passive emission test showed a considerable build up of CH\textsubscript{4} and N\textsubscript{2}O (577 and 10 ppm after 60 minutes respectively) in the headspace of the IVC and indicated enhanced microbial activity combined with significant anaerobic zone development (Czepiel et al. 1996). Evidence for this anoxic zone formation was also observed from CH\textsubscript{4} and N\textsubscript{2}O measurements taken from the interior of the composting mass showing increased build up of CH\textsubscript{4} and N\textsubscript{2}O with depth. The concentration of CH\textsubscript{4} (4214 ppm at 150 cm depth) closely matches data reported in Jackel et al. (2004), although CH\textsubscript{4} concentrations reported for that study of thermophilic CH\textsubscript{4} production are for material 8 weeks after composting started.

What isn’t clear from the data is the amount of CH\textsubscript{4} and N\textsubscript{2}O released to air from these systems. Measurements taken from the IVC when SSHW was being processed from both the headspace and the recirculation pipes were taken to potentially show the loss of CH\textsubscript{4} and N\textsubscript{2}O from the headspace prior to recirculation. These data proved inconclusive, as they cannot be used to estimate release of CH\textsubscript{4} and N\textsubscript{2}O to air, and in fact demonstrate the effectiveness of the air recirculation system. Measurements of bio-aerosols taken from the IVC while RW was being processed also do not show an emission to air. Bacteria and fungi present within the headspace were not detected in the sampling zone 1 m outside the roof of the IVC system, however it does not mean there were no micro-organisms in this zone, only that they did not survive the sampling process which was typical of an outdoor sample at the time and duration used for sampling (personal communication with Dr T. Gladding, The Open University).

It is worth noting that levels of bio-aerosols present in the headspace of the IVC fall somewhat below Environment Agency thresholds (personal communication with Dr T. Gladding, The Open University), and could, as well, reflect the moisture restricted microbial activity within the RW. More successful as a measure of potential emission to air from the RW IVC process were measurements of NH\textsubscript{3}, CO\textsubscript{2}, total VOC, CH\textsubscript{4}, and N\textsubscript{2}O taken from the zone 1 m outside the roof of the IVC system. All readings showed an
increase over ambient concentrations and indicate some leak from the system. These data cannot realistically be used to quantify emission to air from the IVC system but do highlight the need for further study of systems of this type. The Tenax tube VOC analysis also showed evidence of potential emission from the IVC system, in particular concentrations of limonene in the headspace and zone 1 m outside the roof of the IVC system (99 and 65 mg m\(^{-3}\) respectively). Limonene is known as a compound with a high odour potential (Haug 1993), and may present localised problems. Smet et al. (1999) highlights limonene as a compound requiring biofiltration from the anaerobic/aerobic composting of biowastes. Brown (2001) details an IVC system that produces an output of 28.9 mg m\(^{-3}\) of limonene that is reduced to 9.6 mg m\(^{-3}\) by biofiltration. The size of the concentration of limonene observed in the study of this IVC certainly warrants further investigation.

4.5 Summary and conclusions

This study was aimed at determining the effect of waste type on the performance of an in-vessel composting system and on gaseous emissions with particular regard to emission of CH\(_4\) and N\(_2\)O. A respirometry system was developed and used to determine the biodegradability of the SSHW and RW under investigation. Methods, equipment and protocols were developed to measure CH\(_4\) and N\(_2\)O production and emission from the in-vessel composting system studied, and a full scale trial was set up to assess the emission during in-vessel composting of both SSHW and RW.

Emissions of CH\(_4\), N\(_2\)O, NH\(_3\), and volatile organic compounds were produced from both SSHW and RW, although drying of the RW throughout composting resulted in lower gas production, and stabilization rate than for SSHW. The emission to air from the air-recirculation IVC systems studied was, however, difficult to quantify and further investigation would be required to both enable a comparison of emissions to air to be
made with emission standards in other countries, and potentially identify this process as an effective CH₄ and N₂O mitigation option.
5 N₂O and CH₄ emissions from vermicomposting: effect of processing temperature

5.1 Introduction

In Chapter 1 some of the factors driving the current and future expansion of the composting sector were briefly introduced and the changing technological profile of the sector was explored. One important implication from this was that the sector is likely to embrace much greater diversity in plant design and waste types composted than it has in the recent past. However, although it is often assumed that the new composting technologies are more effective at stabilising waste allied with a reduced environmental impact compared with open-air windrow systems, there is little published data relating to emissions to air from such systems, as highlighted in a recent Government report (DEFRA 2004). Hence, in Chapters 3 and 4 much emphasis was placed on studying the performance and the environmental impact of greenhouse gas emissions associated with some of the new composting technologies that have been introduced into the UK, with particular focus on in-vessel composting technologies.

One of the most innovative composting technologies to be introduced into the UK in recent years has been vermicomposting, which is the use of selected species of earthworms to stabilise organic matter. Although this composting method is typically practised on a domestic scale in the UK, there are examples of large-scale operations processing many thousands of tonnes of waste per year and there is some evidence that the number of operations involving vermicomposting is likely to increase (Slater et al. 2005).

The theory and practice of vermicomposting varies considerably compared to other more traditional methods of composting. Firstly, the processing conditions required for
vermicomposting are very different to those employed by more traditional composting methods. In particular, vermicomposting is carried out in the mesophilic temperature range, typically 15 – 25 °C (Edwards & Neuhauser 1988) rather than at the higher temperatures (70 °C or greater) associated with in-vessel systems (Chapter 4).

Secondly, vermicomposting systems tend to be operated continuously on a long-term basis with waste being applied frequently in layers to a processing bed containing earthworms, rather than as large-scale batch operations as with traditional composting (Edwards & Bohlen 1996). Thirdly, vermicomposting systems are particularly suited to processing very wet, highly putresible sludges, such as biological sludges from food processing or paper manufacture, which are not easily amenable to traditional composting methods (Loehr et al. 1988; Short et al. 1999). Finally, in contrast to traditional composting methods, the use of very large populations of earthworms as the main processing agent in vermicomposting may contribute significantly to the environmental impact of these systems through increased nitrous oxide emission.

While much is known about the performance and optimisation of vermicomposting systems, their environmental impact, in particular their potential to produce greenhouse gases, has not been well researched to date. However, while comparatively little is known about emission of N₂O and CH₄ from large-scale composting systems employing earthworms as the main processing agent, many authors have linked enhanced emission of N₂O to earthworms in studies of forest and garden soil (Matthies et al. 1999, Horn et al. 2003). In each of these studies, denitrification within the partially anaerobic gastrointestinal tract of earthworms has been identified as being the source of N₂O.

Karsten & Darke (1997) found that the guts of the species *Lumbricus rubellus* contained high levels of denitrifying bacteria and reported nitrous oxide emissions from earthworms under aerobic conditions and from their gut contents under anaerobic conditions. They further speculated that the earthworm gut might constitute a microsite for enriched aerobic
as well as anaerobic processes. While nitrous oxide was clearly linked with earthworm activity, they also reported that no methane was detected from *Lumbricus rubellus* or its gut contents. In one of very few studies investigating the environmental impact of vermicomposting, Frederickson & Howell (2002) identified potentially significant N\textsubscript{2}O emissions from a large-scale vermicomposting system and this potential source of environmental pollution would appear to warrant further research. It would appear that nitrous oxide emission rather than methane is primarily associated with vermicomposting, but further studies are needed to confirm this. Consequently, this chapter aims to investigate emissions of N\textsubscript{2}O and CH\textsubscript{4} from a typical large-scale vermicomposting system.

Vermicomposting (VC) is the biodegradation of organic material at ambient temperatures through interactions between earthworms and micro-organisms maintained under aerobic conditions (Arancon et al. 2002). It is increasingly becoming a large-scale automated process (Sherman 1997) as detailed by Travalini (2002) describing a Californian cardboard paper sludge vermicomposting process that occupies 70 acres and receives 300 tonnes of cardboard fibre waste daily. A variety of wastes are considered to be suitable for vermicomposting. Examples of the types of waste processed using vermicomposting include yard trimmings (Sherman 1997), food waste (Simko 2000), waste paper sludge (Short et al. 1999), and human sewage (Lotzof 2000).

Vermicomposting operates under mesophilic conditions and does not therefore provide the level of waste sanitisation offered by other types of composting methods carried out in the thermophilic range (Sherman-Huntoon 2000). However, it is generally accepted that the lower vermicomposting temperatures can result in compost containing enhanced available nutrient content. The low temperature nature of vermicomposting can reduce N volatilisation typical of thermophilic composting processes, an effect noted by Buckerfield et al. (1999) who found increased nutrient content within vermicomposts and in particular enhanced N that promoted increased plant growth. This effect of vermicompost
application was also described by Arancon et al. (2003) showing increased tomato yields when vermicompost fertiliser was used compared to the use of inorganic fertilisers.

Vermicomposting has also been found to accelerate the stabilisation of waste compared with windrow composting (Frederickson et al. 1997) and promote the production of nitrate (NO$_3^-$) during waste processing (Short et al. 1999). Simko (2000), however, concluded that earthworms had a negative impact on the decomposition process, although mention of pungent odour and mould growth during the composting process under investigation indicated poor vermicomposting management. While vermicomposting has been described as a pollution-free process (Lotzof 2000), very little research has focused on assessing the environmental impact of such systems, in particular emission of N$_2$O and CH$_4$.

Nitrous oxide (N$_2$O) contributes to global warming (around 6% of the enhanced global greenhouse effect) and stratospheric ozone depletion. The production and emission of N$_2$O originates from the microbial transformations of nitrogen (N) as organic material degrades. At the start of decomposition fresh organic material undergoes ammonification, this is when organic N molecules (such as proteins, nucleic acid, and amino acids) are microbially released into ammonium (NH$_4^+$) (Katterer 2002). Once N has been mineralised to NH$_4^+$ it becomes available to organisms that convert the NH$_4^+$ to nitrate (NO$_3^-$) (Caton 2002). This is a two-stage process under aerobic conditions, firstly NH$_4^+$ is microbially transformed to nitrite (NO$_2^-$), then to NO$_3^-$ (Hagopian and Riley 1998). It is during the first stage of nitrification (NH$_4^+$ $\rightarrow$ NO$_2^-$) that N$_2$O is produced under low O$_2$ conditions (Alleman & Preston 1992). The second stage of nitrification under low O$_2$ conditions can result in nitric oxide (NO) emission but not N$_2$O (Hagopian & Riley 1998).

Nitrous oxide can also be produced during denitrification; the transformation of NO$_3^-$ to N$_2$. This is performed by a wide variety of micro-organisms that can inhabit both aerobic and anaerobic environments (Trogler 1999). Nitrate (NO$_3^-$) reduction to NO is the first step in
denitrification followed by further reduction to N$_2$O and finally to N$_2$ (Katterer 2002). Under aerobic conditions denitrifiers metabolise O$_2$, when conditions become anaerobic they switch to using NO$_3^-$ as the terminal electron acceptor. It is under anaerobic or limited O$_2$ conditions that optimal denitrification N$_2$O production occurs (Gejlsbjerg et al. 1998, Czepiel et al. 1996, De Weaver et al. 2002).

Many factors may affect the capacity of vermicomposting to produce N$_2$O, such as waste characteristics and processing conditions. Frederickson & Howell (2002) found that the level of N$_2$O emitted during a vermicomposting experiment was positively correlated with earthworm density. They also identified potentially significant N$_2$O emissions from a large-scale vermicomposting system that appeared to show seasonal variation in N$_2$O flux, with much larger fluxes of N$_2$O in summer compared to winter. This suggests that earthworm density and processing temperature may be related to N$_2$O emissions for vermicomposting systems.

Processing temperature appears to be a particularly important factor in determining potential emission of N$_2$O from vermicomposting. Since nitrous oxide emission from vermicomposting operations has been linked to denitrification processes taking place within the guts of the earthworms, earthworm density would appear to be a factor in the overall level of emissions. Processing temperature has been shown to greatly affect the carrying capacity of the vermicomposting system and the number of earthworms contained within the processing bed.

Reproduction rates for *Dendrobaena veneta* appear to be highly temperature dependent. For example, Fayolle et al. (1997) found that *D. veneta* kept at 10 °C produced around eight times fewer cocoons worm$^{-1}$ than those maintained at 15 °C, while Neuhauser et al. (1988) reported that *D. veneta* failed to produce any cocoons at 15 °C. Viljoen et al. (1992) found that cocoon production for *D. veneta* was 0.28 cocoons worm$^{-1}$ day$^{-1}$ at 25 °C but only 0.17 cocoons worm$^{-1}$ day$^{-1}$ at 15 °C. Higher earthworm densities within the
Earthworm processing beds have also been shown to result in increased waste decomposition reflected in increased waste processing rates. Gajalakshmi et al. (2002) showed that the rate of waste processing could be doubled by an initial threefold increase in earthworm density from 50 to 150 earthworms litre$^{-1}$. Ndewa et al. (2000) also found that waste processing rates increased with increasing earthworm density. Hence, increasing the processing temperature for vermicomposting systems up to the considered maximum of 25 °C is likely to result in higher earthworm densities and greater processing rates. However, high earthworm densities may also impact on the potential emission of N$_2$O due to increased waste decomposition and the potential for increased activity from gut-associated denitrifying bacteria.

Temperature also has a role in determining nitrification and denitrification rates. The bedding material present within the vermicomposting processing beds is known to provide strongly nitrifying conditions and many authors have associated high levels of nitrate with vermicompost (Short et al. 1999). Matthies et al. (1999) contended that gut-associated denitrifying bacteria were responsible for emissions of nitrous oxide and showed that these emissions increased when earthworms were moistened with nitrate or nitrite. Temperature is known to influence nitrification and denitrification rates with lower temperatures inhibiting activity within both communities (Holtan-Hartwig et al. 2002, Pfenning & McMahon 2002, and Dincer & Kargi 2000). Moreover, increased levels of nitrous oxide from soil during summer compared to winter months may be explained by the temperature dependence of both nitrification and denitrification (Machefert et al. 2002), where other factors are not limiting.

Few studies have addressed the environmental impact of large-scale vermicomposting systems but on the basis of very limited research evidence it appears that nitrous oxide emission rather than methane is primarily associated with this type of system. Further studies are needed to confirm this. In addition, the processing temperature during vermicomposting seems to play an important role in determining the emission of nitrous
oxide. Increasing the processing temperature in order to increase the size of the earthworm population and carrying capacity of the system has been shown to maximize waste processing capacity. However, it also appears that higher temperatures have been linked to increased nitrous oxide emission. It is therefore important to determine the relationship between processing temperature and nitrous oxide emission so that operators of vermicomposting systems can impose processing conditions to maximize waste throughput while minimizing the environmental impact of the system.

This chapter details a two-part field investigation to explore the relationship between processing temperature and the emission of N\textsubscript{2}O from a large-scale vermicomposting system and to better understand the mechanisms for N\textsubscript{2}O production and emission. The first part of the study relates to a pilot experiment which sought to develop experimental skills and to establish the nature and level of gaseous emissions. The second study aimed to test the hypothesis that increased processing temperatures for large-scale vermicomposting systems (within a defined operating range) will enhance N\textsubscript{2}O emissions, thereby increasing the environmental impact of such systems.

5.2 Part 1: Preliminary assessment of CH\textsubscript{4} and N\textsubscript{2}O emissions from a large-scale vermicomposting system using two temperature regimes

The project aim
To monitor emissions of CH\textsubscript{4} and N\textsubscript{2}O from a vermicomposting system operating under high and low temperature regimes.

The project objectives
1. To set up a large-scale vermicomposting system appropriate to the aim of the project.
2. To understand how vermicomposting systems may be controlled and to establish effective mechanisms with particular reference to temperature control.
3. To develop methods for monitoring CH₄ and N₂O emissions from vermicomposting.

5.2.1 Materials and Methods

This pilot study was started in October 2002. An experimental vermicomposting system was established at the Worm Research Centre, Yorkshire, UK. The system comprised a block of vermicomposting beds which was constructed using breeze block walls 0.4 m high, 30 m long and 1.5 m wide. Figure 5.1 shows an image of the vermicomposting facility. The block had thermostat controlled heating and leachate drainage, and was covered. The block was subdivided into 6 beds which were physically isolated from each other in terms of earthworm migration. There were 5 active vermicomposting beds plus a control bed. Each bed contained a 20 cm layer of bedding material (mixed coir and woodchip) and the five vermicomposting beds were stocked with 2 kg m⁻² of earthworms (species *Dendrobaena veneta*). There were two possible options for the configuration of the control bed: bedding and waste, and bedding only. The second option was chosen as the first would have resulted in the waste drying on the surface of the bedding since in the absence of earthworms the waste would not have been incorporated into the bedding.

![Figure 5.1 The Worm Research Centre vermicomposting facility, Yorkshire, UK](image)

Figure 5.1 The Worm Research Centre vermicomposting facility, Yorkshire, UK
For this study pulped potato waste (PPW) was used as the material to be vermicomposted, and was applied in two 20 cm-wide layers to the surface of the bedding (40 L per application). Further PPW was applied to the vermicomposting beds only and this was carried out when the previous application had been processed.

Each of the five vermicomposting beds and the control bed was assessed for its potential to emit CH₄ and N₂O. Two sequential monitoring trials were undertaken with the active beds being operated under two different temperature regimes. The control bed was at ambient temperatures throughout the study. Firstly emissions from vermicomposting were determined for the 5 beds when maintained at 20°C. The bed heating was then turned off and the 5 beds allowed to cool to ambient temperatures before the second series of emission monitoring on the 5 beds was begun. The mean temperature for the 5 beds under ambient conditions was approximately 10°C.

Physico-chemical characteristics of the PPW and vermicomposting bedding material are shown in Table 5.1. Methods for the determination of the chemical constituents listed in Table 5.1 are detailed in section 2.6 of the Methods Chapter.
Table 5.1 Physico-chemical characteristics of pulped potato waste (PPW) and vermicomposting bedding material (VCBM)

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Ec (mS cm⁻¹)</th>
<th>Dry solids (%)</th>
<th>Volatile solids (%)</th>
<th>Total N (%)</th>
<th>Total P (%)</th>
<th>Total K (%)</th>
<th>Na (mg kg⁻¹)</th>
<th>NH₄⁺ (mg kg⁻¹)</th>
<th>K (mg kg⁻¹)</th>
<th>Mg (mg kg⁻¹)</th>
<th>Ca (mg kg⁻¹)</th>
<th>F (mg kg⁻¹)</th>
<th>Cl (mg kg⁻¹)</th>
<th>NO₃⁻ (mg kg⁻¹)</th>
<th>PO₄³⁻ (mg kg⁻¹)</th>
<th>SO₂⁻ (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPW</td>
<td>7.12</td>
<td>249.8</td>
<td>24.6</td>
<td>81.5</td>
<td>3.2</td>
<td>0.65</td>
<td>4.83</td>
<td>1700</td>
<td>4500</td>
<td>34300</td>
<td>1100</td>
<td>800</td>
<td>1500</td>
<td>4300</td>
<td>200</td>
<td>2200</td>
<td>1800</td>
</tr>
<tr>
<td>VCBM</td>
<td>6.81</td>
<td>125.9</td>
<td>21.5</td>
<td>84.5</td>
<td>0.8</td>
<td>0.78</td>
<td>0.22</td>
<td>300</td>
<td>0</td>
<td>1800</td>
<td>200</td>
<td>300</td>
<td>0</td>
<td>200</td>
<td>0</td>
<td>1300</td>
<td>0</td>
</tr>
</tbody>
</table>
Gas samples (n = 10; 2 flux chambers used on each of the 5 vermicomposting beds simultaneously, one chamber situated over the PPW and one over the VC bedding as shown in Figure 5.2) were taken from the surface of the beds when the systems was maintained at a bedding temperature of 20 °C. A further sampling exercise was performed when the bedding temperature had lowered to ambient temperature. The control bed, containing neither earthworms nor waste, was maintained at ambient temperatures throughout the study and was subjected to CH₄ and N₂O flux sampling (n = 10) at the same time flux samples were taken from the vermicomposting beds. Gas samples were taken using the static flux chamber method (as described in the Methods Chapter, section 2.1) at 0 minutes (when the chambers were sealed) then at 10, 20, and 30 minutes. The temperature of the bedding was logged at the time of gas sampling using a hand-held temperature monitor fitted with a 30 cm spike probe.

Figure 5.2 Vermicomposting emission sampling using the static flux chamber method
5.2.2 Vermicomposting emission results

Individual fluxes of CH$_4$ and N$_2$O from heated, ambient temperature, and control (bedding only) vermicomposting beds are shown in Table 5.2. Emission of CH$_4$ from all beds was negligible. N$_2$O was released from both the heated and ambient temperature vermicomposting beds at a mean rate of 1.76 mg N$_2$O m$^{-2}$ hr$^{-1}$ and 2.68 mg N$_2$O m$^{-2}$ hr$^{-1}$ respectively. Mean N$_2$O flux rate from all vermicomposting beds system at both heated and ambient temperature conditions was 123 kg N$_2$O-N ha$^{-1}$ yr$^{-1}$. The highest N$_2$O flux was 15.35 mg N$_2$O m$^{-2}$ hr$^{-1}$ from the ambient temperature bed. Emission of N$_2$O from the control bed was negligible.

Table 5.2 Individual fluxes of CH$_4$ and N$_2$O from heated, ambient temperature, and control vermicomposting (bedding only) beds. Mean flux from all 10 measurements is also shown

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Maintained at 20°C</th>
<th>Ambient conditions</th>
<th>Control bed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_4$ mgm$^{-2}$ hr$^{-1}$</td>
<td>N$_2$O mgm$^{-2}$ hr$^{-1}$</td>
<td>CH$_4$ mgm$^{-2}$ hr$^{-1}$</td>
</tr>
<tr>
<td>1</td>
<td>0.03</td>
<td>2.01</td>
<td>-0.10</td>
</tr>
<tr>
<td>2</td>
<td>0.00</td>
<td>1.43</td>
<td>-0.01</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>3.14</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
<td>3.39</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.01</td>
<td>1.53</td>
<td>-0.02</td>
</tr>
<tr>
<td>6</td>
<td>0.01</td>
<td>1.27</td>
<td>-0.03</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>1.64</td>
<td>-0.03</td>
</tr>
<tr>
<td>8</td>
<td>0.01</td>
<td>1.00</td>
<td>-0.01</td>
</tr>
<tr>
<td>9</td>
<td>0.00</td>
<td>1.12</td>
<td>-0.02</td>
</tr>
<tr>
<td>10</td>
<td>0.00</td>
<td>1.15</td>
<td>-0.02</td>
</tr>
<tr>
<td>Mean</td>
<td>0.01</td>
<td>1.77</td>
<td>-0.02</td>
</tr>
</tbody>
</table>
5.2.3 Discussion

Emission of CH\textsubscript{4} from all beds was negligible, confirming the findings of Frederickson & Howell (2002) for a similar large-scale vermicomposting system and also Karsten & Darke (1997) who reported the absence of CH\textsubscript{4} associated with a particular species of earthworm typically used for vermicomposting purposes.

N\textsubscript{2}O was produced and released from both the heated and ambient temperature beds at a rate of 123 kg N\textsubscript{2}O-N ha\textsuperscript{-1} yr\textsuperscript{-1}. A previous study undertaken by Frederickson & Howell (2002) showed a similar vermicomposting process releasing 275 kg N\textsubscript{2}O-N ha\textsuperscript{-1} yr\textsuperscript{-1} which appeared to be related to earthworm density. The significance of this emission is clear when compared to agricultural buffer zones (one of the largest emitters) releasing around 38 kg N\textsubscript{2}O-N ha\textsuperscript{-1} yr\textsuperscript{-1} (Machefert et al. 2002). A study by Patni et al. (2000) found N\textsubscript{2}O release from vermicomposting at a rate of 0.05 mg N\textsubscript{2}O-N m\textsuperscript{2} hr\textsuperscript{-1} from cattle and hog manure slurries, about an order of magnitude lower than the fluxes found in this study (Table 5.2). This was possibly due to differing N content of the waste being vermicomposted affecting N\textsubscript{2}O emission (although no waste N content data was given in their study).

N\textsubscript{2}O emission can be attributed to the combination of incomplete nitrification and denitrification at low O\textsubscript{2} conditions. This cause of N\textsubscript{2}O emission from the vermicomposting bedding material is, however, unlikely because of the low CH\textsubscript{4} emission and at times CH\textsubscript{4} oxidation observed in the beds indicating sufficient aeration. Studies by Ihussen et al. (2003), Horn et al. (2003), Matthies et al. (1999), and Karsten & Drake (1997 & 1995) have demonstrated the effect of earthworms on the emission of N\textsubscript{2}O. It is the enhanced population of denitrifying combined with the low O\textsubscript{2} conditions within the earthworm gut that provides optimum N\textsubscript{2}O production (Czepiel et al. 1996).
The cause of high flux rate of 15.35 mg m\(^{-2}\) hr\(^{-1}\) was undetermined and could have been
due to a number of factors. Firstly, the compression of the VC bedding material when the
static chambers were installed could have caused a pulse of N\(_2\)O to be released.
Compression of the VC bed would have reduced the pore space in the bedding material
forcing out any pockets of gas present. It is unlikely however that the compression of the
bed would have caused this high pulse as time was allowed for this pulse to exit the
chamber before flux measurement began. This period of equilibration was applied to all
flux measurements. The N\(_2\)O pulse effect of bedding material compression can also be
produced by water entering the pore spaces and forcing out gas, but as the VC beds were
covered this effect was minimised and is not considered the cause of the high N\(_2\)O flux.
By excluding this anomalous result the ambient temperature mean flux rate was revised to
1.27 mg m\(^{-2}\) hr\(^{-1}\), which was not statistically different to the flux from the bed which was
maintained at 20\(^\circ\)C (p = 0.13 using a t-test for independent samples – Statistica). The
reason for the lack of difference could be due to a lag in the time between enhanced
nitrification and increased denitrification to N\(_2\)O in the earthworm gut as a response to a
change in temperature. To test this further study of the effect of temperature on N\(_2\)O
emissions from VC should be undertaken with different VC bed temperatures maintained
over a longer period.

5.2.4 Summary and conclusions

Emissions of CH\(_4\) and N\(_2\)O were monitored from a large-scale vermicomposting system
operating at a high and low temperature. A large scale VC bed was set up and procedures
were developed to monitor CH\(_4\) and N\(_2\)O emissions when the system was heated (to 20
\(^\circ\)C) and at ambient temperature.

At both heated and ambient conditions VC was shown to emit significant N\(_2\)O and
negligible CH\(_4\) fluxes, however flux rates were broadly similar under both temperature
regimes. The short duration of this study is unlikely to have been sufficient to identify
differences in the effect of processing temperature on large-scale VC emission and highlights the need for a longer-term experiment.
5.3 Part 2: N$_2$O emission from large-scale vermicomposting beds operating at a range of temperatures

The project aim

To monitor emissions of CH$_4$ and N$_2$O from a vermicomposting system operating under a range of different continuous temperature regimes.

The project objectives

1. The main objective of this study is to test the hypothesis that increasing the vermicomposting processing temperature will promote enhanced N$_2$O emissions.
2. A secondary objective is to confirm that properly functioning vermicomposting systems, operating under normal circumstances, are unlikely to emit CH$_4$.

5.3.1 Materials and methods

This study was started in December 2002. As for the first part of this experimental programme, the experimental vermicomposting system at the Worm Research Centre, Yorkshire, UK was employed. The system comprised a block of vermicomposting beds which was constructed using breeze block walls 0.4 m high, 30 m long and 1.5 m wide. The block had thermostat controlled heating, leachate drainage and was covered. The block was subdivided into 6 beds which were physically isolated from each other in terms of earthworm migration. There were 5 active vermicomposting beds (A to E) and a control bed (Bed F) which was not supplied with waste or stocked with earthworms. Each bed contained a 20 cm layer of bedding material (mixed coir and woodchip) and the five vermicomposting beds were stocked with 2 kg m$^{-2}$ of earthworms (species *Dendrobaena veneta*). As for the experiment in Part 1, the control bed comprised bedding only.
A separate sample of pulped potato waste (PPW), different to that used for the previous experiment, was vermicomposted. This was applied in two 20 cm wide layers to the surface of the bedding (40 L per application). Further PPW was applied to the beds when the previous application had been processed and a record of the total amount of PPW applied to each VC bed over the 85-day study period was kept by the VC facility operator. Methods for the determination of the physico-chemical characteristics listed in Table 5.3 are detailed in section 2.6 of the Methods chapter. The layout of the block, indicating the location of each temperature controlled bed is shown in Figure 5.3.

The temperatures of individual beds (E, A, D and C) were set at 10, 15, 20 and 25 °C respectively with the remaining two beds (B) and (F Control) being left at ambient temperatures (Figure 5.3). Actual bed and air temperatures were continually logged (at 10 minute intervals) in duplicate during the 85-day study period using two probes located approximately 15 cm deep in the VC bedding material. The placement of the temperature probes was intended to gain a measure of the temperature in the zone that the earthworms inhabit. Figure 5.4 shows the configuration of the individual VC beds.

Figure 5.3 Layout of the vermicomposting block, indicating the location of each temperature controlled bed and control bed
A record of the total amount of feed applied to each bed was made for the 85-day trial period. CH₄ and N₂O emissions were measured during 7 visits to the VC facility at 15-day intervals using the static chamber method (detailed in the Methods Chapter, section 2.1) on days 0, 15, 29, 44, 58, 71, and 85. For each sampling visit 12 flux chambers were used simultaneously. Two chambers were used on each bed (A – F), one chamber placed over the PPW feed and one over the bedding. Flux sampling was performed between 12:00 and 14:00 hrs and only during dry weather. Flux chambers were placed on the VC beds at least 2 hours prior to flux sampling to reduce gas emissions caused by pressing the chambers into the surface of the VC bed interfering with the flux measurement.

Gas samples were analysed within 24 hours using a gas chromatograph (GC 94m Al Cambridge) equipped with a porapakQ column, a flame ionisation detector for CH₄, and an electron capture detector for N₂O. Fluxes were calculated using equation 2.1 detailed in the Methods Chapter (section 2.1). When comparing the N₂O flux rates from each VC bed a t-test for dependent variables was used to measure the significance of the difference between the N₂O flux rates from VC beds maintained at differing temperatures.
(using Statistica software package). When comparing mean flux rates from the VC beds a p-level of 0.05 or below was considered an indicator of significant difference.

The initial bedding material and PPW samples were analysed for their physico-chemical characteristics to identify changes occurring during the vermicomposting process. Analysis was performed on a sub-sample of 3 combined samples of PPW and VCBM (Table 5.3). Samples (n = 3, each 0.5 kg) of vermicomposting bedding material were taken from the upper layer (0-5 cm) of the bedding material and from 5-10 cm below the surface from random locations from each bed on day 15 of the study after the first application of PPW had been processed. The 3 samples were then combined and a sub-sample was subjected to the same physicochemical analysis as the initial PPW and VCBM. Methods for this physico-chemical analysis are detailed in section 2.6 of the Methods Chapter.
Table 5.3 Physico-chemical characteristics of pulped potato waste (PPW) and vermicomposting bedding material (VCBM)

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH (water extract)</th>
<th>Ec (mS cm⁻¹)</th>
<th>Dry solids (%)</th>
<th>Volatile solids (%)</th>
<th>Total N (%)</th>
<th>Total P (%)</th>
<th>Total K (%)</th>
<th>Na mg kg⁻¹</th>
<th>NH₄⁺ mg kg⁻¹</th>
<th>K mg kg⁻¹</th>
<th>Mg mg kg⁻¹</th>
<th>Ca mg kg⁻¹</th>
<th>F mg kg⁻¹</th>
<th>Cl⁻ mg kg⁻¹</th>
<th>NO₃⁻ mg kg⁻¹</th>
<th>PO₄³⁻ mg kg⁻¹</th>
<th>SO₄²⁻ mg kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPW</td>
<td>6.6</td>
<td>237.8</td>
<td>22.0</td>
<td>83.0</td>
<td>2.9</td>
<td>0.8</td>
<td>4.87</td>
<td>1500</td>
<td>4300</td>
<td>32800</td>
<td>1100</td>
<td>800</td>
<td>2000</td>
<td>4300</td>
<td>100</td>
<td>1800</td>
<td>1600</td>
</tr>
<tr>
<td>VCBM</td>
<td>6.8</td>
<td>125.9</td>
<td>21.5</td>
<td>84.5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.22</td>
<td>300</td>
<td>0</td>
<td>1800</td>
<td>200</td>
<td>300</td>
<td>0</td>
<td>200</td>
<td>0</td>
<td>1300</td>
<td>0</td>
</tr>
</tbody>
</table>

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5.3.2 Results

5.3.2.1 Temperature

There was considerable fluctuation in individual bed temperatures due to the influence of ambient air temperatures. Table 4.4 shows the actual mean bed temperatures recorded and the maximum and minimum values observed during the 85-day study period.

Vermicomposting bed B and control bed F during this study had the highest fluctuation in observed temperature from the 85-day mean (41% and 79% respectively). Unheated bed B had a mean temperature of 6.7°C, which was significantly higher (p < 0.01) than the control bed F (5°C). This may have been due to the enhanced microbial activity in the active vermicomposting bed B. Vermicomposting beds A, D, and E had maximum/minimum temperature deviations from the mean of 27% 31% and 39% respectively, with VC bed C having the lowest maximum/minimum temperature deviation of 11% from the 85-day average. This suggests that the VC bed that was set to the highest temperature was influenced by the external ambient conditions to a lesser extent than unheated or lower temperature VC beds.
Table 5.4 Set and observed bed temperatures (°C) during 85 days vermicomposting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bed A</th>
<th>Bed B</th>
<th>Bed C</th>
<th>Bed D</th>
<th>Bed E</th>
<th>Control Bed F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set temperature (°C)</td>
<td>15</td>
<td>ambient</td>
<td>25</td>
<td>20</td>
<td>10</td>
<td>ambient</td>
</tr>
<tr>
<td>Actual mean temperature (°C)</td>
<td>12.0</td>
<td>6.7</td>
<td>24.6</td>
<td>14.6</td>
<td>11.7</td>
<td>5.0</td>
</tr>
<tr>
<td>(85 days) (range of temperature in brackets)</td>
<td>(8.8 – 15.2)</td>
<td>(3.3 – 9.4)</td>
<td>(22.1 – 27.9)</td>
<td>(8.65 – 19.5)</td>
<td>(8.15 – 19.2)</td>
<td>(-0.2 – 8.8)</td>
</tr>
<tr>
<td>Minimum observed temperature (°C)</td>
<td>8.8</td>
<td>3.6</td>
<td>22.1</td>
<td>9.7</td>
<td>8.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Maximum observed temperature (°C)</td>
<td>15.2</td>
<td>9.1</td>
<td>27.9</td>
<td>18.9</td>
<td>18.1</td>
<td>8.5</td>
</tr>
</tbody>
</table>

5.3.2.2 Flux observations

CH₄ and N₂O fluxes observed for each sampling day (mean of 2 replicates) and vermicomposting bed temperature recorded at the time of flux sampling are shown in Table 5.5.

Table 5.6 shows CH₄ flux from the VC beds over the 85-day study period, these were found to be negligible and are likely to be a reflection of the aerobic nature of the VC beds. N₂O fluxes from VC beds A-E (Table 5.7) were significantly higher than the mean zero flux of N₂O from unheated unfed control bed F which comprised bedding material.
only \((p \leq 0.01\) in all cases). Bed C, which was the bed with the highest mean temperature, also recorded the highest mean flux \((6.1 \text{ mg N}_2\text{O m}^{-2} \text{ hr}^{-1})\). This flux rate was significantly greater than those flux rates observed from all of the other beds \((p < 0.05\) in all cases).

From Table 5.7 it can be seen that the variability of surface \(\text{N}_2\text{O}\) flux over the 85-day study period from the VC beds is evident, particularly for the higher temperature VC bed C. The mean \(\text{N}_2\text{O}\) flux from the VC bed (bed B) with the lowest mean temperature \((2.7 \text{ mg N}_2\text{O m}^{-2} \text{ hr}^{-1})\) was significantly less \((p = 0.02)\) than the flux from the highest temperature bed \((6.1 \text{ mg N}_2\text{O m}^{-2} \text{ hr}^{-1})\). The difference in \(\text{N}_2\text{O}\) flux between beds B and C can be expressed approximately as a 1.5x increase in \(\text{N}_2\text{O}\) flux for every 10°C rise in temperature over the temperature range studied. Mean VC bed temperature recorded at the time of flux sampling and 85-day mean VC bed temperature is shown in Table 5.5.

The correlation between specific \(\text{N}_2\text{O}\) flux rates for each bed and bed temperature taken at the time of sampling was found to be low \((R^2 = 0.21)\). Specific \(\text{N}_2\text{O}\) flux rates for each VC bed were also found to be poorly correlated with the relevant 85-day mean temperatures \((R^2 = 0.23)\). However, it was found that the 85-day mean \(\text{N}_2\text{O}\) fluxes and the 85-day mean temperatures were strongly correlated \((R^2 = 0.91)\). A plot of the relationships between mean \(\text{N}_2\text{O}\) flux and mean temperature, and mean \(\text{N}_2\text{O}\) flux and total feed application is shown in Figure 5.5. The 85-day mean \(\text{N}_2\text{O}\) flux for each VC bed and the total PPW application rate (Table 5.8) over the 85-day study period for each VC bed were found to be positively correlated \((R^2 = 0.68)\). The total amount of feed applied to each VC bed was also found to be positively correlated with the relevant 85-day mean temperature for the beds \((R^2 = 0.65)\).
Figure 5.5 Relationships between mean N\textsubscript{2}O flux and mean temperature, and mean N\textsubscript{2}O flux and total feed application

![Figure 5.5](image)

- \textbullet\textbullet\textbullet\textbullet\textbullet = N\textsubscript{2}O flux against temperature (R\textsuperscript{2} = 0.91)
- \square\square\square\square = N\textsubscript{2}O flux against feed rate (R\textsuperscript{2} = 0.68)

Table 5.5 Mean vermicomposting bed temperature recorded at the time of flux sampling, and 85-day mean vermicomposting bed temperature

<table>
<thead>
<tr>
<th>Sampling day</th>
<th>Bed A Temperature (°C)</th>
<th>Bed B Temperature (°C)</th>
<th>Bed C Temperature (°C)</th>
<th>Bed D Temperature (°C)</th>
<th>Bed E Temperature (°C)</th>
<th>Bed F Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.5</td>
<td>10.5</td>
<td>16.8</td>
<td>11.0</td>
<td>10.9</td>
<td>8.3</td>
</tr>
<tr>
<td>8</td>
<td>14.1</td>
<td>8.9</td>
<td>23.8</td>
<td>13.8</td>
<td>11.6</td>
<td>8.5</td>
</tr>
<tr>
<td>15</td>
<td>11.8</td>
<td>8.9</td>
<td>22.1</td>
<td>16.6</td>
<td>11.1</td>
<td>8.5</td>
</tr>
<tr>
<td>29</td>
<td>9.4</td>
<td>4.6</td>
<td>24.5</td>
<td>18.1</td>
<td>15.3</td>
<td>2.8</td>
</tr>
<tr>
<td>44</td>
<td>9.8</td>
<td>8.7</td>
<td>24.7</td>
<td>21.0</td>
<td>10.1</td>
<td>8.0</td>
</tr>
<tr>
<td>58</td>
<td>12.5</td>
<td>4.0</td>
<td>23.9</td>
<td>16.9</td>
<td>11.5</td>
<td>2.1</td>
</tr>
<tr>
<td>71</td>
<td>13.6</td>
<td>7.0</td>
<td>23.5</td>
<td>18.4</td>
<td>10.2</td>
<td>4.7</td>
</tr>
<tr>
<td>85</td>
<td>12.5</td>
<td>3.5</td>
<td>23.7</td>
<td>16.3</td>
<td>10.1</td>
<td>1.8</td>
</tr>
<tr>
<td>85 day Mean</td>
<td>12.0</td>
<td>6.7</td>
<td>25</td>
<td>15</td>
<td>12</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Table 5.6 Mean CH$_4$ fluxes observed during each sampling day and 85-day mean CH$_4$ flux. Individual repetitions are shown in brackets

<table>
<thead>
<tr>
<th>Sampling day</th>
<th>Bed A (mg CH$_4$ m$^{-2}$ hr$^{-1}$)</th>
<th>Bed B (mg CH$_4$ m$^{-2}$ hr$^{-1}$)</th>
<th>Bed C (mg CH$_4$ m$^{-2}$ hr$^{-1}$)</th>
<th>Bed D (mg CH$_4$ m$^{-2}$ hr$^{-1}$)</th>
<th>Bed E (mg CH$_4$ m$^{-2}$ hr$^{-1}$)</th>
<th>Control bed F (mg CH$_4$ m$^{-2}$ hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.2 (0.1, 0.3)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.5 (0.3, 0.7)</td>
<td>0.6 (0.5, 0.6)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>8</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.1 (0.0, 0.2)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.7 (0.4, 0.9)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>15</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.2 (0.1, 0.4)</td>
<td>0.3 (0.2, 0.3)</td>
<td>0.0 (0.0, 0.1)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>29</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.1 (0.0, 0.2)</td>
<td>0.3 (0.1, 0.5)</td>
<td>0.2 (0.0, 0.4)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>44</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.1 (0.0, 0.1)</td>
<td>0.4 (0.3, 0.5)</td>
<td>0.6 (0.2, 1.1)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>58</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.1)</td>
<td>0.0 (0.0, 0.1)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>71</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>85</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (-0.1, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>85 day Mean</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
<td>0.1 (0.0, 0.0)</td>
<td>0.2 (0.0, 0.0)</td>
<td>0.2 (0.0, 0.0)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
</tbody>
</table>
Table 5.7 Mean N₂O fluxes observed during each sampling day, and 85-day mean N₂O fluxes. Individual repetitions are shown in brackets

<table>
<thead>
<tr>
<th>Sampling day</th>
<th>Bed A mg N₂O m⁻² hr⁻¹</th>
<th>Bed B mg N₂O m⁻² hr⁻¹</th>
<th>Bed C mg N₂O m⁻² hr⁻¹</th>
<th>Bed D mg N₂O m⁻² hr⁻¹</th>
<th>Bed E mg N₂O m⁻² hr⁻¹</th>
<th>Control bed F mg N₂O m⁻² hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.7 (2.2, 5.2)</td>
<td>2.7 (1.2, 4.2)</td>
<td>7.5 (6.4, 8.6)</td>
<td>2.2 (2.1, 2.3)</td>
<td>3.5 (1.6, 5.3)</td>
<td>0.0 (0.0, 0.1)</td>
</tr>
<tr>
<td>8</td>
<td>5.1 (3.6, 6.7)</td>
<td>2.9 (2.1, 3.7)</td>
<td>3.7 (1.1, 6.4)</td>
<td>5.3 (3.2, 7.5)</td>
<td>5.6 (3.3, 8.0)</td>
<td>0.1 (0.1, 0.1)</td>
</tr>
<tr>
<td>15</td>
<td>2.7 (1.4, 4.0)</td>
<td>4.8 (4.7, 4.9)</td>
<td>10.7 (6.8, 14.5)</td>
<td>3.7 (3.5, 3.9)</td>
<td>2.3 (0.9, 3.6)</td>
<td>-0.1 (-0.2, 0.0)</td>
</tr>
<tr>
<td>29</td>
<td>2.3 (1.5, 3.0)</td>
<td>1.4 (1.0, 1.7)</td>
<td>4.9 (2.6, 7.1)</td>
<td>4.2 (3.0, 5.4)</td>
<td>3.0 (1.6, 4.3)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>44</td>
<td>2.3 (0.8, 3.9)</td>
<td>2.2 (1.8, 2.7)</td>
<td>4.4 (2.8, 6.0)</td>
<td>3.7 (2.2, 5.2)</td>
<td>1.7 (1.4, 1.9)</td>
<td>0.1 (0.1, 0.1)</td>
</tr>
<tr>
<td>58</td>
<td>4.4 (2.1, 6.7)</td>
<td>1.7 (0.8, 2.6)</td>
<td>3.3 (3.2, 3.4)</td>
<td>3.8 (2.9, 4.7)</td>
<td>1.9 (1.7, 2.0)</td>
<td>0.0 (0.0, 0.1)</td>
</tr>
<tr>
<td>71</td>
<td>5.3 (4.0, 6.6)</td>
<td>3.8 (2.3, 5.4)</td>
<td>8.9 (6.9, 10.9)</td>
<td>5.9 (2.9, 8.8)</td>
<td>2.3 (2.2, 2.4)</td>
<td>0.0 (0.0, 0.0)</td>
</tr>
<tr>
<td>85</td>
<td>2.1 (1.7, 2.4)</td>
<td>1.9 (1.0, 2.8)</td>
<td>4.6 (2.8, 6.5)</td>
<td>2.7 (2.2, 3.2)</td>
<td>2.3 (0.8, 3.7)</td>
<td>0.1 (0.1, 0.1)</td>
</tr>
<tr>
<td>85 day Mean</td>
<td>3.5</td>
<td>2.7</td>
<td>6.1</td>
<td>3.9</td>
<td>2.8</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Two exceptionally high N₂O flux readings were omitted from the data sets relating to beds C and D, with fluxes of 38.8 mg N₂O m⁻² hr⁻¹ and 43.2 mg N₂O m⁻² hr⁻¹ respectively. Although these data points were omitted when comparing fluxes from differing VC beds, these high readings were considered to be valid. Possible reasons for the presence of such large readings are explained in the discussion section.
Table 5.8 Volume of pulped potato waste applied to each vermicomposting bed during the 85-day study period

<table>
<thead>
<tr>
<th>Vermicomposting bed</th>
<th>Feed applied over 85 days(^1) (Litres)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed A</td>
<td>490</td>
</tr>
<tr>
<td>Bed B</td>
<td>330</td>
</tr>
<tr>
<td>Bed C</td>
<td>530</td>
</tr>
<tr>
<td>Bed D</td>
<td>490</td>
</tr>
<tr>
<td>Bed E</td>
<td>370</td>
</tr>
<tr>
<td>Control bed F</td>
<td>none</td>
</tr>
</tbody>
</table>

5.3.2.3 Physico-chemical characteristics

Physico-chemical characteristics of the VC bedding material at both the surface (0-5 cm) and at depth (5-10 cm) are shown in Table 5.9. In general the VC bedding material acidified with depth, increased in density, lost \(\text{NH}_4^+\) and gained \(\text{NO}_3^-\). The most likely cause for the increase in \(\text{NO}_3^-\) observed for the active vermicomposting beds was aerobic nitrification. This is a characteristic of vermicomposting and was not evident in the control bed (bed F). It is possible that some volatilisation of \(\text{NH}_4^+\) as \(\text{NH}_3\) occurred, although this was less likely because of the mesophilic temperature regime of the VC system (Sommer & Dahl 1999).
Table 5.9 Physico-chemical analyses of the vermicomposting bedding material upper layer (0-5 cm) and lower layer (5-10 cm) after 15 days of vermicomposting for beds A – E and control bed F

<table>
<thead>
<tr>
<th>Vermicompost bed</th>
<th>Sample depth (cm)</th>
<th>pH (water extract)</th>
<th>Ec (mS cm(^{-1}))</th>
<th>Dry solids (%)</th>
<th>Volatile solids (%)</th>
<th>Total N (%)</th>
<th>Total P (%)</th>
<th>Total K (%)</th>
<th>Na g kg(^{-1})</th>
<th>NH(_4) g kg(^{-1})</th>
<th>K g kg(^{-1})</th>
<th>Mg g kg(^{-1})</th>
<th>Ca g kg(^{-1})</th>
<th>F g kg(^{-1})</th>
<th>Cl g kg(^{-1})</th>
<th>NO(_3) g kg(^{-1})</th>
<th>PO(_4) g kg(^{-1})</th>
<th>SO(_4) g kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 0-5</td>
<td>7.4</td>
<td>539</td>
<td>17.4</td>
<td>82.5</td>
<td>2.3</td>
<td>0.7</td>
<td>0.5</td>
<td>14.3</td>
<td>91.6</td>
<td>725</td>
<td>6.2</td>
<td>19.4</td>
<td>1.0</td>
<td>94.6</td>
<td>7.7</td>
<td>109.7</td>
<td>65.7</td>
<td></td>
</tr>
<tr>
<td>A 5-10</td>
<td>6.5</td>
<td>577</td>
<td>17.7</td>
<td>73.3</td>
<td>1.6</td>
<td>1.1</td>
<td>0.8</td>
<td>30.1</td>
<td>3.8</td>
<td>802</td>
<td>16.7</td>
<td>38.0</td>
<td>0.8</td>
<td>82.8</td>
<td>1002</td>
<td>207.5</td>
<td>98.2</td>
<td></td>
</tr>
<tr>
<td>B 0-5</td>
<td>7.5</td>
<td>363</td>
<td>18.1</td>
<td>81.1</td>
<td>2.1</td>
<td>0.7</td>
<td>0.4</td>
<td>4.4</td>
<td>45.9</td>
<td>530</td>
<td>7.2</td>
<td>22.4</td>
<td>0.1</td>
<td>60.0</td>
<td>20.9</td>
<td>106.0</td>
<td>34.7</td>
<td></td>
</tr>
<tr>
<td>B 5-10</td>
<td>6.9</td>
<td>469</td>
<td>17.4</td>
<td>75.3</td>
<td>1.7</td>
<td>1.2</td>
<td>0.9</td>
<td>11.5</td>
<td>2.1</td>
<td>669</td>
<td>10.9</td>
<td>29.6</td>
<td>0.2</td>
<td>71.5</td>
<td>759</td>
<td>182.4</td>
<td>44.2</td>
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</tr>
<tr>
<td>C 0-5</td>
<td>7.5</td>
<td>573</td>
<td>15.6</td>
<td>83.8</td>
<td>2.0</td>
<td>0.7</td>
<td>0.5</td>
<td>19.0</td>
<td>113.3</td>
<td>914</td>
<td>12.0</td>
<td>27.3</td>
<td>1.2</td>
<td>106.9</td>
<td>3.7</td>
<td>149.5</td>
<td>66.5</td>
<td></td>
</tr>
<tr>
<td>C 5-10</td>
<td>6.7</td>
<td>444</td>
<td>17.7</td>
<td>77.6</td>
<td>1.7</td>
<td>1.4</td>
<td>0.7</td>
<td>34.4</td>
<td>4.1</td>
<td>673</td>
<td>9.5</td>
<td>25.3</td>
<td>0.0</td>
<td>60.0</td>
<td>730</td>
<td>190.2</td>
<td>46.6</td>
<td></td>
</tr>
<tr>
<td>D 0-5</td>
<td>7.1</td>
<td>445</td>
<td>17.7</td>
<td>82.3</td>
<td>2.0</td>
<td>0.6</td>
<td>0.5</td>
<td>13.2</td>
<td>42.0</td>
<td>651</td>
<td>14.6</td>
<td>41.4</td>
<td>0.0</td>
<td>70.0</td>
<td>6.7</td>
<td>198.5</td>
<td>61.8</td>
<td></td>
</tr>
<tr>
<td>D 5-10</td>
<td>6.0</td>
<td>490</td>
<td>17.1</td>
<td>74.9</td>
<td>1.5</td>
<td>1.4</td>
<td>0.7</td>
<td>11.3</td>
<td>3.1</td>
<td>693</td>
<td>16.5</td>
<td>38.8</td>
<td>0.5</td>
<td>77.3</td>
<td>890</td>
<td>240.6</td>
<td>61.4</td>
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</tr>
<tr>
<td>E 0-5</td>
<td>7.6</td>
<td>686</td>
<td>15.8</td>
<td>80.4</td>
<td>2.1</td>
<td>0.6</td>
<td>0.5</td>
<td>9.9</td>
<td>118.8</td>
<td>1238</td>
<td>12.7</td>
<td>19.8</td>
<td>0.9</td>
<td>122.7</td>
<td>15.0</td>
<td>210.4</td>
<td>110.4</td>
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<tr>
<td>E 5-10</td>
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<td>477</td>
<td>17.1</td>
<td>76.4</td>
<td>1.8</td>
<td>1.3</td>
<td>0.9</td>
<td>18.8</td>
<td>5.2</td>
<td>793</td>
<td>16.5</td>
<td>37.7</td>
<td>1.9</td>
<td>98.2</td>
<td>1033</td>
<td>183.7</td>
<td>72.0</td>
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<tr>
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<td>226</td>
<td>58.9</td>
<td>80.5</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>11.6</td>
<td>0.2</td>
<td>80</td>
<td>3.8</td>
<td>7.2</td>
<td>0.6</td>
<td>14.8</td>
<td>14.5</td>
<td>33.0</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>F 5-10</td>
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<td>214</td>
<td>56.2</td>
<td>76.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>24.7</td>
<td>0.9</td>
<td>77</td>
<td>3.2</td>
<td>8.0</td>
<td>0.1</td>
<td>8.8</td>
<td>7.2</td>
<td>43.9</td>
<td>3.5</td>
<td></td>
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</table>
5.4 Discussion

The main aim of this study was to test the hypothesis that increasing the vermicomposting processing temperature would promote enhanced N\textsubscript{2}O emissions. It would appear that the data presented in the results section supports this hypothesis, with the 85-day mean N\textsubscript{2}O fluxes and the 85-day mean temperatures being strongly correlated ($R^2 = 0.91$). A secondary aim was to confirm that properly functioning vermicomposting systems, operating under normal circumstances, are unlikely to emit CH\textsubscript{4}. This was confirmed from analysis of the CH\textsubscript{4} fluxes from the VC beds over the 85-day study period. These were found to be negligible and this is likely to be a reflection of the aerobic nature of the vermicomposting beds.

N\textsubscript{2}O emission from composting originates from the microbial transformations of N as organic material degrades. Fresh organic material at the start of composting undergoes ammonification. Once N has been mineralised to NH\textsubscript{4}+ it becomes available to nitrifiers that convert the NH\textsubscript{4}+ to NO\textsubscript{3}\textsuperscript{-} (Katterer 2002, Caton 2002). N\textsubscript{2}O and NO are possible by-products of nitrification in low O\textsubscript{2} environments. An accumulation of NO\textsubscript{3}\textsuperscript{-} within the VC bedding material and the acidification associated with nitrification (Dincer & Kargi 2000) was observed in this study (Table 5.9) matching the findings of Frederickson & Howell (2003) and Short et al. (1999). Denitrifiers (transforming NO\textsubscript{3}\textsuperscript{-} to N\textsubscript{2}) under aerobic conditions metabolise O\textsubscript{2}, when conditions become anaerobic they switch to using NO\textsubscript{3}\textsuperscript{-} as the terminal electron acceptor. Czepiel et al. (1996) showed that denitrification undertaken at low O\textsubscript{2} conditions results in N\textsubscript{2}O production. Low temperatures greatly inhibit denitrifying communities (Holtan-Hartwig et al. 2002), an effect shown by Pfenning & McMahon (2002) who found that reduction of temperature from 22°C to 4°C resulted in a decrease in denitrification of 77%. It is the effect of temperature variation on nitrification and denitrification that is of most concern in this study.
There is evidence for good aeration within the VC beds such as negligible CH$_4$ emission (Table 5.3) and a high level of aerobic nitrification observed (Table 5.5), therefore N$_2$O from low O$_2$ denitrification is unlikely to originate from the VC bedding material (as was shown by a lack of N$_2$O emission from the control bed Table 5.3). Nitrification activity in low O$_2$ environments is also a potential source of N$_2$O emission, however earthworms require a well-aerated environment as the exchange of O$_2$ and CO$_2$ occurs at a thin moist layer on their skin. Indicators of a poorly aerated VC bed would be earthworm mortality and CH$_4$ emission, since neither were observed it can be inferred that the VCs bed were well aerated (to which earthworms make a considerable contribution) and the N$_2$O flux was unlikely to have originated as a by-product of nitrification. Therefore it was likely that earthworms were directly contributing to the formation of N$_2$O in the vermicomposting beds.

Earthworms have been shown to significantly contribute to the emission of N$_2$O from forest soils that are normally well aerated (Karsten & Darke 1997). Estimates of the proportion of N$_2$O emitted from soils that can be directly attributed to earthworms range from 16% to 33% for beech forest and garden soils respectively (Karsten & Drake 1997, Matthies et al. 1999). The partially anaerobic gastro-intestinal tract of earthworms (Matthies et al. 1999) is inhabited by a population of ingested denitrifying bacteria at a proportion higher than that of the surrounding material (Horn et al. 2003). It is the combination of partial anaerobicity, the enhanced population of denitrifying bacteria and the readily available supply of NO$_3^-$ within the VC bedding material that makes the earthworm gut an ideal zone for N$_2$O production. The high availability of NO$_3^-$ in the VC system may also have had the effect of enhancing N$_2$O emission. Denitrifiers will preferentially use NO$_3^-$ as the terminal electron acceptor (De Weaver et al. 2002), therefore any produced N$_2$O is less likely to be denitrified to N$_2$ either within the worm gut or the NO$_3^-$ enriched VC bed.
Since earthworm body temperatures reflect that of their immediate surroundings, the temperature of the material they inhabit has an influence on the rate of microbial activity within the earthworm gut (Edwards & Bohlen 1996). In order to assess how the rate of N₂O flux from large-scale vermicomposting is affected by the temperature of the immediate environment, VC beds were designed with heating and temperature controls. Diurnal temperature fluctuations and changes in weather conditions had a strong influence on the VC bed temperature. Unheated beds fluctuated up to 79% from the mean temperature, significantly higher than the temperature controlled VC beds. The occurrence of temperature fluctuation in the heated beds as a response to ambient conditions does, however, highlight the need for better temperature control systems to be used in VC processes of this type.

In order to better understand the relationship between N₂O flux and processing temperature three temperature N₂O flux relationships were investigated:

1. VC bed temperature at the time of sampling and individual N₂O flux rates for each sampling visit.

2. Individual N₂O flux rates and 85-day mean VC bed temperature.

3. 85-day mean N₂O flux rates and 85-day mean VC bed temperature.

Although a relationship between increased N₂O flux with increased temperature was found when using the first and second comparisons, this relationship was weak. However, there are a number of reasons why a strong relationship between N₂O and temperature at the time of sampling would not be expected for such a system.

Firstly the temperature at the time of sampling did not reflect the predominant temperature of the VC bed in the period leading up to the sampling event. It is in this period that the
NO$_3^-$, subsequently denitrified to N$_2$O by the earthworms, would have been generated. The response to temperature change of nitrifiers in the VC bed would have been rapid (Kammann et al. 1998) but a time lag would have occurred between VC bed nitrification and denitrification within the earthworm guts, similar to the time lag observed by Machefert et al. (2002) between temperature elevation and increased N$_2$O emission from riparian zones. Based on this it is conceivable that a high N$_2$O flux could have been observed at a relatively low temperature as a response to an earlier higher VC bed temperature, and vice versa. Without a measure of VC bed nitrification rates throughout the course of the 85-day study period, accounting for the effect and duration of this lag is not possible.

Secondly, the earthworm population within the VC beds is dynamic, with individual earthworms capable of travelling many metres in one day (Bastardie et al. 2003). Also witnessed when sampling material was the tendency for earthworms to 'ball up' into clusters containing tens of individuals. The effect of the population dynamics on N$_2$O flux from the VC beds used in this study cannot be quantified but goes some way to explaining the variability of data when analysed as individual data points. This variability is also displayed in Table 5.5 which shows individual flux rates observed throughout the study reflecting the variation of flux in response to temperature fluctuation and earthworm population dynamics.

Another possible cause of the poor correlation between sampling temperature and N$_2$O flux could be the effect temperature has on complete denitrification to N$_2$. Holtan-Hartwig et al. (2002) found that N$_2$O consumption has a higher activation energy than N$_2$O production, therefore the ratio of N$_2$O/N$_2$ production increases with decreasing temperature. The effect of low temperature inhibition of N$_2$O reductase would need to be taken into account when assessing the potential global release of N$_2$O from VC. A more useful method of comparing the effect of temperature on N$_2$O flux from the VC beds used in this study is to use the 85-day mean flux rates and 85-day mean observed
temperatures for each VC bed where N$_2$O flux rate showed good positive correlation with temperature ($R^2 = 0.91$).

Management of the VC beds involved the replenishment of PPW after that previously applied had been processed, Table 5.6 shows total PPW applied to the bed during the 85-day study period. The total amount of PPW applied positively correlated to the mean temperature of the VC bed ($R^2 = 0.65$). NO$_3^-$ within the bedding material was derived from ammonification and nitrification of the organic N compounds within the pulped potato waste, and this NO$_3^-$ was fuelling the in-vivo emission of N$_2$O from the earthworms. The 85-day mean temperature ($R^2 = 0.91$) appeared to have had greater influence on N$_2$O flux than total PPW applied to the VC beds ($R^2 = 0.68$). However, these two influences are closely related. The increased temperature appeared to provide more microbially-active conditions and earthworm metabolic activity which in turn increased the waste processing rate, elevating NH$_4^+$ input, subsequent nitrification to NO$_3^-$, and production/emission of N$_2$O.

Two very high N$_2$O flux rates observed from VC beds C and D of 38.8 mg N$_2$O m$^{-2}$ hr$^{-1}$ and 43.2 mg N$_2$O m$^{-2}$ hr$^{-1}$, respectively, were observed during the study period. These N$_2$O flux pulses were omitted from the dataset as being significant outliers, but were considered as valid (not being due to disturbance of the pore space beneath the flux chambers at the time of sampling). Very high short-lived pulses of N$_2$O flux have been observed from soils as a response to a short-term change in environmental conditions. Increased moisture or a sudden increase in temperature can trigger an N$_2$O flux pulse (Mummey et al. 1997, Prieme & Christensen 2001), as can the introduction of NO$_3^-$ to a denitrifying community (De Weaver et al. 2002). With all these factors being dynamic within the VC beds it is conceivable that a combination of factors occurred that gave rise to the very high N$_2$O fluxes. The frequency and duration of these pulses and therefore how much they contribute to the total N$_2$O release from VC cannot be ascertained in this study and requires future consideration.
The implications of \( N_2 O \) flux from vermicomposting are discussed in Chapter 8 where fluxes from this study are scaled up (and based on mass of waste processed) to provide comparison of the global warming potential of VC emissions with other composting methods. It was shown in this study that an increase in VC temperature gives faster waste processing rates, but also gives rise to higher \( N_2 O \) fluxes. It is therefore important that consideration must be given to the environmental impact of VC when deciding upon process operating temperature. Significant mitigation of emission can be achieved by lowering the operating temperature of VC, this and other emission mitigation options are discussed in Chapter 8.

5.5 Summary and conclusions

Emissions of \( CH_4 \) and \( N_2 O \) from a vermicomposting system operating under a range of different continuous temperature regimes were monitored. This study showed that increasing the vermicomposting processing temperature promotes enhanced \( N_2 O \) emissions, and that for a rise in vermicomposting processing temperature of \( 10^\circ C \), emission of \( N_2 O \) increased 1.5 times (up to \( 25^\circ C \)).

\( CH_4 \) fluxes from the VC beds over the 85-day study period were found to be negligible and is a reflection of the aerobic nature of the vermicomposting beds. Further studies are necessary to identify how other factors may influence the emission of \( N_2 O \), especially when considering the varied nature of organic material that may be subjected to vermicomposting due to EU landfill directive compliance.
6.1 Introduction

A particular theme throughout this thesis has been the emphasis on developing experimental skills and on acquiring new knowledge about emissions of CH$_4$ and N$_2$O from composting processes. Specific process types were selected to reflect the rapidly changing profile of sustainable waste management practices in the UK and in particular the composting sector. To this end much of the practical research that has been undertaken and much of the research emphasis has been focused on the environmental impact of the innovative composting technologies and novel composting practices being introduced into the UK. This theme is continued in this chapter.

In Chapter 1, the changing profile of the UK composting sector was briefly discussed. While it is clear from this review that the current predominance of green waste composting using open-air, mechanically turned windrow systems will continue in the short to medium term, more advanced and more environmentally benign systems will also be required in the near future. Several factors and new legislation were identified as drivers for change in the composting sector promoting the development and adoption of cost-effective enclosed and in-vessel composting systems. A particular feature of Chapters 3 and 4 was the emphasis on monitoring short-term gaseous emissions during the early stages of composting for enclosed and in-vessel composting systems. To a large degree, the focus on monitoring short-term effects was the result of the role that in-vessel and enclosed composting is perceived to play, by Government and the composting industry, in the overall management of biodegradable wastes.
By contrast, in Chapter 5 a longer-term study of CH₄ and N₂O emissions from vermicomposting was presented. This study clearly demonstrated the need for long-term monitoring of greenhouse gases from these types of composting systems, as the highest N₂O fluxes were recorded after 71 days. An important aim of this chapter will be to build on previous work by addressing the potential of partially composted material to produce CH₄ and N₂O emissions during an extended period of compost maturation. In particular, the study aims to contribute much-needed empirical data for CH₄ and N₂O emissions relating to the latter stages of composting, as little research has been conducted on this phase of composting. The study on which the chapter is based first stabilised source segregated household using in-vessel technology before setting up a comparative experiment relating to the compost maturation phase, which sought to evaluate the performance and environmental impact of two types of composting systems. The two composting methods used to mature the partially composted waste, which were selected for this study, were mechanically-turned windrow technology and vermicomposting.

The study commenced in 2002 and was based on a new system of composting which was introduced into the UK in 2003 as a result of the introduction of the Animal By-Products Regulations (DEFRA 2003). These regulations have been highly influential in promoting the development of in-vessel and enclosed composting systems. The effect of the Animal By-Products Regulations (ABPRs) on shaping composting technology and composting practices is an important consideration in this study. Since the scope of the Animal By-Products Regulations was discussed in Chapter 1, these regulations will not be considered here in detail. However, with the introduction of the ABPRs in 2003 in the UK, legislation was put in place to ensure that composting of the category of waste referred to as "catering wastes" was undertaken using a risk-based barrier system. The catering waste category was taken to encompass source segregated household waste if kitchen waste was included. The first closed reactor barrier was defined as thermophilic composting of waste using enclosed windrows or in-vessel technology. This was to be followed by either composting in a second barrier using a similar treatment regime (if meat
was present in the waste) or storage of material for a defined time if meat was not present. Hence, novel composting systems such as vermicomposting would not be considered to be a suitable technology for the first barrier treatment of source segregated household waste (containing kitchen waste). This is because it operates in the lower temperature mesophilic range. However, for non-meat containing wastes, low temperature processes such as vermicomposting can be used to satisfy the ABPR "18-day storage" requirement. The use of vermicomposting to accelerate the compost maturation process and to enhance the characteristics of the partially-composted material from the closed reactor stage would appear to be a viable option for some composting operations. Indeed, there are some good examples of this approach having been adopted (Finance Wales 2004). Combining the closed reactor stage with vermicomposting for the treatment of source segregated household waste may offer many benefits. However, very little research has been carried out into this type of combined system. In particular, the environmental impacts and many practical aspects of combining these systems are unclear. For example, at the time of the study it was not known if hot, partially composted material from in-vessel systems could be applied directly to earthworm beds without killing earthworm populations.

For non-meat containing wastes, other composting systems such as open air mechanically turned windrow systems would also be suitable for satisfying the ABPR "storage" requirement for the second stage. Although vermicomposting is known to accelerate the maturation process for some wastes and to enhance product characteristics, it was not known if maturation could be achieved more rapidly than other cost-effective processes, such as windrow composting systems. Also, in terms of the environmental impact of vermicomposting and windrow composting systems when operated in combination with in-vessel systems, it is important to assess the greenhouse gas emissions from both approaches. This is especially important in terms of generating sound data for use in Lifecycle Analysis. Finally, it should be noted that although the ABPRs focus on establishing risk-based bio-processing methods for minimising disease
transmission, there is a requirement for most composting systems to produce marketable compost. This requires longer-term compost maturation in addition to satisfying short term stabilisation and sanitation needs. This study investigated the composting of source segregated household waste, not containing kitchen waste, using in-vessel technology as the first thermophilic barrier. This was followed by a "storage" and maturation stage, which involved a comparative composting experiment using a traditional windrow system and a vermicomposting system. An Important feature of this study was the direct comparison of CH₄ and N₂O emissions for these contrasting composting systems, using identical waste.

Project Aim

To investigate the effect on CH₄ and N₂O emissions from composting and vermicomposting during long term maturation of pre-treated source segregated household waste.

Project Objectives

1. To explore experimentally key aspects of combining in-vessel composting systems with vermicomposting technology in order to further stabilise and mature selected wastes.

2. To investigate the effect of in-vessel composting on source segregated waste and assess its suitability to undergo further maturation.

3. To apply partially composted material from an in-vessel system to vermicomposting beds and to monitor vermicompost maturation rates using respirometry.

4. To windrow compost partially composted material from an in-vessel system and monitor the compost maturation rate using respirometry.
5. To develop suitable methods for the comparative monitoring of greenhouse gas emissions from vermicomposting and from windrow composting when operated in combination with an in-vessel composting system.

6.2 Materials and Methods

The study was undertaken from November 2002 to February 2003. The waste used in this study was shredded source segregated household waste (SSHW), containing mostly green waste with some non-meat kitchen waste and inert contaminants. Initial 7-day in-vessel treatment of the material (approximately 12 tonnes) was undertaken. The in-vessel system used was the Sirocco System, manufactured by Waste Mechanics. After pre-treating the material for 1 week and subjecting the material to the required temperature conditions for compliance with animal by-product regulations (DEFRA 2003), the unit and its contents were transported to the experimental site for further stabilisation and maturation. The material was deposited at the Worm Research Centre experimental site on 12 November 2002. Figure 6.1 shows the unloading of the source segregated household waste at the Worm Research Centre. Half of the material (3.5 t) was formed into a windrow (2 m high, 10 m long and 3 m wide) which was situated on a concrete surface and covered with a porous membrane. Temperature probes provided continuous logging of pile temperature. The windrow was turned every 7 days for the first 4 weeks, then every 2 weeks thereafter. The remaining material was deposited as a layer 10-15 cm deep onto the surface of 4 vermicomposting beds, each with a bed area of 10 m$^2$, as described in Chapter 5. No further material was added during the vermicomposting process. The duration of maturation was 85 days. A fifth vermicomposting bed was set up as a control without worms or surface compost layer. These purpose-built vermicomposting beds were of concrete and brick construction with built-in drainage/leachate collection, electric cable heating and continuous temperature data logging. The bedding material used to contain the worms consisted of mixed woodchips to
a depth of 20 cm. The beds were maintained at a constant 20 °C and were stocked with *Dendrobaena veneta* at a mean density of 2 kg m$^{-2}$ of bed.

Figure 6.1 Unloading of the source segregated household waste at the Worm Research Centre

After being allowed to equilibrate for 1 day, gas and material samples were taken from both the windrow and vermicomposting systems. Gas and material samples were taken every week for the first 3 weeks then every fortnight for the following 10 weeks. The static chamber method was used for gaseous emission measurements from the surface of the compost material from both systems. Sampling comprised locating static chambers on the windrow ($n = 4$), on the vermicomposting bed ($n = 4$) and on the control bed ($n = 4$) simultaneously. The static chamber method is described in detail in section 2.6 of the Methods Chapter. CH$_4$ and N$_2$O concentrations were determined within 24 hours using a gas chromatograph (Ai Cambridge GC 94m with porapakQ column) fitted with a flame ionisation detector for CH$_4$ and an electron capture detector for N$_2$O. Figure 6.2 shows static flux chamber locations on the surface of the vermicomposting bed. After gas
sampling, solid material from both processes was sampled. Samples (15 kg) were analysed for nitrate (NO$_3$) content (using a Dionex DX-100 ion chromatograph (IC)) and respirometry was used to determine waste stability. Respirometric analysis allowed comparison of the effectiveness of windrow and vermicomposting in degrading organic material. The respirometer design was adapted from the basic system recommended by the manufacturer (Sable Systems, Connecticut, USA) and is described in Chapter 4.

Figure 6.2 Static flux chambers located on the surface of the vermicomposting bed

6.3 Results

Table 6.1 shows chamber CH$_4$ fluxes and operating temperatures for the windrow, vermicomposting beds and control bed from day 7 of the experiment, Days 1-6 relate to composting the material in the in-vessel system. The flux figures are the means of the recorded flux chamber data (n = 4). The temperature readings represent the means of data gathered both at the time of sampling (via spike probe) and from continuous logging. Some small negative fluxes are indicated and can be attributed to a slight drop in ambient
CH₄ concentration within the flux chamber. This is probably due to oxidation of the ambient CH₄ by aerobic microorganisms conditions (Ferry 2002).

Table 6.1 Measured static chamber CH₄ flux from windrow, vermicomposting and control (n = 4). Range of results shown in brackets

<table>
<thead>
<tr>
<th>Day</th>
<th>Windrow CH₄ flux mg m⁻² hr⁻¹</th>
<th>Windrow temperature (°C)</th>
<th>Vermicomposting CH₄ flux mg m⁻² hr⁻¹</th>
<th>Control CH₄ flux mg m⁻² hr⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>6.60 (0.00 - 37.08)</td>
<td>36.1 (33.2 - 38.3)</td>
<td>0.01 (0.01 - 0.10)</td>
<td>0.00 (0.00 - 0.00)</td>
</tr>
<tr>
<td>14</td>
<td>4.10 (0.10 - 10.18)</td>
<td>40.8 (36.3 - 48.4)</td>
<td>0.06 (0.04 - 0.09)</td>
<td>-0.01 (-0.01 - 0.00)</td>
</tr>
<tr>
<td>21</td>
<td>1.05 (0.00 - 1.70)</td>
<td>60.9 (57.2 - 67.1)</td>
<td>0.02 (0.00 - 0.05)</td>
<td>-0.01 (-0.01 - 0.00)</td>
</tr>
<tr>
<td>35</td>
<td>6.12 (1.71 - 15.59)</td>
<td>50.1 (45.3 - 58.9)</td>
<td>0.04 (0.00 - 0.15)</td>
<td>0.00 (0.00 - 0.00)</td>
</tr>
<tr>
<td>50</td>
<td>5.02 (0.00 - 13.99)</td>
<td>46.7 (35.6 - 49.7)</td>
<td>0.08 (0.02 - 0.20)</td>
<td>-0.01 (-0.01 - 0.00)</td>
</tr>
<tr>
<td>64</td>
<td>0.86 (0.25 - 1.38)</td>
<td>18.8 (15.3 - 26.8)</td>
<td>0.02 (0.00 - 0.13)</td>
<td>0.00 (0.00 - 0.00)</td>
</tr>
<tr>
<td>78</td>
<td>0.05 (0.01 - 0.12)</td>
<td>14.2 (12.9 - 18.6)</td>
<td>0.03 (0.00 - 0.08)</td>
<td>-0.01 (-0.01 - 0.00)</td>
</tr>
<tr>
<td>92</td>
<td>0.22 (0.15 - 0.39)</td>
<td>8.6 (7.1 - 10.2)</td>
<td>0.38 (0.01 - 0.75)</td>
<td>0.02 (0.01 - 0.02)</td>
</tr>
</tbody>
</table>

Table 6.2 shows flux chamber N₂O data from the windrow, vermicomposting beds and control bed. The mean measured N₂O release from the control bed was 0.035 mg N₂O m⁻² hr⁻¹. Vermicomposting emission up to day 64 was at a mean rate of 0.51 mg N₂O m⁻² hr⁻¹, approximately 15 times greater than the emission rate of the control. N₂O flux measured on days 78 and 92 showed emission rates of 1.0 mg N₂O m⁻² hr⁻¹ and 1.5 mg N₂O m⁻² hr⁻¹ respectively showing a large increase in flux toward the end of the 92 day period.
Figure 6.3 shows changes in waste stability as determined by respirometry. The figure displays data from day 0, which relates to the fresh source segregated household waste prior to in-vessel treatment. It can be seen that the effect of the initial 7-day in-vessel pre-treatment was to rapidly increase the stability of the composting material.

Table 6.2 Measured static chamber N\textsubscript{2}O flux from windrow, vermicomposting and control (n = 4). Range of results shown in brackets

<table>
<thead>
<tr>
<th>Day</th>
<th>Windrow N\textsubscript{2}O flux mg m\textsuperscript{-2} hr\textsuperscript{-1}</th>
<th>Vermicomposting N\textsubscript{2}O flux mg m\textsuperscript{-2} hr\textsuperscript{-1}</th>
<th>Control N\textsubscript{2}O flux mg m\textsuperscript{-2} hr\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.37 (0.00 - 2.43)</td>
<td>0.43 (0.08 - 0.92)</td>
<td>0.03 (0.02 - 0.03)</td>
</tr>
<tr>
<td>14</td>
<td>0.27 (0.00 - 0.41)</td>
<td>0.81 (0.18 - 1.56)</td>
<td>0.12 (0.00 - 0.02)</td>
</tr>
<tr>
<td>21</td>
<td>0.01 (0.00 - 0.01)</td>
<td>0.12 (0.00, 0.21)</td>
<td>-0.07 (-0.02 - 0.01)</td>
</tr>
<tr>
<td>35</td>
<td>0.03 (0.00 - 0.13)</td>
<td>0.63 (0.10 - 1.14)</td>
<td>0.03 (0.02 - 0.04)</td>
</tr>
<tr>
<td>50</td>
<td>0.63 (0.05 - 2.13)</td>
<td>0.53 (0.27 - 0.95)</td>
<td>0.08 (0.04 - 0.09)</td>
</tr>
<tr>
<td>64</td>
<td>0.03 (0.00 - 0.07)</td>
<td>0.54 (0.07 - 1.08)</td>
<td>0.03 (0.02 - 0.03)</td>
</tr>
<tr>
<td>78</td>
<td>0.01 (0.00 - 0.05)</td>
<td>1.01 (0.00 - 3.42)</td>
<td>-0.01 (-0.01 - 0.00)</td>
</tr>
<tr>
<td>92</td>
<td>0.03 (0.00 - 0.06)</td>
<td>1.46 (0.87 - 2.42)</td>
<td>0.07 (0.05 - 0.08)</td>
</tr>
</tbody>
</table>
Figure 6.3 Respiration rates for material subjected to in-vessel composting, windrow and vermicomposting processes. Error bars show range of results.

Change in total carbon and nitrogen contents before and after the 7 day in-vessel treatment is displayed in Table 6.3. During this 7 day period approximately 23% of total carbon and 47% of total nitrogen was lost from the waste. Total Kjeldahl N and total organic C content of the windrow and vermicomposting material on day 92 of the study was 0.9% N and 26% C, and 1.1% N and 25% C respectively. Table 6.4 displays water soluble NO$_3$ content of the material throughout the process. Samples were analysed for NO$_3$ content at the same interval as for those subjected to respirometric analysis.
Table 6.3 Total organic carbon and nitrogen content of the waste before and after in-vessel treatment. The range of results is shown in brackets.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before in-vessel treatment (%)</th>
<th>After in-vessel treatment (%)</th>
<th>Estimated total loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile solids content</td>
<td>65.0 (53.8 - 72.7)</td>
<td>50.4 (45.1 - 56.4)</td>
<td>22.5</td>
</tr>
<tr>
<td>Total organic carbon content:</td>
<td>36.0 (29.9 - 40.4)</td>
<td>27.9 (25.1 - 31.3)</td>
<td>22.5</td>
</tr>
<tr>
<td>Total nitrogen content:</td>
<td>1.63 (1.22 - 2.09)</td>
<td>1.23 (1.11 - 1.29)</td>
<td>47.0</td>
</tr>
</tbody>
</table>

Nitrogen loss was corrected for the concentration effect due to the reduction in organic matter during composting. Ash (%DM) was used as a baseline, assumed to remain at a constant total mass (Stentiford and Pereira Neto 1985).

Using the theory of ash conservation, dry mass (DM) contents can be calculated based on the following equation:

\[
X_{\text{loss}} = 1 - \frac{\text{(%X}_t \times \text{%Ash}_0)}{\text{(%X}_0 \times \text{%Ash}_t)}
\]

\[
X \%\text{loss} = X_{\text{loss}} \times 100
\]

where:

\(x = \text{nutrient; } \%\text{ASH}_0 = \text{initial ash content (\%DM); } \%X_0 = \text{initial nutrient content (\%DM; } \%\text{ASH}_t = \text{final ash content (\%DM) after composting duration (t); } \%X_t = \text{final nutrient content (\%DM) after composting duration (t) (adapted from Bernal et al. 1996).}}\)
Table 6.4 Nitrate formation over the course of the experiment for windrow and vermicomposting. Range of results is shown in brackets.

<table>
<thead>
<tr>
<th>Sample period (days)</th>
<th>Windrow NO$_3$ concentration mg kg$^{-1}$ (n = 3)</th>
<th>Vermicomposting NO$_3$ concentration mg kg$^{-1}$ (n = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>34.9 (23.3 – 44.5)</td>
<td>34.9 (19.2 – 48.8)</td>
</tr>
<tr>
<td>14</td>
<td>48.9 (25.9 – 67.5)</td>
<td>38.4 (24.5 – 46.3)</td>
</tr>
<tr>
<td>21</td>
<td>20.6 (18.1 – 32.9)</td>
<td>23.1 (17.2 – 29.7)</td>
</tr>
<tr>
<td>35</td>
<td>28.9 (23.4 – 37.8)</td>
<td>104.1 (75.3 – 132.7)</td>
</tr>
<tr>
<td>50</td>
<td>85.6 (66.2 – 1.2.5)</td>
<td>122.8 (98.3 – 151.9)</td>
</tr>
<tr>
<td>64</td>
<td>118.4 (101.2 – 129.8)</td>
<td>212.8 (175.3 – 240.3)</td>
</tr>
<tr>
<td>78</td>
<td>103.4 (87.7 – 122.6)</td>
<td>504.9 (427.1 – 603.2)</td>
</tr>
<tr>
<td>92</td>
<td>166.4 (101.7 – 232.8)</td>
<td>571.4 (512.5 – 631.4)</td>
</tr>
</tbody>
</table>

6.4 Discussion

In terms of flux chamber measured emissions the windrow system produced more CH$_4$ than the vermicomposting beds during the 85-day maturation process. The microbial production of methane, the final step in the decomposition of biomass under strictly anaerobic conditions (Ferry 2002), indicates that significant anaerobic zones developed within the windrow pile. The comparatively intensive windrow management practises undertaken in this study (i.e. regular turning) appeared not to prevent significant anaerobic zones developing within the windrow pile. Equally the rapid formation of CH$_4$ suggests that the methanogen population began CH$_4$ production soon after windrow formation. Rapid CH$_4$ production is not surprising given that several species of methanogen are tolerant of O$_2$ exposure and will retain their methane-producing viability after exposure to O$_2$ (Barber
& Ferry 2001). Hao et al. (2001) demonstrated that O\textsubscript{2} levels within a windrow pile can fall to less than 3% within 12 hours after turning and that a considerable amount of carbon can be emitted from composting as CH\textsubscript{4}.

Windrows have only recently been identified in a number of studies as being a significant source of CH\textsubscript{4} emission, with emission of CH\textsubscript{4} from composting processes being highly variable. Hellebrand (1998) states that 1.8 g CH\textsubscript{4} m\textsuperscript{-2} hr\textsuperscript{-1} can be emitted from dung windrows, and Beck-Friis et al. (2000) measured up to 5 g CH\textsubscript{4} m\textsuperscript{-2} hr\textsuperscript{-1} from MSW composting. The fluxes detected during this study were much lower than those stated above. One reason for the low levels of CH\textsubscript{4} detected in this study could be the effect of in-vessel pre-treatment. During this phase the volatile solids content and total organic carbon content of the waste fell by approximately 23%, reducing the amount of microbially-available carbon within the material, which was subsequently subjected to further stabilisation and maturation. This loss in volatile solids and carbon content due to the relatively short 7 day in-vessel composting would appear to be consistent with volatile solids and carbon losses observed for other materials and longer composting processes. For example, Michel et al. (1996) reported a 60% loss in volatile solids for food waste and leaves, 52% for cattle manure (Tarre et al. 1987); 75% for green waste (Frederickson et al. 1997); and 55% for a mixture of waste paper sludge, chicken litter and yard waste (Sesay et al. 1997).

Microbiological respiration was greatly reduced (by 75%) after in-vessel treatment and reflects the loss of available carbon. This loss in substrate would have the effect of decreasing the amount of carbon available for microbial decomposition thereby reducing the potential of CH\textsubscript{4} emission during subsequent composting. Carbon loss during this in-vessel stage will require further investigation to determine whether it originates from oxidising (CO\textsubscript{2} production) or reducing (CH\textsubscript{4} production) conditions within the enclosed organic matter. The fact that around 80% of composting operations in the UK (Slater & Frederickson, 2001) employ the mechanically turned windrow method clearly highlights the problem of CH\textsubscript{4} emission. It must be considered that some management practices
(e.g. infrequent turning) and use of large windrows may further enhance CH$_4$ emission. Fukumoto (2003) found that the size of a compost pile was a major factor in gas emission rates with larger windrow piles developing more anaerobic zones and therefore CH$_4$. Sommer & Moller (2000) found density to be a major factor in CH$_4$ production with lower densities (after amending material with straw) giving rise to lower CH$_4$ production.

During this study, the significant drop in windrow CH$_4$ flux readings for day 21 may be explained by the high (60 °C) temperatures recorded during sampling. At this temperature only the thermophile portion of the methanogen population could function (Barber & Ferry 2001). This effect of high temperature inhibition of CH$_4$ generation was also noted by Pier & Kelly (1997).

The windrow and vermicomposting systems in this study operated under different temperature regimes and aerobic conditions. It is clear that, although the windrow was regularly turned, anaerobic zones (and associated CH$_4$ production) were established for most of the course of the experiment. In the case of the vermicomposting system, which utilised thin layers of bedding and waste, comparatively little CH$_4$ was emitted. It was therefore concluded that the development of anaerobic zones was prevented or else sufficiently aerobic conditions were maintained to sustain the aerobe population and oxidise any produced CH$_4$.

N$_2$O release from the windrow in this study was comparatively low, with the vermicomposting material producing much higher fluxes throughout the course of the study and increasingly toward the end. These differing N$_2$O fluxes may be explained in terms of the fate of the organic N present at the start of the two processes. The data obtained from the respirometry studies indicates that a significant reduction in microbial activity had taken place as a result of in-vessel treatment. Furthermore, much organic nitrogen was lost during this stage (47%). High nitrogen losses are typical for composting processes. Witter and Lopez-Real (1988) reported that losses of nitrogen could amount to 50% of initial nitrogen and considered that nearly all nitrogen lost is due to ammonia
volatilisation during the early stages of composting. However, nitrogen losses during composting have also been attributed to emissions of nitrous oxide and nitrogen as well as ammonia (He et al. 2002). Nitrogen losses ranging from 9 to 68% during the composting of cattle manure have also been reported and particularly high losses have been attributed to very high levels of ammonium (NH$_4$) within the manure prior to composting (Gibbs et al. 2002, Eghball et al. 1997).

The N present at the start of composting in this study would have been present either as organic nitrogenous macromolecules, such as proteins, or would have already become mineralised by decomposer organisms to ammonium (NH$_4$) (Kätterer 2002). After division into the two processes the material was subjected to differing temperature regimes and levels of aerobicity. The material formed into a windrow quickly became hot and remained that way for around 50 days, during this time it is likely that some nitrogen would have been lost through volatilisation of NH$_3$ due to these high temperatures. Sommer (2001) observed this N loss pathway in his study of cattle litter composting, as did Smars et al. (1999) who recorded 40% N loss as NH$_3$ during the first 31 days of SSHW composting. Tiquia & Tam (2000) also attributed NH$_3$ volatilisation to high pile temperatures. Nitrogen losses as NH$_3$ may also have been exacerbated by mechanical turning of the windrow system. De Bertoldi et al. (1983) reported that the N loss was greater with mechanical turning (18% N loss) than with forced aeration (5% N loss) suggesting that mechanically-turned systems tend to liberate considerable amounts of ammonia to air during turning. Hence it can be assumed that reduced N loss as NH$_3$ volatilisation for the vermicomposting process was likely, due to the mesophilic temperature regime and system of passive aeration employed. This reduced N loss was reflected in the higher total Kjeldahl N content of the vermicomposting material compared to the windrow (1.1% N compared to 0.9 % N).

Because it is likely that reduced NH$_3$ loss occurred from the vermicomposting system and because of the mesophilic conditions prevailing, it may be predicted that enhanced
microbial nitrification would have occurred earlier and to a greater extent in the vermicomposting beds compared with the windrow. This effect was observed as reflected in the higher levels of NO$_3$ found in the vermicomposted material over the course of the experiment (Table 6.4). Nitrification is the process by which NH$_4$ is oxidised microbially to nitrite (NO$_2$) by *Nitrosomonas* bacteria, then to nitrate (NO$_3$) by *Nitrobacter* (Dincer & Kargi, 2000), both requiring strictly aerobic mesophilic conditions (Hagopian & Riley 1998, Fukumoto *et al.* 2003). This greater production of NO$_3$ in vermicomposting compared to windrow was also identified by Short *et al.* (1999) in their study of waste paper sludge composting. It is via this conversion from NH$_3$ to NO$_3$ that N$_2$O can be formed and emitted. He *et al.* (2000) suggested a N$_2$O generation pathway via nitrification of NO$_2$. This hypothesis was also put forward by Czepiel *et al.* (1996) who states that the determining factor for N$_2$O production during nitrification is availability of O$_2$, with low O$_2$ concentrations enhancing nitrifier N$_2$O production. Because the CH$_4$ fluxes from vermicomposting in this study were insignificant it was assumed that anaerobic or low O$_2$ conditions had not developed within the vermicomposting material and therefore N$_2$O emission from vermicomposting was unlikely to originate from low O$_2$ nitrification. This was also the case for nitrifier denitrification, this being the microbial process of anaerobic reduction of NO$_2$ to N$_2$O by bacteria that can also oxidise NH$_4$ (Machefert *et al.* 2002). These bacteria, which include some *Nitrosomonas* species, have the ability to switch between oxic and anoxic environments (Gejlbsbjerg *et al.* 1998), but as the vermicomposting system has been shown to be sufficiently aerated, their contribution to N$_2$O release from vermicomposting is not regarded to be important in this study.

Microbial denitrification can also result in emission of N$_2$O. Complete denitrification (NO$_3$\textarrow{}NO$_2$\textarrow{}N$_2$O\textarrow{}N$_2$) is the reduction of NO$_3$ to N$_2$ under anaerobic conditions, and is a process by which microbes utilise NO$_3$ instead of oxygen as the terminal electron acceptor in respiration in the absence of O$_2$ (Kätterer 2002). N$_2$O can originate from this process as a result of incomplete denitrification. In the presence of low O$_2$ conditions, complete denitrification is interrupted and instead of terminating at N$_2$ production, the process ends
at N₂O formation and subsequent emission (Czepiel et al. 1996, He et al 2000; Sommer 2001, De Weaver et al. 2002). These low O₂ environments do not seem to have predominated within the vermicomposting material and are not seen as the major contributor of N₂O production from this system. Some fungi are able to denitrify within aerobic environments and their denitrifying capability terminates at N₂O formation (Payne 1999, Kätterer 2002), therefore contribution to N₂O emission from fungal denitrification within the vermicomposting material in this study cannot be eliminated.

Data from previous studies measuring emission from vermicomposting, and habitats occupied by worms of the type used in vermicomposting, have shown that N₂O production rates are greatly enhanced by the presence of worms. Karsten & Drake (1997) in their study of the microflora of earthworm gastro-intestinal tracts found populations of denitrifying bacteria present in the worm gut proportionally higher than that of the surrounding soil. They also found that the worms emitted N₂O via internal denitrification while inhabiting an aerobic environment, with up to 16% of the total emission of N₂O from forest soils being attributed to worms. Matthies et al. (1999) further confirmed the association of earthworms and N₂O emission, arriving at an estimate of worms contributing 33% of the N₂O released from garden soils. They also stimulated N₂O production by moistening the earthworms with a sterile NO₃ solution, with the application of a NH₄ solution producing no N₂O. Therefore the contribution to emission of N₂O from vermicomposting from worms must be assumed. In their study of vermicomposting, Frederickson & Howell (2002) found that an increase in earthworm density led to greater N₂O emission and that vermicomposting favours NO₃ production. The N₂O emission from vermicomposting detected in this study was low compared to that reported in Frederickson & Howell (2002). One reason for this comparatively low emission rate may have been that total N for the waste in this study was around 3 times lower than that used in Frederickson & Howell (2002) (1.23% N compared to 3.6% N). A considerable amount of the total N (47%) was lost during the in-vessel stage in this study, thereby reducing the
amount of available N for nitrification and denitrification during vermicomposting and reducing the N$_2$O emission potential.

6.5 Summary and conclusions

The effect of in-vessel pre-treatment on CH$_4$ and N$_2$O emissions from source segregated household waste composting and vermicomposting was studied in this chapter. The in-vessel composting pre-treatment was characterised by significant C and N loss, after which both windrow and vermicomposting stabilized the waste at a similar rate.

Emissions of CH$_4$ and N$_2$O were detected during windrow composting and vermicomposting using the static flux chamber method. Emission of CH$_4$ and N$_2$O from windrow and vermicomposting measured in this study was lower than levels reported in other studies, likely due to the effect of in-vessel pre-treatment reducing the amount of available C and N for subsequent composting. Discussion on the use of in-vessel pre-treatment as an option for mitigating emissions, and a comparison of CH$_4$ and N$_2$O emissions (by mass of waste processed) is detailed in Chapter 8.
7 Relationship between waste biodegradability and CH₄ and N₂O emissions from composting

7.1 Introduction

The main focus of this thesis has been monitoring and assessing greenhouse gas emissions from large-scale composting systems. An important aim has been to address the lack of reliable data, in both the professional and academic literature relating to CH₄ and N₂O emissions, in particular from advanced composting systems. It was recognised from the outset of this research programme that it was also important to understand how the physico-chemical characteristics of the waste undergoing composting affected the nature and level of emissions. To this end, much work has been devoted to developing equipment and a set of experimental techniques based on respirometry principles. This was to enable waste characterisation and in particular waste biodegradability to be assessed during key stages of the composting process.

To enable the relationship between waste biodegradability and emission of CH₄ and N₂O to be investigated in more detail, a laboratory-based experiment was designed. This experiment is the main subject of this chapter and is presented in Part 2. Its aim was to monitor emission of CH₄ and N₂O from composting for two synthetic wastes (high and low biodegradability) operating under conditions of high and low aeration. In Part 1, the chapter also contains a detailed account of the experimental research, which led to the development of a new respirometry method, now called the DR4. The development of the test was commissioned by the Environment Agency and was recently adopted as one of two national tests for monitoring the biodegradability of pre-treated household waste prior to landfill. The DR4 test was used in the study presented here to determine levels of biodegradability for the synthetic wastes used in the experiment.
7.1.1 Introduction

The respirometry test method which was used in the study presented in this chapter to measure waste biodegradability was developed and extensively refined during the duration of the research programme. It is a dynamic method and is based on a modified version of ASTM D5975-96. Although a variety of respirometry methods have been developed and used by other researchers to determine levels of waste stability, respirometry has not been widely adopted as a research tool. The section contains a review of the many methods, including respirometry, that have been used to characterise wastes during biological processing. It is particularly important to note the use of two forms of respiration test that have been developed to determine stability levels for mechanically and biologically treated (MBT) household waste, prior to landfill in Germany, Austria and Italy. The tests are known as the dynamic respiration index (DRI) and the static respiration index (SRI) and are used extensively.

With the need for local authorities in the UK to meet their Landfill Allowance Targets for biodegradable waste, there is now considerable interest in the use of Mechanical and Biological treatment processes (Slater & Frederickson 2001). A brief introduction to MBT can be found in Chapter 1, but in summary, the biological processing technology used as part of MBT systems, is used to reduce the biodegradable content of municipal solid waste (MSW) prior to landfill. For many countries in continental Europe, de minimus respiration rates are in place, which restrict and regulate the landfilling of biodegradable wastes according to waste stability (Binner 2003). However, in the UK a mass balance approach to landfilling pre-treated biodegradable waste has been adopted. This requires the use of a newly developed testing regime comprising respiration test (DR4) and biochemical methane potential test (BM100). This testing regime is needed to determine the actual amounts of biodegradable material landfilled, for particular MBT plants.
Part 1 of this chapter presents the final experimental results relating to the development of the DR4 test which was carried out by this author at the Open University. The research was commissioned by the Environment Agency and was undertaken in collaboration with WRc PLC. The DR4 test was used to determine waste biodegradability for the wastes used in the experiment presented in Part 2.

The amount of biodegradable substrates within municipal solid waste (MSW) has been estimated at approximately 68% (DETR 2000). The types of organic molecules that constitute the waste material govern the rate of microbial biodegradation of these wastes when composted. In order to assess the level of stability, biodegradability, or degree of maturity of a waste sample a number of tests have been developed. These tests either directly measure organic compounds in the waste, or assess microbial activity or biomass behaviour within the waste. Tests solely focussing on the material being composted include Kalbitz et al (2003) on the use of UV absorbance to assess the amount of dissolved organic compounds in compost extracts, and the measurement of water soluble carbon concentration and humic/fulvic acid content analysis by Fourier transform infra-red spectroscopy performed by Castaldi et al (2005). Other methods of compost material biodegradability analysis include; volatile organic acid content (Brinton et al 2001), the relationship between carbon and nitrogen transformations (Hirai et al 1983), and near infra-red spectroscopy relating to water content (Johansson & Brundin 2002), Calorimetry and thermal analysis (Dell'Abate et al. 1998, Dell'Abate et al. 2000), and phytotoxicity measurement using seed germination tests (Zucconi et al. 1981). Methods such as these that are concerned with the chemical constituents do not however take into account the potential for wastes to be microbially broken down. The most widely used way to assess waste material biodegradability is by monitoring microbial activity (Haug 1993), and this is done using two main approaches, i) direct measurement of the amount or behaviour of the microbial biomass residing in the waste, and ii) measurement of gaseous transfer (CO₂ production or O₂ uptake) associated with microbial activity. The former approach has been made using a number of methods. Bellon-Maurel et al. (2003) used a variety of sensing
systems to monitor the microbial biomass content of waste which included infra-red spectrometry, artificial vision, and magnetic resonance imaging. Reactive forms of N extracted by the fumigation extraction technique were used by Mondini et al. (2002) and were found to correlate strongly with microbial biomass content. The measurement of phospholipid fatty acid and RNA material in composting waste were measured by Carpenter-Boggs et al. (1998) and Liwarska-Bizukojc & Ledakowicz (2003), both as a way of tracking microbial communities during composting. The techniques used for biomass measurements were likely to have been suitable as methods of assessing the biodegradability of wastes, however most techniques used are complex and may prove to vary in replication.

Measurement of the CO₂ production or O₂ uptake associated with aerobic microbial activity has been in use for some time to monitor the composting process. It is commonly termed ‘respirometry’ and can provide data that reflects the rate of organic matter decomposition (Haug 1993). This method of composting analysis was first employed as a way of understanding the composting process. Clark et al. (1978) used the measurement of CO₂ production to test the effects of varying moisture content, temperature and N content on the composting process using a laboratory composting system (described in Clark et al. (1977)). Similar tests were undertaken by Suler & Finstein (1977) using a laboratory ‘compost production system’ to measure both CO₂ production and O₂ uptake. Mote and Griffis (1978) (and more recently VanderGheynst et al. 1997) also used a bench scale system for compost process analysis demonstrating the self heating properties of various wastes. The good reproducibility of data using a system with temperature control was described by Ashbolt & Line (1982), with Deschamps et al. (1982) demonstrating similar reproducibility in the study of the improvement of solid urban waste composting. Both Magalhaes et al. (1993) and Sikora et al. (1983) describe the simulation of composting in the laboratory using respirometry systems as being a good simulation of large-scale systems.
Laboratory respirometry systems are now commonly used to assess the degree of stabilisation in a compost sample, as was first described by Pressel & Bidlingmaier (1981) in the use of respirometry to indicate the state of decomposition. Stability of a waste is regarded as being the degree to which readily degradable organic matter has decomposed (Lasaridi & Stentiford 1998), therefore respirometry gives a good indication of the biodegradability of a waste. A variety of tests have been developed to assess biodegradability using respirometry. Lasaridi & Stentiford (1998) describe the use of an aqueous respirometry system to measure the specific oxygen uptake rate (SOUR) of a compost sample in suspension. This system maximises oxygen uptake rate. However the size of the samples used (3 – 8 g) may be too small due to the heterogeneity of municipal solid waste (MSW). Two other methods of determining the respiration rate of the microbial population within a compost sample are commonly referred to as the dynamic respiration index (DRI) and static respiration index (SRI). The latter refers to the method of measuring CO$_2$ production and O$_2$ uptake by measuring concentration change over time in the headspace of a closed vessel containing a compost sample (Iannotti et al. 1993). The SRI however has been shown to result in an underestimation of the O$_2$ consumption potential of a sample by over 200% (Scaglia et al. 2000). Measurement of biological stability is most commonly made using the DRI method which measures CO$_2$ and O$_2$ concentrations before and after air has been passed through a compost sample. The CO$_2$ production and O$_2$ uptake of waste sample can be made from calculations using gas analysis data before and after the sample, air flow rate through the waste, amount of waste tested, and duration of the test. This method is used in Adani et al. (2001) on the study of MSW stability (reporting the mean of 24 hours of highest O$_2$ uptake rate) and has been made the standard test method for waste stability in the USA (ASTM D5975-96) and Germany (AT4) (both calculating the 4 day cumulative O$_2$ uptake). The biodegradability of plastics are also assessed using dynamic respiration, as described in Jayasekara et al. (2001), and British Standard BS ISO 14855:1999. The respirometer used in Chapters 2, 3, and 5 of this study operates using the dynamic system for either CO$_2$ production or O$_2$ uptake.
The respirometer developed throughout the course of this study (Chapters 2, 3, 5, and 6) was used to perform a variety of tests to arrive at a suitable method of biodegradability determination. The details of the various methods used are described in section 7.1.2, and results of these tests are presented in section 7.1.3. The final method (now called the DR4) was considered to be the most suitable for this analysis is described in 7.1.4 and was applied in the experiment to better understand the relationship between biodegradability and CH$_4$ and N$_2$O generation and emission detailed in Part 2 of this chapter.

7.1.2 Materials and methods

The respirometer used throughout this study was adapted to perform analysis required for the development of a UK standard test for the determination of waste biodegradability commissioned by the Environment Agency. Adaptations made to the respirometer used in other chapters were the extension of the number of sample chambers to 12 smaller chambers (120 cm diameter, 40 cm high cylinders) allowing more variables to be tested with better replication. To compare with simultaneous tests being undertaken WRc PLC the 4-day cumulative O$_2$ uptake rate was used for reporting and was referred to as the DR4 amount.

A number of variations in the preparation of the waste samples to be tested and the operating parameters of the respirometer were made to optimise the DR4 test. This optimisation of the method was performed to produce a test that would be reproducible when done at different laboratories (using different apparatus), involve minimal sample preparation, and provide the best indication of waste biodegradability. The main aim of the research was to identify those key parameters, which most influenced the level of respiration for appropriate sample types. Secondly, selected parameters such as particle size were set at levels to enable comparisons to be made with respiration rates as
determined by the Open University "draft standard method" which is described in section 2.5 of the Methods Chapter.

Table 7.1 shows the sample preparation and respirometer operation parameters used during the development of the DR4 test. Unless stated otherwise this draft standard test method was used; the samples were tested at 35°C (maintained by water bath), were prepared to a moisture content of 50%, contained 100 g dry matter test waste sample and 100 g dry matter seed compost (used to provide an inoculating bacterial population), the aeration flow rate used was 500 ml minute⁻¹, and the waste sample was taken from the organic fraction of MSW (shredded to 20 mm unless otherwise stated). Respiration rates shown are the mean of three replicates. Waste samples were supplied unprepared by WRc PLC. 30kg of MSW were collected from the waste processing site (5 samples of approximately 6kg each) operating a mechanical and biological treatment batch process. Waste sampling was undertaken by WRc PLC.
Table 7.1 Treatments tests during development of the DR4 waste biodegradability test.

Unless stated otherwise the draft standard test method was used

<table>
<thead>
<tr>
<th>Test method</th>
<th>Variation in sample preparation method</th>
<th>Variation in respirometer operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (draft standard)</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>None</td>
<td>Test performed room temperature (around 20°C)</td>
</tr>
<tr>
<td>3</td>
<td>None</td>
<td>Test performed at 50°C</td>
</tr>
<tr>
<td>4</td>
<td>Different inoculum used (provided by WRc PLC)</td>
<td>None</td>
</tr>
<tr>
<td>5</td>
<td>None</td>
<td>Flow rate set to 250 ml minute⁻¹</td>
</tr>
<tr>
<td>6</td>
<td>Double amount inoculum and waste test sample</td>
<td>None</td>
</tr>
<tr>
<td>7</td>
<td>Inert plastic added, doubling sample volume</td>
<td>None</td>
</tr>
<tr>
<td>8</td>
<td>Test sample shredded to &lt;10 mm particle size</td>
<td>None</td>
</tr>
<tr>
<td>9</td>
<td>Waste sample dried and ground (prepared by WRC)</td>
<td>None</td>
</tr>
<tr>
<td>10</td>
<td>Supplementing sample with N and P*</td>
<td>None</td>
</tr>
</tbody>
</table>

*40 ml of 2 M NH₄Cl per 100 g of test sample (dry weight) – supplying 0.28 g N and 8 ml of 2 M KH₂PO₄ per 100 g test sample (dry weight) – supplying 0.124 g P.

In addition to work described above, an inter-laboratory trial was undertaken. This was carried out to test the reproducibility of the DR4 method, four different samples of MBT waste that had been partially composted were tested by four separate test laboratories.

7.1.3 Results

Table 7.2 below gives respiration rates for the various treatments selected for the development of the DR4 test (described in Table 7.1). The treatments giving the highest
respiration rates were selected for incorporation into the DR4 test method. The DR4 test method was subjected to inter-laboratory trial with each laboratory measuring the biodegradability of four different wastes that had been partially composted. Results showing a comparison of Open University with results from WRc PLC only are presented in Figure 7.1. There is strong correlation between the data derived by WRc PLC and the Open University ($R^2 = 0.97$).

Table 7.2 Respiration rates for the selected treatments as described in Table 7.1. The range of results is shown in brackets

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Respiration rate (mgO$_2$ kgDM$^{-1}$ 96hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46948 (38779 – 61345)</td>
</tr>
<tr>
<td>2</td>
<td>16767 (single rep)</td>
</tr>
<tr>
<td>3</td>
<td>59951 (59353 – 62612)</td>
</tr>
<tr>
<td>4</td>
<td>42167 (single rep)</td>
</tr>
<tr>
<td>5</td>
<td>67717 (single rep)</td>
</tr>
<tr>
<td>6</td>
<td>62837 (single rep)</td>
</tr>
<tr>
<td>7</td>
<td>52203 (single rep)</td>
</tr>
<tr>
<td>8</td>
<td>64690 (single rep)</td>
</tr>
<tr>
<td>9</td>
<td>48203 (43945 – 52460)</td>
</tr>
<tr>
<td>10</td>
<td>57640 (51348 – 61388)</td>
</tr>
</tbody>
</table>
7.1.4 DR4 test method

A brief description of the standard test method (DR4) used in Part 2 of this chapter for biodegradability determination is as follows:

- **Respirometer vessels**
  Cylindrical vessels of 100 – 120 mm diameter and 2.5 litres volume with a perforated false bottom that allows an even gas purge in an upward direction, and sealed at the top with a bung and gas exhaust outlet.

- **Inoculum compost source**
  The inoculum compost should be a mature compost derived from a commercial composting site preferably treating MSW or green waste.
• Inoculum storage
The inoculum compost may be stored in a cold room at < 5 °C until required. The microbial activity to be restored before use by incubating the compost seed at room temperature for at least 48 hours before use.

• Inoculum preparation and analysis
The inoculum compost should be sieved through a 10 mm sieve to remove all large particles. The sieved material should be analysed for moisture and dry matter content, loss on ignition and ash content, TOC, total N, and P.

• Test organic waste
This should comprise the BMW (biodegradable municipal waste) sample prepared by drying at 80°C and grinding. The dried and ground sample dry matter (at 103°C) and loss on ignition (at 550°C) should be determined. The prepared test material should be stored cold at < 5°C until required but used within weeks of preparation to avoid any decomposition before testing.

• Mixture of inoculum and test organic waste
The test mixture is prepared by mixing thoroughly 100 g by dry weight of test waste with 100 g by dry weight of seed compost. The green waste inoculum is also used as control and is composed of 200 g by dry weight.

• Nutrient addition (N and P) and moisture adjustment
The (100 g) test mixture is supplemented with the following nutrients as a measure to ensure sufficient nutrients are present for microbial growth. The amounts added should supplement any deficiency in the mixture and are 10 ml of 2 M NH₄Cl (supplying approximately 0.28 g N per 100 g test substrate dry weight), and 2 ml of 2 M KH₂PO₄ (supplying 0.124 g P per 100 g test substrate). The test mixture is
supplemented with distilled or de-ionised water to give a final moisture content of 50% on a wet weight basis, i.e. 200 g total water. The amount of water added takes into account the moisture already in the waste and seed, and that added in the nutrient additions. The water and nutrient are mixed first and then added to the seed/compost mixtures and thoroughly mixed to ensure the mixture is evenly wetted. Calculation of the required water addition is made as follows: Water added = 200 - (g moisture in inoculum + g moisture in test waste + 12).

- Setting up the system

Each test vessel is supplied with 400 g of prepared test mixture (200 g test waste, 200 g inoculum, thoroughly mixed at 50% moisture content). Each respirometry run should consist of at least: 1 empty blank, 1 inoculum control, and 3 test waste samples.

- Respirometry temperature

The respirometry temperature is set at 35°C.

- Air supply

This may be provided by a pump or gas cylinder, or by a pump that sucks the gas through the system, i.e. after the composting stage. Ideally the system should be free from leaks.

- Exhaust gas monitoring

Connect the exhaust gas streams to the on-line CO₂ and/or O₂ monitor. Ensure the gas is dewatered before it enters the monitoring instruments.

- Air flow

Set the airflow to 2.5 l/kg dry matter minute⁻¹ in each vessel, i.e. 500 ml minute⁻¹.
• On-line exhaust gas monitoring
If the exhaust gas is monitored automatically by an on-line monitor then it is vital that accurate gas flow measurements are taken as well and therefore careful monitoring of the gas flow rate is required.

• Results expression
The results are expressed in terms of a DR4 value (four day cumulative oxygen consumption) by summing the data of the four days and expressing the results in terms of both loss on ignition (LOI) and dry matter (DM), i.e. mg O kg\(^{-1}\) LOI and mg O kg\(^{-1}\) DM respectively.
Part 2 Effect of waste biodegradability on CH₄ and N₂O production

7.2.1 Introduction

A number of studies have been undertaken to identify causes of emission, however the relationship between the organic carbon forms (and therefore biodegradability) and emission of CH₄ and N₂O however hasn't been fully studied. There has been a recent drive, in the waste industry, to apply composting techniques to the processing of other organic wastes (Slater et al. 2005). The purpose of this processing is not to produce a compost product but to render organic wastes as stable (stability definition – Chapter 2) prior to landfill in compliance with the EU landfill directive. Many of these wastes have much higher putrescible organic material content (kitchen waste and MSW) than green waste, and therefore potentially more labile organic compounds (Liwarska-Bizukojc et al. 2002). The effect this change in waste composition would have on the way composting produces and emits CH₄ & N₂O and the timing of the release is unknown. A comparison of the potential to emit CH₄ & N₂O from wastes of differing biodegradability may give an indication of the effect of diverting organic wastes away from landfill.

Gilbert et al. (2004) studied biodegradation and waste characterisation in a study of the biological mitigation of acid mine drainage and found that the lower the lignin content in the organic substrate, the higher the biodegradability and capacity for developing microbial activity. This effect of lignin on inhibition of biodegradability is detailed by Haug (1993) finding that lower lignin content correlates with higher biodegradability. Lignin is one of the three major constituents of plant cell wall material (Richard 1996), the others being cellulose and hemicellulose. The biodegradability of these components of organic waste has been described by Haug (1993) as being 90, 70, and 0% for cellulose, hemicellulose and lignin respectively. Therefore the relative amounts of these compounds
within a composting mass will dictate the extent of degradation potential (Komilis & Ham 2003). Figure 7.2 shows the types and typical amounts of carbon found in plant residues as they enter the waste stream. Cellulose consists of chains of simple sugar molecules (mostly glucose and are, along with hemicellulose the major structural molecules used by plants (Haug 1993). Cellulose is readily degradable requiring only a small number of enzymes to be broken down (Richard 1996). Hemicellulose is more recalcitrant than cellulose as it is comprised of branched polymers of sugars that also cross link with lignin providing a challenge to microbial degradation (Lynch 1992). Lignin is the organic compound most resistant to biodegradation, it is a complex polymer of phenylpropane molecules (Richard 1996), it is hydrophobic (Gracia-Gomez *et al.* 2005), and is described by Ahmed *et al.* (2001) as being a molecular network in the plant cell wall such that the whole of the plant contains a continuously connected lignin molecule. The purpose of lignin within plant cell structures is to provide protection from pathogen invasion (Haug 1993) and it is this function that results in its resistance to biodegradation. Eklind & Kirchmann (2000) in the study of C and N turnover and losses from composting, a study which highlighted hardwood as being more biodegradable that softwood due to higher lignin contents in the soft wood.

![Graph showing types and typical amounts of carbon compounds in plant residues](image)

Figure 7.2 Types and typical amounts of carbon compounds present in plant residues as they enter the waste stream (from Brady 1997)
Studies detailed in the previous chapters have shown that in all cases composting is a source of both \( \text{CH}_4 \) and \( \text{N}_2\text{O} \). A number of the operational parameters of a composting process have been identified throughout the course of this study as having an influence on greenhouse gas emissions including; composting \( \text{O}_2 \) load, composting system type, and composting process temperature and moisture content. All these factors have an influence on the microbial activity and therefore \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) production. Understanding of the carbon decomposition dynamics was considered as being important in the overall understanding of the composting process. Composting has been found to be a complex process where aerobic degradation occurs alongside anaerobic microbial processes at differing temperatures and oxygen concentrations. In this chapter the effect of the biodegradability of the waste being composted on emission of \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) is examined.

Project Aim

To monitor emission of \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) from composting for two synthetic wastes (high and low biodegradability) when supplied with either sufficient or insufficient \( \text{O}_2 \).

Project objectives

1. To test the hypothesis that increasing the biodegradability of a synthetic material, as determined by the DR4 test, would increase \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) emissions, when composted using either high or low aeration rates.
2. To test the hypothesis that increased aeration during composting would reduce emission of \( \text{CH}_4 \) and that this effect would be more pronounced for the high biodegradable material compared with the low biodegradable material.
3. To test the hypothesis that increased aeration during composting would increase emission of \( \text{N}_2\text{O} \) and that this effect would be more pronounced for the high biodegradable material compared with the low biodegradable material.
7.2.2 Materials and methods

7.2.2.1 Sample preparation

Two simulated organic wastes were produced to test the relationship between biodegradability and CH$_4$ and N$_2$O emission. Table 7.3 shows the lignin, hemicellulose, cellulose, protein, fat, starch, glucose, and hot water soluble matter content of a variety of wastes. To simulate two wastes of differing biodegradability laboratory grade organic compounds were obtained and made up to provide artificial high and low biodegradability samples, the C:N of the samples was kept equal, and throughout biodegradability and CH$_4$ and N$_2$O emission analysis the moisture content of the samples was adjusted to 50%. Table 7.4 shows C, N, and H$_2$O content of the organic compounds used to produce the two simulated wastes (mean of 2 replicates, methods for these analyses are described in the Methods Chapter, section 2.6). The compounds used were; untreated softwood as a lignin substitute (having approximately 40% lignin (Ahmed et al. 2001), cellulose, corn starch, albumen (simulating protein), and pectin (to simulate hot water soluble matter).
Table 7.3 Lignin, hemicellulose, cellulose, protein, fat, starch, glucose, and hot water soluble matter content of a variety of wastes

<table>
<thead>
<tr>
<th>Waste</th>
<th>Lignin %DW</th>
<th>Hemicellulose %DW</th>
<th>Cellulose %DW</th>
<th>Protein %DW</th>
<th>Fats %DW</th>
<th>Starch %DW</th>
<th>Glucose %DW</th>
<th>Hot water soluble matter %DW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh plant³</td>
<td>15</td>
<td>20</td>
<td>50</td>
<td>5</td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Green waste¹</td>
<td>25</td>
<td>-</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biosolids</td>
<td>25</td>
<td>-</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MSW¹²</td>
<td>10</td>
<td>10</td>
<td>55</td>
<td>4</td>
<td>8</td>
<td>7</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Tree &amp; brewery¹</td>
<td>28</td>
<td>26</td>
<td>35</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Olives &amp; cotton¹</td>
<td>42</td>
<td>30</td>
<td>22</td>
<td>-</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Olives &amp; leaves¹</td>
<td>37</td>
<td>26</td>
<td>13</td>
<td>-</td>
<td>15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Food waste²</td>
<td>12</td>
<td>0</td>
<td>46</td>
<td>-</td>
<td>13</td>
<td>6</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>Yard waste²</td>
<td>24</td>
<td>11</td>
<td>27</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Mixed paper²</td>
<td>16</td>
<td>7</td>
<td>70</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>MSW²²</td>
<td>17</td>
<td>7</td>
<td>47</td>
<td>-</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Grass²</td>
<td>17</td>
<td>17</td>
<td>40</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>Leaves²</td>
<td>33</td>
<td>4</td>
<td>10</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Branches²</td>
<td>42</td>
<td>13</td>
<td>15</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Office paper²</td>
<td>6</td>
<td>7</td>
<td>70</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Dutch MSW</td>
<td>10</td>
<td>10</td>
<td>13</td>
<td>3</td>
<td>-</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>News paper²</td>
<td>21</td>
<td>16</td>
<td>61</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Agrarian residue⁴</td>
<td>-</td>
<td>17</td>
<td>32</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cassava residue⁴</td>
<td>4</td>
<td>40</td>
<td>4</td>
<td>2</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mean</td>
<td>21</td>
<td>15</td>
<td>35</td>
<td>3</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

- denotes no data given

Source:
¹Garcia-Gomez et al. (2005).
²Komilis & Ham (2003).
³Haug (1993).
⁴Eklind & Kirchmann (2000).
Table 7.5 shows amounts of each fraction of organic compound used to simulate the high and low biodegradability organic wastes and were based around the mean of the organic fractions shown in Table 7.3. The lower biodegradability sample had higher lignin (untreated softwood used), and lower protein (albumen used) and starch contents than the mean. The higher biodegradability simulated sample had lower lignin, and higher protein and starch contents than the mean. Both mixtures were made up to a C:N of 26:1 (within the optimal 20 – 30:1 range for composting (Fricke & Vogtmann 1993)).

Table 7.4 C, N, and $\text{H}_2\text{O}$ content of the untreated softwood, cellulose, corn starch, albumen, and pectin used to produce the two simulated wastes (mean of two replicates). Individual repetitions are shown in brackets.

<table>
<thead>
<tr>
<th>Organic fraction</th>
<th>Organic C%</th>
<th>Total Kjeldahl N%</th>
<th>$\text{H}_2\text{O}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pectin</td>
<td>37.9</td>
<td>0.4</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>(37.1, 38.6)</td>
<td>(0.4, 0.4)</td>
<td>(7.5, 7.6)</td>
</tr>
<tr>
<td>Albumen</td>
<td>53.1</td>
<td>12.9</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>(52.9, 53.3)</td>
<td>(12.7, 13.1)</td>
<td>(5.6, 5.6)</td>
</tr>
<tr>
<td>Starch</td>
<td>41.4</td>
<td>0.1</td>
<td>11.9</td>
</tr>
<tr>
<td></td>
<td>(41.2, 41.6)</td>
<td>(0.1, 0.1)</td>
<td>(11.8, 11.9)</td>
</tr>
<tr>
<td>Cellulose</td>
<td>54.4</td>
<td>0.0</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>(54.1, 54.7)</td>
<td>(0.0, 0.0)</td>
<td>(5.7, 5.8)</td>
</tr>
<tr>
<td>Softwood</td>
<td>51.8</td>
<td>0.3</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>(51.4, 52.1)</td>
<td>(0.3, 0.4)</td>
<td>(23.7, 24.5)</td>
</tr>
</tbody>
</table>

Table 7.5 Amounts of each fraction of organic compound listed in Table 7.4 used to simulate 100 g of the high and low biodegradability organic wastes.

<table>
<thead>
<tr>
<th>Organic fraction</th>
<th>High biodegradability (g dry matter)</th>
<th>Low biodegradability (g dry matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pectin</td>
<td>7.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Albumen</td>
<td>8.0</td>
<td>7.6</td>
</tr>
<tr>
<td>Starch</td>
<td>25.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Cellulose</td>
<td>50.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Soft Wood</td>
<td>10.0</td>
<td>70.0</td>
</tr>
</tbody>
</table>
Table 7.7 shows the results of physico-chemical analysis (ion chromatography analysis, C:N, conductivity, pH, acid detergent fibre (ADF), and neutral detergent fibre content (NDF)) of the high and low biodegradability simulated organic wastes (methods for this analysis are described in section 2.6 of the Methods Chapter). Neutral Detergent fibre is the total hemicellulose, cellulose and lignin content, and acid detergent fibre consists primarily of lignin and cellulose. Table 7.6 gives results of the respiration rates of the high and low biodegradability simulated organic wastes (mean of three replicates, using the DR4 standard method described in Part 1 of this chapter).

Table 7.6 gives results of the respiration rates of the high and low biodegradability simulated organic wastes (mean of three replicates, using the DR4 standard method). The range of results is shown in brackets.

<table>
<thead>
<tr>
<th>Artificial organic waste sample</th>
<th>Respiration rate (DR4) (mgO2 kgVS⁻¹ 96hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 High biodegradability</td>
<td>320400 (288500 – 313000)</td>
</tr>
<tr>
<td>2 Low biodegradability</td>
<td>129900 (120000 – 141100)</td>
</tr>
</tbody>
</table>

The apparatus used for DR4 respiration analysis was used to test the potential of the two artificial organic wastes to produce CH₄ and N₂O under simulated composting conditions. The twelve chambers of the DR4 system were used in which four treatments were tested (described in Table 7.8). The four treatments comprised 3 replicates of the high biodegradability waste aerated with sufficient O₂ supply, 3 replicates of the high biodegradability waste with insufficient O₂ supply, 3 replicates of the low biodegradability waste at sufficient O₂ supply, and 3 replicates of the low biodegradability waste at...
insufficient O₂ supply. The two aeration flow rates used for this test were chosen to provide both sufficient O₂ supply (250 ml minute⁻¹) and insufficient O₂ supply (10 ml minute⁻¹) to the composting waste. Calculation of the O₂ requirement of the two samples was made based on the results from the DR4 data which showed the low biodegradability waste demanded up to approximately 11 mg O₂ minute⁻¹ (equating to approximately 40 ml minute⁻¹ air flow rate), and the high biodegradability waste demanded up to approximately 19 mg O₂ minute⁻¹ (equating to approximately 75 ml minute⁻¹ air flow rate).

In an attempt to replicate actual composting conditions the temperature of the test period was maintained within the thermophilic range (50°C). This temperature was as close to the thermophilic methanogenesis maximum temperature of 55°C as was practical for the apparatus. Mata-Alvares (2003) give 55°C as being the temperature at which biogas yield is maximised during the anaerobic digestion of MSW.

The sample size used was double that for the DR4 test (200 g dry matter waste sample and 200 g dry matter inoculum), this therefore allowed a higher flow rate to be used at a more manageable level (flow rates were difficult to maintain below 10 ml minute⁻¹), particularly for the low biodegradability waste supplied with insufficient O₂ supply. The samples were subjected to these conditions for 21 days, as was the case in the biochemical methane potential test used by Heo et al. (2003) in the study of MSW solubilisation, and was deemed a suitable test duration as it was shown by Hansen et al. (2004) that 80-90% of methane potential was produced during the first 8-10 days of a similar test. Measurement of the CO₂ and O₂ concentration (%) of the air exiting the chambers was taken daily for the 21 days test period using (Sable systems CO₂ and O₂ analysers used in the DR4 test). Samples were also taken for GC analysis of CH₄ and N₂O (using a 60 ml brufix syringe) from the exhaust of the chambers. Exhaust air was also analysed for NH₃ (Drager Multiwarn), and VOC content (using a dual flame ionisation detector and photo ionisation detector TVA1000B hydrocarbon analyser). Flow rates were checked 3 times per day to ensure a steady flow rate into the chambers.
Table 7.8 Number of replicates of the four treatments used to test the effect of biodegradability on CH₄ and N₂O production

<table>
<thead>
<tr>
<th></th>
<th>250 ml minute⁻¹ aeration rate</th>
<th>10 ml minute⁻¹ aeration rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 High Biodegradability</td>
<td>3 replicates</td>
<td>3 replicates</td>
</tr>
<tr>
<td>2 Low biodegradability</td>
<td>3 replicates</td>
<td>3 replicates</td>
</tr>
</tbody>
</table>

On completion of the 21 day test period the 12 samples were taken from the chambers, weighed, and the physico-chemical characteristics of the samples were measured (organic C, total Kjeldahl N, pH, conductivity, and Ion chromatograph analysis).
Table 7.7 Physico-chemical characteristics (includes; ion chromatography analysis, C:N, conductivity, pH, acid detergent fibre, and neutral detergent fibre content) of the high and low biodegradability simulated organic wastes. Individual repetitions are shown in brackets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH (water extract)</th>
<th>Conductivity Ec (mS cm⁻¹)</th>
<th>C:N</th>
<th>Na mg kg⁻¹</th>
<th>NH₄ mg kg⁻¹</th>
<th>K mg kg⁻¹</th>
<th>Mg mg kg⁻¹</th>
<th>Ca mg kg⁻¹</th>
<th>F mg kg⁻¹</th>
<th>Cl mg kg⁻¹</th>
<th>NO₃ mg kg⁻¹</th>
<th>PO₄ mg kg⁻¹</th>
<th>SO₄ mg kg⁻¹</th>
<th>Acid detergent fibre (%)</th>
<th>Neutral detergent fibre (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 High Biodegradability</td>
<td>4.6</td>
<td>1.0</td>
<td>26:1</td>
<td>0.0</td>
<td>(0.0, 0.0)</td>
<td>17</td>
<td>(16, 19)</td>
<td>413</td>
<td>72</td>
<td>(63, 81)</td>
<td>(358, 467)</td>
<td>(128, 179)</td>
<td>(319, 340)</td>
<td>318</td>
<td>17 (12, 23)</td>
</tr>
<tr>
<td>2 Low Biodegradability</td>
<td>4.5</td>
<td>1.8</td>
<td>26:1</td>
<td>0.0</td>
<td>(0.0, 0.0)</td>
<td>19</td>
<td>(14, 25)</td>
<td>393</td>
<td>90</td>
<td>(60, 120)</td>
<td>(326, 459)</td>
<td>(59, 117)</td>
<td>(191, 327)</td>
<td>0.0</td>
<td>16 (14, 18)</td>
</tr>
</tbody>
</table>
7.2.3 Results

Tables 7.9 – 7.15 show the measured concentrations of CH₄ (ppm), N₂O (ppm), CO₂ (%), O₂ (%), NH₃ (ppm), VOC (ppm - flame ionisation detector), and VOC (ppm - photo ionisation detector) in the exhaust air of the chambers (mean of 3 replicates) for each day of the 21 day study period. Concentrations of these gases in the exhaust air for each individual repetition are shown in Tables A.I.3 – A.I.9. Comparison of the mean emission concentrations during the 21 day test period of CH₄ and N₂O from each treatment was made using a repeated measure multivariate test of significance (Statistica software), in all cases the difference in 21 day mean emission between all four treatments was found be significant (p < 0.01).

Table 7.16 shows the physico-chemical characteristics including ion chromatography analysis, organic C, total Kjeldahl N (mean of 3 repetitions), conductivity, and pH, of the four treatments after the 21 day test period. Table 7.17 shows loss of C and N from the treatments as CH₄ and N₂O (based on the 21 day mean CH₄ and N₂O emission rates and converted to weight using equation 2.5 in the methods chapter), total organic C and Kjeldahl N (g) loss from the waste samples (measurement of C and N is detailed in section 2.6 of the Methods Chapter, loss of N was corrected for the concentration effect due to the reduction in organic matter during composting as described in Chapter 5), and weight loss of the samples (g) after the 21 day test period (all mean of 3 replicates).
Table 7.9 Mean concentration of CH$_4$ (ppm) in the exhaust air from the chambers for each day of the 21 day study period (CH$_4$ concentration in exhaust air for each individual repetition is shown in Table A.I.1)

<table>
<thead>
<tr>
<th>Sampling day</th>
<th>CH$_4$ (ppm) (low biodegradability with insufficient aeration)</th>
<th>CH$_4$ (ppm) (high biodegradability with insufficient aeration)</th>
<th>CH$_4$ (ppm) (low biodegradability with sufficient aeration)</th>
<th>CH$_4$ (ppm) (high biodegradability with sufficient aeration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>4</td>
<td>4.8</td>
<td>5.2</td>
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Table 7.10 Mean concentration of N\textsubscript{2}O (ppm) in the exhaust air from the chambers for each day of the 21 day study period (N\textsubscript{2}O concentration in exhaust air for each individual repetition is shown in Table A.1.2)

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<th>N\textsubscript{2}O (ppm) (high biodegradability with insufficient aeration)</th>
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Table 7.11 Mean concentration of CO₂ (%) in the exhaust air from the chambers for each day of the 21 day study period (CO₂ concentration in exhaust air for each individual repetition is shown in Table A.I.3)

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Table 7.12 Mean concentration of $O_2$ (%) in the exhaust air from the chambers for each day of the 21 day study period ($O_2$ concentration in exhaust air for each individual repetition is shown in Table A.1.4)

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Table 7.13 Mean concentration of NH₃ (ppm) in the exhaust air from the chambers for each day of the 21 day study period (NH₃ concentration in exhaust air for each individual repetition is shown in Table A.1.5)

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-Denotes not detected.
Table 7.14 Mean concentration of VOC (ppm - flame ionisation detector (FID)) in the exhaust air from the chambers for each day of the 21 day study period (VOC concentration in exhaust air for each individual repetition is shown in Table A.I.6)

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<td>169.2</td>
</tr>
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<td>12</td>
<td>1073</td>
<td>2642</td>
<td>10.3</td>
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<td>2680</td>
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<td>7.0</td>
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<td>760</td>
<td>2494</td>
<td>6.8</td>
<td>14.9</td>
</tr>
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<td>740</td>
<td>2383</td>
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<td>667</td>
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<td>6.2</td>
<td>11.5</td>
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<td>5.1</td>
<td>9.6</td>
</tr>
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<td>2007</td>
<td>3.0</td>
<td>9.6</td>
</tr>
<tr>
<td>Mean</td>
<td>914</td>
<td>2273</td>
<td>12.3</td>
<td>149.9</td>
</tr>
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</table>
Table 7.15 Mean concentration of VOC (ppm - flame ionisation detector (PID)) in the exhaust air from the chambers for each day of the 21 day study period (VOC concentration in exhaust air for each individual repetition is shown in Table A.1.7)

<table>
<thead>
<tr>
<th>Sampling day</th>
<th>VOC (ppm PID) (low biodegradability with insufficient aeration)</th>
<th>VOC (ppm PID) (high biodegradability with insufficient aeration)</th>
<th>VOC (ppm PID) (low biodegradability with sufficient aeration)</th>
<th>VOC (ppm PID) (high biodegradability with sufficient aeration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>3.2</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>22.9</td>
<td>43.9</td>
<td>6.0</td>
<td>9.3</td>
</tr>
<tr>
<td>3</td>
<td>23.8</td>
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<td>4</td>
<td>30.1</td>
<td>47.8</td>
<td>7.0</td>
<td>15.4</td>
</tr>
<tr>
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<td>41.2</td>
<td>4.9</td>
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</tr>
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<td>26.1</td>
<td>28.4</td>
<td>4.0</td>
<td>15.1</td>
</tr>
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</tr>
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<td>28.9</td>
<td>3.1</td>
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</tr>
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<tr>
<td>12</td>
<td>15.7</td>
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<td>1.0</td>
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<tr>
<td>13</td>
<td>10.1</td>
<td>26.0</td>
<td>1.0</td>
<td>8.0</td>
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<tr>
<td>14</td>
<td>9.0</td>
<td>25.6</td>
<td>1.1</td>
<td>6.0</td>
</tr>
<tr>
<td>15</td>
<td>8.2</td>
<td>25.5</td>
<td>1.0</td>
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</tr>
<tr>
<td>16</td>
<td>7.0</td>
<td>19.2</td>
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<td>4.0</td>
</tr>
<tr>
<td>17</td>
<td>7.2</td>
<td>15.9</td>
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<tr>
<td>18</td>
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<td>19</td>
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<td>-</td>
<td>1.0</td>
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<tr>
<td>20</td>
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<td>1.0</td>
</tr>
<tr>
<td>21</td>
<td>2.0</td>
<td>13.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mean</td>
<td>15.4</td>
<td>26.2</td>
<td>2.3</td>
<td>7.8</td>
</tr>
</tbody>
</table>

-Denotes not detected.
Table 7.16 Physico-chemical characteristics (includes; weight of sample, ion chromatography analysis, C:N, conductivity, pH,) of the four treatments after the 21 day test period. The range of results are shown in brackets

| Sample                        | pH water extract | Conductivity Ec (mS cm⁻¹) | Organic C (%) | Total Kjeldahl N (%) | Na mg kg⁻¹ | NH₄⁺ mg kg⁻¹ | K mg kg⁻¹ | Mg mg kg⁻¹ | Ca mg kg⁻¹ | F mg kg⁻¹ | Cl mg kg⁻¹ | NO₃⁻ mg kg⁻¹ | PO₄³⁻ mg kg⁻¹ | SO₄²⁻ mg kg⁻¹ |
|-------------------------------|------------------|---------------------------|---------------|----------------------|------------|--------------|-----------|------------|-----------|-----------|-------------|----------------|----------------|
| Low biodegradability         | 7.7              | 0.71                      | 32 (31-33)    | 1.4                  | 150 (143-157) | 76 (28-112) | 44 (397-520) | -          | 303 (40-788) | 5.0       | 226 (96-437) | 49 (16-52)       | -              | 154 (99-260)     |
| with insufficient aeration    |                  |                           |               |                      |            |              |           |            |           |           |             |                 |                 |
| High biodegradability        | 6.7              | 0.81                      | 31 (31-32)    | 1.5                  | 167 (137-202) | 63 (49-74)  | 411 (363-465) | -          | 247 (125-362) | 0.5       | 93 (75-112)  | 3.5 (2.2-7.5)    | -              | 22 (16-26)        |
| with insufficient aeration    |                  |                           |               |                      |            |              |           |            |           |           |             |                 |                 |
| Low biodegradability         | 7.9              | 0.60                      | 29 (28-30)    | 1.5                  | 110 (95-121) | 32 (17-42)  | 378 (333-436) | -          | 96 (58-142)  | 0.4       | 113 (67-166) | 17 (12-21)       | -              | 85 (57-127)       |
| with sufficient aeration      |                  |                           |               |                      |            |              |           |            |           |           |             |                 |                 |
| High biodegradability        | 6.8              | 0.58                      | 28 (27-29)    | 1.6                  | 158 (151-168) | 58 (30-98)  | 373 (324-434) | -          | 354 (69-907) | 0.4       | 86 (34-172)  | 24 (5-59)        | -              | 24 (16-28)        |
| with sufficient aeration      |                  |                           |               |                      |            |              |           |            |           |           |             |                 |                 |

- Denotes not detected.
Table 7.17 Loss of C and N (g) from the four treatments as CH$_4$ and N$_2$O during the 21 day study period (based on the 21 day mean CH$_4$ and N$_2$O emission rates), total organic C and Kjeldahl N (g) loss from the waste samples, and wet weight of the samples after the 21 day test period (all mean of 3 replicates). Range of results is shown in brackets.

<table>
<thead>
<tr>
<th></th>
<th>Total C loss as CH$_4$ (g)</th>
<th>Total N loss as N$_2$O (g)</th>
<th>Total organic C loss (g)</th>
<th>Total Kjeldahl N loss (g)</th>
<th>Total weight loss of samples (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>low biodegradability with Insufficient aeration</td>
<td>0.12 (0.11 - 0.13)</td>
<td>0.003 (0.003 - 0.004)</td>
<td>59.6 (57.2 - 60.9)</td>
<td>1.12 (1.02 - 1.31)</td>
<td>113 (122 - 106)</td>
</tr>
<tr>
<td>high biodegradability with Insufficient aeration</td>
<td>0.34 (0.30 - 0.38)</td>
<td>0.004 (0.003 - 0.004)</td>
<td>60.9 (58.8 - 62.5)</td>
<td>1.31 (1.22 - 1.37)</td>
<td>148 (137 - 161)</td>
</tr>
<tr>
<td>low biodegradability with sufficient aeration</td>
<td>0.03 (0.03 - 0.03)</td>
<td>0.011 (0.010 - 0.013)</td>
<td>63.1 (59.4 - 65.3)</td>
<td>0.95 (0.85 - 1.10)</td>
<td>104 (95 - 114)</td>
</tr>
<tr>
<td>high biodegradability with sufficient aeration</td>
<td>0.55 (0.52 - 0.58)</td>
<td>0.020 (0.019 - 0.021)</td>
<td>71.3 (69.5 - 73.3)</td>
<td>1.18 (0.76 - 1.94)</td>
<td>133 (126 - 141)</td>
</tr>
</tbody>
</table>

7.2.4 Discussion

The first project objective in this study was to test the hypothesis that increasing the biodegradability of a synthetic material, as determined by the DR4 test, would increase CH$_4$ and N$_2$O emissions, when composted using either high or low aeration rates. The total amounts of CH$_4$ and N$_2$O emitted from each of the four treatments tested in this study were found to be statistically different. At a low aeration rate (10 ml minute$^{-1}$) a mean 0.17 g of CH$_4$ and 0.010 g of N$_2$O was released from the low biodegradability treatments during the 21 day test period. At the same low aeration rate the high biodegradability treatments released 0.46 g of CH$_4$ and 0.013 g of N$_2$O, significantly higher than the lower
biodegradability waste (calculation of these amounts was made using equation 2.5). This pattern was reflected in the samples under a higher aeration regime (250 ml minute\(^{-1}\)) where 0.05 g CH\(_4\) and 0.04 g N\(_2\)O (low biodegradability), and 0.74 g CH\(_4\) and 0.07 g N\(_2\)O (high biodegradability) was recorded. Hence, for each level of aeration, it was found that the material with the higher degree of biodegradability emitted significantly more CH\(_4\) and N\(_2\)O. This would appear to support the hypothesis.

The second project objective was to test the hypothesis that increased aeration during composting would reduce emission of CH\(_4\) and that this effect would be more pronounced for the high biodegradable material compared with the low biodegradable material. The findings from the study did not completely support this hypothesis. Although reduced emission of CH\(_4\) from the low biodegradable material was recorded under the high aeration regime, increased emission of CH\(_4\) from the high biodegradable material was found. The higher aeration rate treatments (intended to provide sufficient aeration to the waste during decomposition) showed significantly higher emission rates for N\(_2\)O from the low biodegradability and increased CH\(_4\) and N\(_2\)O from the high biodegradability wastes. While clear evidence for reduced CH\(_4\) emissions with increased aeration was found for the low biodegradable material, this was not observed for the high biodegradable material. This finding appears to be contrary to other studies of CH\(_4\) and N\(_2\)O that generally directly link aeration rate or availability of O\(_2\) with the formation of greenhouse gases during composting. Studies of this nature have been mentioned in other chapters and include Kuroda et al. (1996) on the study of greenhouse gas emission from swine faeces being enhanced with no aeration, and the effect of composting material density on aeration and subsequent CH\(_4\) and N\(_2\)O production (Sommer & Moller 2000).

However, some studies have reported higher degradation rates for material with higher biodegradability, suggesting that increased levels and rates of carbon mineralisation is expected for highly biodegradable material. For example, Cecchi et al (2002) found that more biodegradable substrates promote faster microbial transformation processes. It is
possible that increased microbial activity, under the highly aerated system, promoted
increased carbon mineralisation for the high biodegradability waste, which in turn gave
rise to the higher level of CH$_4$ emission. The enhanced degradation caused by the higher
substrate availability and high aeration rate would also have resulted in greater microbial
metabolic activity that included methanogens resident in anaerobic microsites within the
waste. These microsites have been shown to be present in all aerobic composting
systems. Atkinson et al. (1996) through microbial growth trials found that approximately
10% of the population of bacteria in composts were anaerobes, and that these organisms
were present at all stages of the composting process.

A similar test to that undertaken in this chapter was conducted by Beck-Friis et al. (2003)
and involved the measurement of CH$_4$ and N$_2$O produced by the composting process at
different O$_2$ concentrations. The procedures adopted in the study were very similar to
those described in this chapter, the temperature was controlled to 55°C, moisture content
was equalised between samples (although at a somewhat higher 65%), and C:N was
amended to an optimum amount (22:1). Where the tests differ is in the study was source
segregated household organic (of unknown content of organic C forms) and the vessel
(only one 200 L chamber used) used to allow monitoring of the biodegradation process
was larger and differed operationally. The chambers detailed in this chapter allowed
continuous aeration of the waste material, changing the flow rate of air through the
chambers allowed a specific rate of O$_2$ to be applied to the waste. The vessel described in
Beck-Friis et al. (2003) was a closed system with constant flow air re-circulation
(somewhat similar to the in-vessel systems described in Chapters 2 and 3 but on a
smaller scale). When O$_2$ concentrations in the vessel had fallen below the desired level,
fresh air was allowed in until the required O$_2$ concentration was achieved. The method of
continuous flow using a reduced O$_2$ concentration air may however exaggerate the
measurement of the potential a waste has for emission of CH$_4$ and N$_2$O. This is because
under a high flow low O$_2$ regime any generated CH$_4$ and N$_2$O via methanogenesis or
incomplete nitrification and denitrification gases would be forced out. The O$_2$
concentrations used in the study were 16, 2.5 and 1%. The 1% oxygen showed the highest CH₄ concentration within the re-circulating air (although the 16% data was not available after day 6 of the 25 day test). However it was stated that at even 16% O₂ anaerobic zones had developed. The pattern of CH₄ and N₂O was essentially the reverse of that observed in this study and seems likely due to the aeration method employed.

The third project objective was to test the hypothesis that increased aeration during composting would increase emission of N₂O and that this effect would be more pronounced for the high biodegradable material compared with the low biodegradable material. The findings from the study supported this hypothesis in the sense that significantly increased emission of N₂O was found for the highly aerated treatments. However, this effect did not appear to be more pronounced for the high biodegradable material compared with the low biodegradable material.

As noted above for the emission of CH₄ many studies have linked aeration rate or availability of O₂ with the formation of greenhouse gases during composting. In general, anaerobic conditions have been attributed to emission of CH₄ and N₂O such as Sommer & Moller 2000 who studied the effect of composting material density on aeration and subsequent CH₄ and N₂O production. However, Beline & Martinez (2002) showed how reducing aeration can also reduce the emission of N₂O from organic waste degradation in the study of pig slurry composting. This study compared the nitrogen transformation that occurred during composting when continuous or intermittent aeration methods were used. Under continuous aeration N₂O emission rate was greatest and approximately 18% of the total N content of the waste was emitted as N₂O. No N₂O emission was reported for the intermittently aerated process. The study suggests that the transition between anoxic and aerobic conditions is very important in terms of interrupting either nitrification or denitrification and can result in enhanced N₂O production. The study detailed in this chapter found that higher aeration rates gave higher N₂O emission. This may be because the higher aeration flow rate more readily changed the intensity and location of the
anaerobic zones within the material giving rise to the interruption of N transformations (as described by Beline & Martinez 2002). It is possible that the low flow rate regime, giving more anoxic conditions, would have had less dynamic aerobic/anoxic fluctuation and resulted in lower N₂O production.

The aeration method used in this study more closely replicates that occurring in large scale composting where O₂ concentrations within some areas of the composting pile are reduced because little fresh air flow can enter the more dense, compacted, water logged zones. It is within these zones that CH₄ and N₂O have been found to originate (detailed in other chapters). It seems conceivable that forced aeration composting, in providing more air to aerobic and porous zones could in turn be transporting the products of anaerobic zones through the compost, and emitting them to air at a faster rate than traditional windrow composting. This effect would be enhanced when composting is done with higher biodegradability wastes. This effect was not noted in Chapter 2 when monitoring CH₄ and N₂O from a forced aeration system compared to a windrow but it seems that there is a requirement for future study on aeration method and the transportation of CH₄ and N₂O from anaerobic zones to air. Studies by Higgins (1982), Lynch & Cherry (1996), and Koenig & Bari (1999) have all identified the improved composting time and increased temperature associate with the use of either forced aeration or improved flow using ducting, effect on emissions of CH₄ and N₂O has however as yet been overlooked.

The concentrations of NH₃, and volatile organic compounds (VOC) in the exhaust gas generally matched the pattern of CH₄ and N₂O concentration. One reason for increased NH₃ and VOC emission from composting is increased operating temperatures (Petersen et al. 1998), however the test used in this study was maintained at equal temperatures, and therefore it is either the air flow rate or differences in available biodegradable compounds that give rise to these differences.
This basic finding has considerable consequence when considering the diverse nature of organic wastes that are going to be diverted from landfill at an increasing rate in the future. As one of the main purposes of the landfill directive is to reduce greenhouse gas emissions the potential of a waste to produce CH$_4$ and N$_2$O must be considered when choosing an appropriate disposal route. The use of respirometry has been shown to give a good indication of the potential of an organic waste to produce CH$_4$ and N$_2$O during composting. This approach to the analysis of wastes should be further investigated to test whether a correlation exists between respiration rate and CH$_4$ and N$_2$O emission for different waste types and composting processes.

When comparing the same samples under differing aeration regimes, the supposed sufficient O$_2$ flow rate resulted in the higher emissions (for all but the total CH$_4$-C (g) from the low biodegradability waste at the higher emission rate). It is likely that CH$_4$ and N$_2$O flux rates observed from composting process may be attributed more to smaller anaerobic microenvironments within well-aerated zones than the predominantly anaerobic dense interior of a pile. It can be concluded that it is the combination of higher biodegradable and aerobic/anoxic conditions within the wastes that can enhance CH$_4$ and N$_2$O emission, and that these emission rates can be increased with forced flow through a composting mass.

### 7.2.5 Summary and conclusions

Emission of CH$_4$ and N$_2$O was monitored from 2 synthetic organic wastes (of high and low biodegradability) for 21 days under sufficient and insufficient aeration. It is clear that the differences in CH$_4$ and N$_2$O produced from wastes of differing biodegradability are as was proposed in project objective 1. It has been shown that more labile substrate within a composting waste provides greater nutrient source for microbial activity and therefore CH$_4$ and N$_2$O production under a single aeration rate.
The hypothesis that increased aeration would result in decreased CH$_4$ emission rates was proved correct for the low but not the high biodegradability waste. The increase in CH$_4$ with higher aeration for high biodegradability waste could have been due to CH$_4$ from methanogen activity in anaerobic microsites (enhanced by higher available substrate content) being forced from the waste by the higher air flow rate.

Emission of N$_2$O increased with higher aeration rate as proposed in objective 3 of this study and was likely due to development of dynamic aerobic and anaerobic zones. Nitrogen transformations were interrupted in these zones resulting in increased N$_2$O emission, and were further enhanced by high biodegradability.
8 – General discussion

8.1 Introduction

This thesis explores the impact on the atmosphere of a variety of large-scale composting systems, currently operating in the UK, with particular focus on the emission of CH\textsubscript{4} and N\textsubscript{2}O. In addition to traditional open windrow composting systems, more advanced composting technologies (including in-vessel systems, vermicomposting and mechanical and biological treatment (MBT) processes) that are being increasingly used to meet European landfill diversion targets (Slater & Frederickson 2001) are evaluated for emissions of CH\textsubscript{4} and N\textsubscript{2}O. The use of advanced composting technologies is likely to comprise an increasing proportion of the proposed expansion in the UK composting sector, and will be used to process a variety of materials including residual and catering wastes. Discussion of the thesis findings is presented in this chapter and it is envisaged that the findings from the research programme will contribute significantly to the knowledge base relating to the performance and environmental impact of composting processes and particularly with regard to emission of CH\textsubscript{4} and N\textsubscript{2}O.

The main aim of this research programme was to explore the emission of CH\textsubscript{4} and N\textsubscript{2}O from a range of composting processes. The objectives of the research programme were to:

1. Develop appropriate sampling protocols and methods for the measurement of these emissions.
2. Assess the nature and level of CH\textsubscript{4} and N\textsubscript{2}O emissions from selected composting processes.
3. Develop a respirometry method for effectively measuring the biodegradability of waste at key stages during composting.
4. Investigate mechanisms of CH$_4$ and N$_2$O production during composting with particular regard to the role of waste biodegradability.

5. Undertake a preliminary assessment relating to the total emissions of CH$_4$ and N$_2$O from the UK composting sector.

6. Suggest technical and process-based options for the mitigation of emission.

Chapters 3 to 7 covered the experimental details and findings for a number of investigations, which were undertaken to address the primary aim of this research programme. This chapter will focus particularly on discussing the implications of the large-scale composting CH$_4$ and N$_2$O emission data derived from chapters 3 to 7 and, for the first time, extrapolating CH$_4$ and N$_2$O emission data to a national scale (UK).

In Chapter 1 it was noted that there have been extensive studies undertaken to assess the total emission of methane from UK landfills and estimates have also been made of total global emission from landfill. However, no similar inventory of greenhouse gas emissions has been attempted for other waste management options and for large-scale composting it is has been assumed that emission of CH$_4$ and N$_2$O is negligible (DEFRA 2005). This thesis has presented clear evidence for the generation of CH$_4$ and N$_2$O during waste processing for a variety of composting processes. While emission of CH$_4$ and N$_2$O from open air windrow composting systems has been shown, it has not been possible to adequately evaluate the level of CH$_4$ and N$_2$O emissions to air for in-vessel systems. Further research is needed to develop protocols and methods of evaluation to determine CH$_4$ and N$_2$O emissions to air for in-vessel systems which incorporate forced air re-circulation systems.

Using emission data from this research programme, mainly derived from open air mechanically turned windrow systems, this Chapter contains a preliminary study aimed at estimating the emission of CH$_4$ and N$_2$O from the composting sector in the UK.
For each individual composting study presented within this thesis, a range of composting process operating parameters (including temperature, moisture content, and waste physico-chemical characteristics) were monitored alongside CH₄ and N₂O production and emission measurements. The development of a respirometry system for measuring the microbial activity within a compost sample progressed throughout the study, and proved to be a useful method of monitoring the performance of the composting process with regard to changes in waste biodegradability and CH₄ and N₂O emission potential. Discussion of the use of respirometry techniques as a means of assessing the potential of a composting process to emit CH₄ and N₂O is also included in this Chapter. A selected range of mitigation options for CH₄ and N₂O are also discussed and this Chapter includes recommendations for future investigations relating to reducing CH₄ and N₂O emission from composting.

8.2 Mechanisms of CH₄ and N₂O emissions during composting

8.2.1 Carbon, nitrogen, and biodegradability

Three windrow composting processes have been investigated in this study. Chapter 3 details the measurement of emission from both a mechanically turned open air windrow (WC1) and a covered static forced aerated windrow composting (CSFAC) pile. Chapter 6 details a longer duration study of a mechanically turned windrow (WC2). All three windrow-type composting processes involved the treatment of source segregated household waste. The waste studied in Chapter 6 (WC2) was first subjected to a 7-day in-vessel composting process prior to windrow formation. Methane flux rates from the windrows were measured as 20.1 mg CH₄ m⁻² hr⁻¹, 15.6 mg CH₄ m⁻² hr⁻¹, and 3 mg CH₄ m⁻² hr⁻¹ for WC1, CSFAC (both determined on day 15 of composting), and WC2 (mean of 85 day composting process) respectively. Nitrous oxide fluxes from the windrows were
measured as 9.3 mg N₂O m⁻² hr⁻¹, 1.8 mg N₂O m⁻² hr⁻¹, and 0.2 mg N₂O m⁻² hr⁻¹ for WC1, CSFAC (both on day 15 of composting), and WC2 (mean of 85 day composting process) respectively. There was considerable variation in surface flux rates of CH₄ and N₂O from the windrow composting systems. Flux rates varied not only between individual repeated measurements on a single sampling run, but also throughout the duration of composting. The variation in CH₄ fluxes from the composting processes studied is reflected in findings from other studies. Examples of this variation are Pier & Kelly's (1997) measurement of 1.68 mg CH₄ m⁻² hr⁻¹ mean flux from sawdust waste composting, 1458 mg CH₄ m⁻² hr⁻¹ mean flux from more putrescible municipal solid waste composting (Beck-Friis et al. 2000), and 1800 mg CH₄ m⁻² hr⁻¹ from dung windrows (Hellebrand 1998).

Nitrous oxide flux from windrow composting has also been reported at variable rates as is evident when comparing the Hellmann et al. (1997) source segregated household waste composting flux of 10 mg N₂O m⁻² hr⁻¹ with 1.5 mg N₂O m⁻² hr⁻¹ from dung windrows (Hellebrand & Kalk 2001). Comparing the operating parameters of the windrow composting systems studied in Chapters 3 and 6 with other reported findings will help in understanding the mechanisms driving CH₄ and N₂O emission. The CH₄ flux rates reported in Pier & Kelly's (1997) study of sawdust waste composting were lower than those measured in Chapters 3 and 6. A static chamber flux sampling method similar to that used in this study was employed to measure emissions. Pier & Kelly (1997) contend that the low emission rates may be due to oxidation of CH₄ within the pile, although they provide no data to support this theory. One limiting factor of methanogenesis is the amount of readily available organic matter that can be converted into suitable substrates (CO₂, acetate, and methanol or methylamines) (Ferry 2002). A physico-chemical analysis of the sawdust waste used was not made although information concerning the forms of C it contained was given. Sawdust waste was stated as having 51.9 % C of which around 15 % was lignin. No information concerning the content of N in sawdust waste was given, although analysis in Chapter 7 of this study showed softwood as having 0.03 % N. When assuming this N content for sawdust waste the C:N ratio for the compost material in their
study may have been around 1700:1. This would have made the availability of N a limiting factor in microbial activity, and is reflected in the comparatively low temperatures attained in the sawdust waste composting piles. The mean temperature within the pile was 37.6 °C at 3 m depth reflecting low microbial reaction rates in the composting material (Koenig & Bari 1999).

The influence of C:N ratios on emission of N₂O may also be inferred when comparing the N₂O emissions from the windrows studied in Chapters 3 and 6 with those detailed in Czepiel et al (1996). Their study focussed on the emission of N₂O from windrows of a mixture of wastewater sludge and wood ash (1:1). A similar static flux chamber method to that used in this study was employed to measure N₂O emission rates. A mean flux rate of 92 mg N₂O m⁻² hr⁻¹ was recorded during a 40 day aerated composting process, considerably higher than those measured in Chapters 3 and 6. The C:N ratio of the wastewater sludge composting mixture was 12.4:1 and could be a main contributing factor to the comparatively high rate of N₂O emission measured. Czepiel et al (1996) state in the introduction to their study that high mineral N availability provides favourable conditions for N₂O production. However, they do not offer any discussion of the effect C:N ratio has on the emission rates they recorded, or how additions of C may provide a more balanced composting mixture and possible reduced emission rates. One interesting finding of their study was an increase in N₂O flux rate at elevated composting aeration rates. This matches the pattern of N₂O emission measured in Chapter 7 where increased aeration rate promoted greater N loss as N₂O compared to a lower aeration rate. The effect of composting aeration rate on production and emission of CH₄ and N₂O is discussed in greater detail in section 8.2.3 of this Chapter.

The effect of C:N ratio on emission of CH₄ and N₂O was also investigated by Sommer & Moller (2000) in the study of the effect of straw content on the composting of deep litter from pig production. Two differing mixtures of composting material were subjected to static flux chamber gas sampling. The mixture without straw amendment (C:N 12.8) had
emission rates of 255 g CH$_4$ t waste$^{-1}$ and 182 g N$_2$O t waste$^{-1}$ for the 140 day composting period. Emission of CH$_4$ and N$_2$O from the straw amended mixture (C:N 16.3) was not detected. Sommer & Moller (2000) concluded that the primary factor in the emission from the windrows was density. The low density straw amended mixture provided higher aeration rates to the interior of the composting mass which in turn lead to increased CH$_4$ oxidation. Absence of any N$_2$O emission from their low density pile may have also been a consequence of the higher O$_2$ concentration within the composting material. Another reason not mentioned in their conclusions for the lack of CH$_4$ and N$_2$O emissions from this low density pile is that it was not actively composting. Oxygen concentrations within the pile (40 cm up from the base) did not fall below 20 % during 140 day composting process, and the internal temperature at the same location fell to below 30 °C after day 10. The notion that the low density pile was not composting is reflected in the amount of CO$_2$ it produced, this being 0.09 kg C t waste$^{-1}$ compared to 7.37 kg C t waste$^{-1}$ for the high density pile. A test of the biodegradability of the composting material during the 140 day process using the respirometric methods used in Chapters 3, 4, 5, and 7 of this study would have confirmed the lack of active composting. The C:N ratio of this low density pile was sufficient for active composting and production of CH$_4$ and N$_2$O. Therefore, another composting parameter may have affected this process and influenced gaseous emissions.

The initial moisture contents of high and low density piles reported in Sommer and Moller (2000) were 76.4 % and 34.8 % respectively. It is likely that the moisture content of the two piles alone were the principal drivers for greenhouse gas production in the piles. The probable cause of CH$_4$ and N$_2$O emission from the high density pile was anaerobic zone formation due to high moisture content. Low moisture content in the low density pile combined with a low C:N ratio was likely to have led to a cessation of microbial activity and no CH$_4$ and N$_2$O emission. Unfortunately Sommer and Moller (2000) failed to identify these fundamental composting operating parameters as being key causes of the observed pattern of CH$_4$ and N$_2$O emission. The potential effect of moisture content on emission of CH$_4$ and N$_2$O is discussed in section 8.2.3 of this Chapter.
It may be concluded that C:N ratios of composting material are an important determining factor of CH$_4$ and N$_2$O emission from composting. A comparable composting process to those studied in Chapters 3 and 6 was detailed in Beck-Friis et al. (2000) where emission of CH$_4$ and N$_2$O from the windrow composting of household waste was investigated. The C:N ratio of the waste used in this study was 22:1 which was similar to the C:N ratio of the windrow systems studied in Chapter 3 (22.7:1) and Chapter 6 (24.8:1). The similarity between the C:N ratios was however not reflected in the flux rate of CH$_4$ and N$_2$O from the windrow studied in Beck-Friis et al. (2000) which were up to 5000 mg CH$_4$ m$^{-2}$ hr$^{-1}$ and 61 mg N$_2$O m$^{-2}$ hr$^{-1}$. It is clear that composting characteristics other than the C:N ratio of the waste determined the differences in these flux rates.

The effect of changing the relationship between the C and N content present in the composting mass and microbial production of N$_2$O during composting was investigated by Hui et al. (2003). This study focussed on the emission of N$_2$O during the composting of a sawdust, garden soil, and nitrogenous landfill leachate mixture. The mixture was periodically amended during the composting period with both landfill leachate and glucose. Their results showed an increase in N$_2$O flux when landfill leachate was added but not when the material was amended with glucose. Hui et al. (2003) concluded that glucose did not have an effect on the flux rate of N$_2$O because sufficient C was available for microbial nitrification/denitrification within the mixture. The addition of the nitrogenous landfill leachate did stimulate N$_2$O emission, therefore fuelling either a nitrifier or denitrifier production of N$_2$O. The C and N balance of the composting material in this study is likely to have had the greatest influence on the emission of N$_2$O. However, information on the composting process such as moisture content, aeration regime, actual C:N ratio, and temperature were absent from this study so no alternative conclusions to the enhanced N$_2$O emissions can be drawn.

As detailed in Chapters 3 and 6, the two composting processes which employed mechanically turned open air windrow systems produced flux rates of 20.1 mg CH$_4$ m$^{-2}$ hr$^{-1}$
and 9.3 mg N₂O m⁻² hr⁻¹ (Chapter 3), and 3 mg CH₄ m⁻² hr⁻¹ and 0.2 mg N₂O m⁻² hr⁻¹ (Chapter 6). Although these were similar windrow systems, and the type of material being processed was similar (source segregated household waste, C:N 22.7 and 24.8 respectively), the characteristics of the waste differed in each case. Flux rates for the mechanically turned windrow system studied in Chapter 6, which was processing pre-treated waste were much lower than those found in Chapter 3 for the system which was processing fresh waste. This may be explained by the loss of C and N (23% and 47% respectively) from the material during the preceding in-vessel pre-treatment phase used in the Chapter 6 study. During the intensive in-vessel pre-treatment phase it is the more readily degradable C and N compounds that would have been removed. Carbon contained in sugars and volatile organics would have been quickly microbially degraded and organic N compounds would have been quickly hydrolysed to NH₃.

An investigation into composting operating parameters other than C:N ratio was made in Chapter 7 of this study. The amounts of C and N within two samples of differing biodegradability were equalised, however the types of organic C and N molecules differed. One conclusion for his study was that waste with a higher biodegradability had greater potential for CH₄ and N₂O generation. The DR4 respiration test showed the higher biodegradability material was around 147 % more biodegradable than the lower biodegradability material (320400 mgO₂ kgVS⁻¹ 96hr⁻¹ compared to 129900 mgO₂ kgVS⁻¹ 96hr⁻¹ respectively). Emission of CH₄ and N₂O is driven by the microbial processes of methanogenesis and nitrification/denitrification which are moderated by the amount of available substrate within the composting material. Kulling et al. (2001) conducted an experiment along a similar line to that detailed in Chapter 7. They investigated how the dietary protein content of animal feed affects CH₄ and N₂O emissions from the storage of the resulting cow manure. The feed mixtures were amended with starch to reduce the initial crude protein content without affecting the supply of energy and amino acids to the cow, or their milk-producing performance. The conclusions of this study were that considerable reduction of N loss (through both NH₃ and N₂O emission) can be achieved.
during the storage of the cow manure when the animal feed contained less crude protein. The magnitude of CH$_4$ emission was found to be governed primarily by the method of storing the cattle manure with the highest rate of emission from a stacked pile of manure (compared to the slurry and urine rich slurry pits). There are a number of parallels between this study and the investigation of compost biodegradability in chapter 7. Both studies assess what effect the C and N configuration of the initial material has on emission of CH$_4$ and N$_2$O during subsequent biodegradation. Both studies also conclude that higher availability of C and N to microbial consumption in the input material result in enhanced CH$_4$ and N$_2$O emissions, and that the processing method can further dictate the pattern of emission. It was found that increasing the aeration rate to the waste mixtures in Chapter 7 resulted in increased CH$_4$ and N$_2$O emission. Kulling et al (2001) recorded enhanced CH$_4$ emission from manure piles compared to slurry and urine rich slurry, with the former being potentially more aerobic (although no data was given to this effect). It was shown in Chapter 7 that waste with a higher biodegradable organic matter content may provide greater potential for CH$_4$ and N$_2$O formation. These products of microbial activity are primarily controlled by the amount of available substrate within the composting material.

Eleazer et al (1997) showed that CH$_4$ yields from laboratory-scale landfills increased as the available C content was increased. It may be concluded that one of the key parameters controlling microbial activity, and therefore CH$_4$ and N$_2$O formation, is substrate availability. Emission of CH$_4$ and N$_2$O from a composting process occurs after methanogenesis and nitrifier/denitrifier formation of N$_2$O, and is moderated by a number of factors. These include oxidation of CH$_4$, denitrification of N$_2$O to N$_2$ within the composting mass (Jackel et al 2005), and the composting aeration method.
8.2.2 Aeration method

CH$_4$ emission is observed from composting when methanogenesis within anaerobic zones in the composting material exceeds the oxidation of CH$_4$ within aerobic zones (Barber & Ferry 2001). The formation and emission of CH$_4$ was found to be rapid for some composting methods possibly being due to a number of methanogen species being tolerant of O$_2$ exposure and retaining their methane producing viability after exposure to O$_2$ (Barber & Ferry, 2001). Evidence for the rapid formation of anaerobic zones in composting material was shown by Hao et al. (2001) where O$_2$ levels within a windrow pile were found to be less than 3% within 12 hours of windrow formation.

Microbial denitrification can also result in emission of N$_2$O. The two pathways for production of N$_2$O during composting are nitrification (an aerobic process) and denitrification (an anaerobic process) at low O$_2$ conditions. CH$_4$ and N$_2$O emission was detected from all composting processes studied and would have originated within anaerobic zones in the composting material. Figure 8.1 shows the formation of CH$_4$ and N$_2$O within anaerobic zones, and is considered to occur on a number of scales (small individual compost particles to larger agglomerated pieces of composting material).
Composting is an aerobic waste treatment process. Therefore, the performance of this process is likely to be primarily governed by the supply of O₂ to microbes utilising available substrates within the composting mass. Complex formulas have been used to model the required method and rate of aeration for composting piles. Lynch & Cherry...
(1996) used an adaptation of Darcy’s Law on flow through porous media to design a system for passively aerated windrow composting. This model however only estimates the required velocity of air through the pile and provides no information on whether the calculated velocity provides sufficient O₂ to the composting material. Higgins (1982) also applied a method of theoretical calculation of air supply to compare the forced aeration techniques of dividing flow and combining flow. Dividing flow was the method of aeration used on the static pile forced aerated windrow and in-vessel composting system studied in Chapter 3, and the in-vessel composting system detailed in Chapter 4. Combining flow is the drawing of air down through the composting mass to a perforated pipe at the base of the pile connected to a vacuum pump. Dividing flow involves blowing air through a perforated pile at the base of the pile and up through the composting material. Higgins (1982) concluded that the dividing flow offered the best solution for forced aeration in sewage sludge/woodchip composting as significantly less airflow resistance was observed using this method. Another benefit of using this air flow regime was that the emissions from composting could be passed through a ‘blanket’ of finished compost on the surface of the windrow, thereby reducing odours. The models described in Lynch & Cherry (1996) and Higgins (1982) unfortunately do not consider formation of CH₄ and N₂O within the pile, or the development of anoxic zones within the composting material.

Some studies have concluded that the formation of CH₄ and N₂O within composting material originates in anaerobic zones, and therefore composting operating parameters that promote the development of these anoxic zones may enhance CH₄ and N₂O production and emission. One such study is on the production and emission of CH₄ and N₂O during the aerated composting of food waste by He et al. (2000). The design of this experiment involved the use of small lab-scale reactors (18 l) in which material of differing food waste, cattle manure, and sawdust was subjected to aerobic composting. A significant finding of this study was that CH₄ and N₂O were produced and emitted even though high O₂ concentrations were maintained within the composting material. He et al. (2000) conclude with the statement that “the results suggest the existence of an anoxic or
anaerobic environment even though ventilation was employed." A previous study of microbial activity in aerated composting by Atkinson et al (1996) also reaches similar conclusions. Their experiment focussed on the isolation of microorganisms from composting material comprised of MSW and paper mill waste. Isolated cultures of microorganisms indicated that aerobes were present in the composting material at much higher numbers than anaerobes (at over 90 % of the population). However, within anaerobic microenvironments in the composting material over 72 % of the metabolic activity was attributed to anaerobes. They conclude the study with the suggestion that anaerobic microenvironments develop within aerobic comports regardless of the aeration system used.

This conclusion has been reached by a number of researchers investigating the composting of various wastes using a variety of methods. Beck-Friis et al (2000 & 2003) concludes both studies of organic household waste composting that zones of aerobic and anaerobic conditions co-exist within heaps of composting material, and that the amount of anaerobic microenvironments increases with the size of the heaps. Their findings are in accordance with Fukumoto et al (2003) who found that the establishment of anaerobic sites within a composting pile increased logarithmically as the scale of the pile increased. This effect of pile scale may explain the difference in flux rates from the windrows studied in Chapters 3 and 6. On day 14 of composting the CH₄ and N₂O fluxes from the windrow in studied in Chapter 3 were 20.1 mg CH₄ m⁻² hr⁻¹ and 9.3 mg N₂O m⁻² hr⁻¹ respectively. On day 15 of composting the CH₄ and N₂O fluxes from the windrow studied in Chapter 6 were 4.1 mg CH₄ m⁻² hr⁻¹ and 0.27 mg N₂O m⁻² hr⁻¹ respectively. Pile scale may be concluded as being a reason for this difference as the pile in Chapter 3 was larger than that in Chapter 6 (3 m wide, 3 m high, 20 m long compared to 3 m wide, 2 m high, 10 m long). It is likely however that the difference in flux between the windrows detailed in Chapters 3 and 6 was due to a combination of factors including pile scale and the amount of available C and N in the composting material, as discussed in section 8.2.1 of this Chapter.
Morand et al. (2005) describe the emission of CH$_4$ and N$_2$O from passively aerated poplar bark and poultry manure composting as being as result of anaerobic zones within the composting material. They suggest that an increase in aeration rate would lead to mitigation of the development of these zones. Hellebrand and Kalk (2001) also conclude that emission of CH$_4$ and N$_2$O during the composting of livestock waste could be abated by increasing the air flow rate to the composting mass. Evidence of the development of anaerobic and semi-aerobic zones was therefore found in the composting methods detailed in Chapters 3, 4, 6, and 7, as emission of CH$_4$ and N$_2$O was measured from these composting systems. This indicated the activity of CH$_4$ producing methanogens (strictly anaerobic bacteria undertaking the last step in the decomposition of biomass, (Ferry 2002, Sommer 2001)), and N$_2$O production from the microbial transformation of N compounds by nitrifying and denitrifying bacteria (both resulting in N$_2$O formation in low O$_2$ environments (Czepiel et al. 1996, Kätterer 2002).

For the two windrow systems studied in Chapter 3, the mechanically turned open air windrow system was found to produce higher CH$_4$ and N$_2$O emissions compared with the covered static forced aeration composting windrow (20.1 mg CH$_4$ m$^{-2}$ hr$^{-1}$ and 9.3 mg N$_2$O m$^{-2}$ hr$^{-1}$ compared to 15.6 mg CH$_4$ m$^{-2}$ hr$^{-1}$ and 1.8 mg N$_2$O m$^{-2}$ hr$^{-1}$ respectively). This suggested that the mechanically turned windrow contained more highly developed anaerobic zones than covered static forced aeration composting pile. This difference could have been due to a number of factors: i) temperature affecting CH$_4$ and N$_2$O production and emission, ii) the biodegradability of the material being composted (i.e. the amount of available carbon for each process when the emission data was collected), iii) compost pile size and compaction, and iv) aeration method employed.

Since both windrow processes studied in Chapter 3 were composting the same material, it may be concluded that the nature of this material (particle size and heterogeneity) would have had little influence on CH$_4$ and N$_2$O emission. Furthermore, flux sampling was conducted simultaneously during a period where both processes were of equal size,
temperature and biodegradability (respiration rate), and therefore differences in these parameters do not explain the different CH$_4$ and N$_2$O emission rates. This large-scale experiment suggested that the forced aeration method of composting led to a reduction in the development of anaerobic zones compared to the mechanically turned windrow method. It would appear that the cause of the lower CH$_4$ and N$_2$O flux rate for the covered static forced aeration composting pile may have been related to the different aeration methods employed.

The forced aeration of a composting mass has also been shown to have the reverse effect on emission of CH$_4$ and N$_2$O to that described in Chapter 3. Emissions measured from the lab-scale experiment detailed in Chapter 7 were higher when the waste was supplied with an increased aeration rate. The mean emission of CH$_4$ and N$_2$O for the low aeration rate was 0.12 g CH$_4$ C and 0.003 g N$_2$O, and 0.34 g CH$_4$ C and 0.004 g N$_2$O for the low and high biodegradable material respectively over the 21 day test period. Mean emissions of CH$_4$ and N$_2$O from the high aeration rate over the 21 day test period were 0.03 g CH$_4$ C and 0.011 g N$_2$O, and 0.55 g CH$_4$ C and 0.020 g N$_2$O for the low and high biodegradable material respectively. The suggestion that increased aeration rate reduces anoxic zone formation and reduces emission is supported when comparing the emission of CH$_4$ from the lower and higher aerated low biodegradability treatments. Emission of CH$_4$ from the higher aerated waste was considerably lower than that measured from the low aeration treatments (0.12 g CH$_4$ C compared to 0.03 g CH$_4$ C over the 21 day test period). This pattern was not reproduced for the high biodegradability waste where a higher aeration rate lead to enhanced CH$_4$ emission. These findings reinforce the suggestion that a combination of O$_2$ supply to the composting mass and the amount of available substrate govern the potential a composting process has to emit CH$_4$ and N$_2$O. Quantifying the relative influence of either composting parameter is not possible from the results of this study. Further research would be required to investigate the relationship between O$_2$ demand, waste biodegradability and emission of CH$_4$ and N$_2$O.
In Chapter 7 a similar pattern of emission of N\textsubscript{2}O from both the low and high biodegradability treatments to that of CH\textsubscript{4} from the high biodegradable treatment was observed where an increase in aeration gave rise to an increase in emission of N\textsubscript{2}O. This conclusion has also been made in a number of studies investigating emission of CH\textsubscript{4} and N\textsubscript{2}O emission from composting processes. Czepiel et al (1996) in the study of organic sludge composting found higher N\textsubscript{2}O emission when active aeration was employed during the composting process. This was attributed to advective air currents flushing the trace gasses out of the pile and into the atmosphere. Hellebrand (1998) concludes the opposite effect of aeration rate on N\textsubscript{2}O emission during the composting of grass and green waste. Emission rates measured in this study suggest that the rate of N\textsubscript{2}O production within the composting pile can be greatly reduced by increasing air flow rate. Czepiel et al (1996) and Hellebrand (1998) appear to offer conflicting results for N\textsubscript{2}O emission dynamics from the same type of waste processing system. It seems likely that the different types of wastes studied are exerting influence on the formation and emission of N\textsubscript{2}O. However, insufficient data detailing the availability of substrates (N in particular) and waste biodegradability was included in either study, therefore no firm conclusions can be drawn.

An interesting study that offers similar findings to that in Chapter 7, and has some parallels with Czepiel et al (1996), is the investigation of N\textsubscript{2}O emission during the aerobic treatment of pig slurry by Burton et al (1993). This study focussed on an adapted aerobic treatment process where a continuously aerated vessel containing composting slurry was periodically amended with fresh slurry. A redox probe was installed in the vessel to measure the aeration level providing a feedback signal to the aeration system. When the O\textsubscript{2} concentration within the composting mass fell the aeration system compensated against this by increasing air flow rate. The conclusions of this study were that application of fresh slurry promoted increased microbial activity, and therefore O\textsubscript{2} consumption, which lead to an increase in flow rate and elevated N\textsubscript{2}O emission. The increase in N\textsubscript{2}O emission (which occurred within minutes of the start of increased aeration rate) was attributed to partial nitrification. The flushing of N\textsubscript{2}O from the composting mass by the increase in
aeration was not considered, although data reported in Chapter 7 demonstrate this to be important.

8.2.3 Moisture content and temperature

The influence of C and N availability, waste biodegradability, and aeration method have been discussed as being key factors in the formation and emission of CH\textsubscript{4} and N\textsubscript{2}O from composting processes. The microbial production of CH\textsubscript{4} and N\textsubscript{2}O not only relies on sufficient substrate availability, it is also governed by the temperature and moisture content of the composting material.

The in-vessel composting systems studied in Chapters 2 and 3 were both re-circulatory closed systems operating by the internal air recirculation, therefore not emitting an exhaust to air. These systems provided high composting temperatures which lead to high oxygen uptake rates and accelerated biodegradation of the composting mass compared with mechanically turned open air windrows. Use of this type of system is increasing (rising 6% to 0.24 Mt between 2002 and 2004) accounting for 20% of the overall increase in the amount of waste composted (Slater et al. 2005). The increased adoption of this type of process can be related to the combined effects of the Animal By-Products Regulations (DEFRA 2003) and Landfill Directive compliance (EU 1999).

The in-vessel composting system studied in Chapter 3 displayed considerable capacity for CH\textsubscript{4} and N\textsubscript{2}O production. The temporal pattern of CH\textsubscript{4} and N\textsubscript{2}O production was found to favour N\textsubscript{2}O during initial stages of the process, while a significant build up of CH\textsubscript{4} was detected after one week of in-vessel composting (reflecting the development of anoxic zones within the composting mass as described in section 8.2.2 of this Chapter). The production of CH\textsubscript{4} and N\textsubscript{2}O occurred alongside the respiratory consumption of O\textsubscript{2} indicating aerobic conditions were present together with anaerobic zones, thus highlighting the complexity of the redox status of the material during composting. The
emission to air from the in-vessel system studied in Chapter 3 could not be quantified as the aeration method employed featured re-circulated air in a closed system. The integrity of this closed system could be questioned, however, as water vapour was observed venting from the roof of the container therefore indicating that the system is not sealed and some CH$_4$ and N$_2$O was emitted. This was also the case for the system studied in Chapter 4.

Chapter 4 detailed a study of the comparison of the in-vessel composting of residual waste (RW) and source segregated household waste (SSHW). The in-vessel composting of SSHW was characterised by intensive thermophilic conditions (up to 76.5°C) due to enhanced exothermic microbial activity (Haug 1993), reduced O$_2$ (as low as 11.6% O$_2$ within the composting mass), significant build up of CH$_4$ and N$_2$O in the composting mass (up to approximately 0.5% CH$_4$ and 8 ppm N$_2$O), and the presence of CH$_4$ and N$_2$O in the re-circulation air (up to 101.5 ppm CH$_4$ and 7.9 ppm N$_2$O measured in the headspace).

The in-vessel composting of RW, using the same system, showed less capacity for self-heating (failing to achieve the 60°C within the composting mass required by animal by-product legislation), displayed higher O$_2$ concentrations within the composting material (19.4% O$_2$), and featured lower CH$_4$ and N$_2$O concentrations both within the composting mass and re-circulation air (23.9 ppm CH$_4$ and 0.8 ppm N$_2$O, and 26.1 ppm CH$_4$ and 0.9 ppm N$_2$O respectively). Tests were carried out to attempt to estimate emission to air from these systems with CH$_4$, N$_2$O, NH$_3$, and VOC concentrations found to be elevated (above ambient concentrations) in the close vicinity (within 1 m) of the in-vessel composting system. It was therefore concluded that the agricultural clamp system studied in that chapter did have the potential to leak CH$_4$ and N$_2$O, however rates of release could not be quantified as the flow rate of gases exiting the system (required in the calculation of flux) could not be assessed using the methods employed.

One notable reason for the differences observed between the in-vessel processing of the two waste types may have been that the moisture content of the residual waste decreased extensively as the material dried during the composting process (82.5% dry mass content...
by the end of the process). This is likely to have severely inhibited the composting process as moisture content plays a very important role in the microbial degradation of organic wastes. Mario & Carvalho (1999) investigated the role of moisture in the windrow composting of municipal solid wastes. The study highlights the importance of moisture in the composting process, and concludes that without control of moisture content, other composting parameters such as O₂ supply and temperature cannot be properly regulated.

The effect of low moisture content was likely to have been the primary cause of low CH₄ and N₂O in the RW described in Chapter 4. This inhibitory effect of low moisture content may also be indicated by the lack of CH₄ and N₂O flux produced by Sommer and Moller's (2000) low density compost pile (as described in section 8.2.1 of this Chapter). Goncalves et al (1999) described difficulties in maintaining thermophilic composting conditions within piles of municipal green waste. They demonstrated that at moisture contents below 40 % microbial productivity was inhibited to the extent that thermophilic composting ceased, and would only be re-instated by the addition of water to the pile.

An in-vessel system similar to that studied in Chapter 6 was the focus of an investigation into the effect of aeration rate on the in-vessel composting of a mixture of food waste and office waste paper by Koenig & Bari (1999). When applying a dividing up-flow aeration regime similar to that described in Chapter 6 the waste dried from the base upwards, with moisture being driven to the surface of the pile. The waste was not reported to have dried to the degree observed for the RW in Chapter 6, and continued composting. This was likely due to the food and waste paper mixture having greater water holding capacity than the RW studied in Chapter 6. The application of a re-circulatory aeration regime, as is used in the in-vessel composting system in Chapter 4, has been shown to achieve more uniform temperature distribution and better organic matter degradation within the composting mass (Bari & Koenig 2001). The temperatures for the SSHW subjected to in-vessel composting reflect this finding. Temperatures for the RW were comparatively low, as was the rate of CH₄ and N₂O formation. It may be concluded that when the RW was subjected to up-flow re-circulatory aeration it lead to a reduction of moisture content, and
resulted in low CH$_4$ and N$_2$O production in the RW. However, the composting rate of the process was also detrimentally affected. In-vessel systems of a similar type have been used successfully for the treatment of other types of organic waste (including the SSHW detailed in Chapter 6). Liao et al (1997) reported on the use of such systems for fish waste composting. They found that in-vessel system composting is an effective method of thermophilic composting for fish waste, and containment of VOC and ammonia emissions. The moisture content of the fish waste was also shown to remain constant throughout the 18 day treatment period. Stelmachowski et al (2003) investigated the in-vessel composting of municipal sewage sludge using a Horstmann bioreactor. The moisture content after the 2-3 week in-vessel process was not found to be significantly lower than in the fresh waste.

The moisture content of composting material plays an important role in rate of composting, when insufficient, microbial activity will quickly cease. When excessive moisture is present in a composting material it will occupy the pores within the composting mass and encourage the development of anaerobic zones described previously in this chapter (Richard & Walker 1999). It is clear that moisture content plays a key role in the formation of CH$_4$ and N$_2$O during composting, and as it is likely that more diverse wastes with different water retention capacities are to be subjected to aerobic treatment as efforts are made to comply with the EU landfill directive. Further research is needed on this subject, particularly on the study of the appropriate methods of composting wastes with diverse characteristics. Emission of CH$_4$ and N$_2$O should be considered as being an important addition to this research.

The results of the study of in-vessel composting in Chapter 4 show that the temperatures achieved within the SSHW exceeded that observed for RW composting. Production of CH$_4$ was also higher in the SSHW treatment process. There have been a number of studies that have highlighted the association of thermophilic composting conditions and elevated CH$_4$ emission, with mesophilic conditions characterised by N$_2$O emission. The windrow studied in Chapter 6 also displayed this pattern to some extent with higher N$_2$O
emission at the start of composting, low fluxes during the thermophilic stage, and sporadic
flux during the latter mesophilic stage. High CH$_4$ fluxes were observed at the initial and
thermophilic stages, but reduced in the latter stages. This windrow process was preceded
by an initial in-vessel composting process so direct comparison with the temperature
driven pattern of CH$_4$ and N$_2$O from some tradition windrow systems may not be made.
The mechanisms of CH$_4$ and N$_2$O emission in relation to temperature may however be
similar to that for other composting systems.

Temperature has been shown to dictate the pattern of CH$_4$ and N$_2$O emission from a
number of composting processes. Hellmann et al (1997) noted that simultaneous
emissions of CH$_4$ and N$_2$O did not occur during the windrow composting of MSW. During
the thermophilic stage of composting they detected only minor N$_2$O emission and inferred
that this was due to N$_2$O production only within the mesophilic outer zones of the pile.
Nitrification and denitrification are generally mesophilic processes requiring higher redox
potential than methanogenesis (Trogler 1999). Simultaneous emission of CH$_4$ and N$_2$O
from the windrow composting process studied in Chapter 6 suggests that the pile
contained zones at mesophilic and thermophilic temperature ranges (as well as anaerobic
zones).

Methane production in the thermophilic stage of composting has been shown to be further
enhanced by Jackel et al (2005) as O$_2$ solubility in water at 60 °C is around 51 % of the
solubility at 20 °C. Thermo-tolerant and thermophilic methanogens were isolated from the
green waste windrow studied, and were found to be of a species similar to that which
occupy hot springs. The pattern of CH$_4$ and N$_2$O emission in relation to temperature,
where N$_2$O is produced at both the early and later mesophilic stages of composting and
CH$_4$ predominantly during the middle thermophilic stage has been recognised and
highlighted in a number of studies (Pier & Kelly 1997, Morand et al 2005, Hellebrand &
2003). The degree to which CH$_4$ emission is enhanced by convective air flow at higher
temperatures has not until now been investigated. The simulated composting experiment in Chapter 7 was conducted within the thermophilic range (50 °C) and for the higher biodegradability waste shows elevated CH₄ emission at an increased air flow rate. This suggests that convective forcing is a key factor in thermophilic CH₄ emission, although, this pattern was not reproduced for lower biodegradability waste.

8.2.4 Emission of CH₄ and N₂O from vermicomposting: Flux and controlling factors

The use of vermicomposting is increasing and is being applied to more diverse waste processing applications. Ghosh (2004) details an investigation into the use of vermicomposting as a method of processing MSW in rural India prior to the application of the waste for fish pond fertilization. Majumdar et al (2005) investigated the use of vermicomposting to compost anti-biotic pharmaceutical wastes. The emission of CH₄ and N₂O was not considered in either study and has been the focus of few investigations involving vermicomposting.

During this research programme there were two main experimental studies that investigated N₂O emissions from vermicomposting. In Chapter 5 vermicomposting of fresh, highly putrescible potato sludge was studied while in Chapter 6, the waste type utilized was pre-composted source segregated household waste. Mean flux rate for N₂O emission from the potato sludge study (Chapter 5) was 123 kg N₂O-N ha⁻¹ yr⁻¹, lower than the flux found by Frederickson & Howell (2002), using a similar system and a similar waste type (275 kg N₂O-N ha⁻¹ yr⁻¹). The duration of the vermicomposting process detailed in Frederickson & Howell (2002) was 80 weeks, considerably longer than the 85 day vermicomposting period detailed in Chapter 5. The duration of the vermicomposting process is therefore likely to have been the cause of the difference in the mean N₂O flux between both systems.
Vermicomposting is a continuous mesophilic process, and provides inhibition of microbial N transformations due to high temperature (Dincer & Kargi 2000). Short et al (1999) investigated the vermicomposting of waste paper sludge and observed greater conservation of N and accumulation of NO$_3$ compared to a windrow process. It is also the aerobic nature of the vermicomposting processes studied that gives rise to them being zones of NO$_3$ accumulation. This was shown in Chapter 5 where NO$_3$ accumulated at approximately three times the rate of NO$_3$ in windrow composting. It may be concluded that the accumulation of NO$_3$ in the vermicomposting system studied in Frederickson & Howell (2003) occurred over a longer duration therefore enhancing N$_2$O emission. Strongly nitrifying conditions, combined with enhanced denitrification (at low O$_2$ conditions) to N$_2$O within the earthworm gut results in enhanced N$_2$O emission from vermicomposting compared with traditional composting systems. This is supported by Frederickson & Howell (2002) who showed that N$_2$O emission was related to earthworm density.

For soil and forest litter ecosystems, studies by Ihussen et al. (2003), Horn et al. (2003), Matthies et al. (1999), and Karsten & Drake (1997 & 1995) discuss in detail, the incomplete denitrification processes taking place within the earthworm gut leading to N$_2$O emission. The studies detailed in Chapters 5 and 6 have shown this process also occurs in vermicomposting at a higher intensity due to the increased amount and N content of the material being broken down. The effect of N content on the emission of N$_2$O may be seen when comparing flux rates in Chapters 5 and 6. The pulped potato waste being vermicomposted in Chapter 5 had 2.93% N and the source segregated household waste vermicomposted in Chapter 6 had 1.63% N. Mean fluxes from the vermicomposting beds from Chapters 5 and 6 were 3.9 mg N$_2$O m$^2$ hr$^{-1}$ and 0.7 mg N$_2$O m$^2$ hr$^{-1}$ respectively thus possibly demonstrating the effect of increased waste N content on N$_2$O flux. Another factor that could have had an influence on N$_2$O emissions was that the wastes were applied to the beds using different methods, continuously for the pulped potato waste, and as a single application for the source segregated household waste.
The highest $\text{N}_2\text{O}$ flux measured in Chapter 5 (1.96 mg $\text{N}_2\text{O}$ N m$^{-2}$ hr$^{-1}$) was considerably higher than the $\text{N}_2\text{O}$ flux measured by Patni et al. (2000) from cattle and hog manure slurry vermicomposting (0.05 mg $\text{N}_2\text{O}$-N m$^{-2}$ hr$^{-1}$). Little information is given in Patni et al (2000) that would aid in identifying the cause of these contrasting $\text{N}_2\text{O}$ flux rates. It may be assumed that the N content of the cattle and hog manure is high however no data is given, as is the case for earthworm stocking density. The configuration of the vermicomposting process detailed in Patni et al (2000) appears to be the direct application of earthworms to a 1:1 mixture of cattle and hog manure. It may therefore be concluded that the waste moisture content was inhibitive to aerobic nitrification to $\text{NO}_3$ and subsequent denitrification to $\text{N}_2\text{O}$ within the earthworm gut. However, as no information on waste moisture content is provided this can only be inferred. Emission of $\text{N}_2\text{O}$ from vermicomposting found in Chapters 5 and 6 has confirmed the finding of Frederickson & Howell (2002) identifying vermicomposting emission as being much higher than agricultural buffer zone (one of the highest natural emitters) emission of 38 kg $\text{N}_2\text{O}$-N ha$^{-1}$ yr$^{-1}$ (Machefert et al. 2002). No significant CH$_4$ fluxes were observed from the vermicomposting processes studied in Chapters 5 and 6, indicating that aerobic conditions predominate in vermicomposting bedding material.

In part 2 of Chapter 5 a study of the effect of temperature on emission of CH$_4$ and $\text{N}_2\text{O}$ from vermicomposting was presented. This study found that vermicomposting processing temperature was correlated with the waste processing rate ($R^2 = 0.65$). Higher vermicomposting temperatures also increased the nitrification rate, leading $\text{NO}_3$ accumulation. If it is assumed that $\text{NO}_3$ is denitrified to $\text{N}_2\text{O}$ within the earthworm gut, then enhanced formation of $\text{NO}_3$ would explain $\text{N}_2\text{O}$ flux rates being strongly correlated with temperature ($R^2 = 0.91$). The microbial processes of both nitrification and denitrification were shown to have increased at higher vermicomposting temperatures (25°C). High, short duration pulses of $\text{N}_2\text{O}$ were observed from the vermicomposting beds studied in both Chapters 5 (43.2 mg $\text{N}_2\text{O}$ m$^{-2}$ hr$^{-1}$) and Chapter 6 (15.35 mg $\text{N}_2\text{O}$ m$^{-2}$ hr$^{-1}$) and may
have been the result of changes in waste/bedding nutrient content, temperature, moisture, aeration, or a combination of a number of these factors (Mummey et al. 1997, Prieme & Christensen 2001, De Weaver at al. 2002, and Beline & Martinez 2002). Further study is required to identify the cause of these high N₂O pulses, and the frequency and duration of their occurrence.

8.3 Estimate of total CH₄ and N₂O emission from the UK composting sector

Emissions from composting are not accounted for in the UK greenhouse gas inventory submitted to the Framework Convention on Climate Change (Baggott et al. 2003) and a recent fact sheet issued by the Department of Environment Food and Rural Affairs lists only CO₂ as a gaseous emission from composting (DEFRA 2005) omitting reference to other greenhouse gases.

The results contained within this thesis clearly demonstrate that emission of CH₄ and N₂O from large-scale composting should be assessed. Composting processes detailed in Chapters 3 – 7 all exhibit significant CH₄ and N₂O fluxes. The generally held view that composting is a pollution free alternative to landfill of organic wastes has been shown to be invalid. Emission of CH₄ and N₂O arise from complex mechanisms of formation where aerobic and anaerobic degradation of substrates occurs simultaneously. Evidence of aerobic/anaerobic processes were found in all the composting systems examined in this study.

Using emission data derived from open air mechanically turned windrow systems, this Chapter contains a preliminary study aimed at assessing the emission of CH₄ and N₂O from the composting sector in the UK. The main focus of the study will be open air windrow composting since approximately 82% of municipal waste is composted using turned windrows in the open-air (Slater et al. 2005). While it is clear that the amount of
waste being composted using more advanced in-vessel systems is significant and that this is predicted to increase further, it is also acknowledged that there are many uncertainties surrounding the estimation of emissions from such systems. Hence, current and future national levels of emissions from in-vessel systems will not be considered further in this study.

The amount of waste composted in the UK has been reported as being approximately 2 million tonnes (Slater et al. 2005). To make an estimate of the total emissions from composting based on the fluxes of CH\(_4\) and N\(_2\)O measured during this study, fluxes need to be converted to a mass basis from the area basis used. In order to do this a number of assumptions and estimates must be made:

i) Amount (weight) of material being processed in the windrows detailed in Chapters 3 and 6 must be estimated and taken as being constant throughout the composting process.

ii) Mean flux rates for all processes studied will be used, potentially omitting high pulse fluxes and release of CH\(_4\) and N\(_2\)O from the interior of the material when it is disturbed (e.g. windrow turning). This means that estimates are likely to underestimate the total UK CH\(_4\) and N\(_2\)O flux from composting.

iii) For the windrows and covered piles the peak of the windrow has been recognised as the area of highest emission (Haug 1986). Hellmann et al. (1997) noted that only half of the windrow surface emitted CH\(_4\) and N\(_2\)O. However, no data was provided in their study and the spatial distribution of CH\(_4\) and N\(_2\)O flux was not measured in the windrows in Chapters 3 and 6. Therefore to calculate the total flux from the windrow on an area basis the total surface area of the pile was considered as being flux emitting. No protocol for the measurement of the emission area has been developed so attributing flux to the entire surface area would give figures for the maximum CH\(_4\) and N\(_2\)O flux possible. In reality the total windrow CH\(_4\) and N\(_2\)O flux may have been
somewhat lower but further work would be required to increase the accuracy of
the emission estimates.

iv) When extrapolating, the actual operating parameters of the processes that are
composting the 2 Mt in the UK are not taken into account.

Table 8.1 Mean flux rates, estimates of the weight of the material processed during
composting, total area of emission, and estimates of CH$_4$ and N$_2$O flux rate on a mass
basis

<table>
<thead>
<tr>
<th>Composting process (chapters in parentheses)</th>
<th>N$_2$O flux (mg m$^{-2}$ hr$^{-1}$)$^b$</th>
<th>CH$_4$ flux (mg m$^{-2}$ hr$^{-1}$)$^b$</th>
<th>Estimate of total weight of material composted (kg)$^c$</th>
<th>Estimate of total area of windrow (m$^2$)$^d$</th>
<th>Estimated N$_2$O flux ($\mu$g kg$^{-1}$ hr$^{-1}$) ($x 1000$)</th>
<th>Estimated CH$_4$ flux ($\mu$g kg$^{-1}$ hr$^{-1}$) ($x 1000$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windrow (3)</td>
<td>9.3</td>
<td>20.1</td>
<td>7000</td>
<td>130</td>
<td>173</td>
<td>373</td>
</tr>
<tr>
<td>Covered windrow (3)</td>
<td>1.8</td>
<td>15.6</td>
<td>7000</td>
<td>130</td>
<td>33</td>
<td>290</td>
</tr>
<tr>
<td>Windrow (6)</td>
<td>0.2</td>
<td>3.0</td>
<td>3500</td>
<td>46</td>
<td>2.6</td>
<td>39</td>
</tr>
</tbody>
</table>

The estimates for CH$_4$ and N$_2$O emission on a mass basis are uncertain as is reflected in
other studies of emission from windrow or pile composting. As a result of this uncertainty
an upper and lower estimate for emissions from composting is calculated. The upper
estimate is flux measured from the windrow studied in Chapter 3 where the composting
material had not been subjected to in-vessel pre-treatment (the current usual practice).
The fluxes were only measured on day 15 of windrow composting so may not be
representative of the mean CH$_4$ and N$_2$O emissions during the 86 day (2064 hours)
composting period. For this estimate mean emissions of CH$_4$ and N$_2$O were 373 $\mu$g CH$_4$
kg$^{-1}$ hr$^{-1}$ and 173 $\mu$g N$_2$O kg$^{-1}$ hr$^{-1}$ (Table 8.1). The flux of CH$_4$ and N$_2$O for the total
composting period can be calculated by multiplying these hourly flux rates by 2064
(duration of the compost process in hours). This gives total flux rates of 770 mg CH₄ kg⁻¹ (or g t⁻¹) and 365 mg N₂O kg⁻¹ (or g t⁻¹).

For the lower estimate mean CH₄ and N₂O fluxes of the windrow studied in chapter 6 during the 85 day (2040 hours) composting period were used. These fluxes are likely to be more representative of the emission of CH₄ and N₂O throughout the duration of the composting process. The changes in the operating parameters such as temperature, C and N availability and moisture content during the composting process gave rise to changes in the pattern of emission. The pattern of emission of CH₄ and N₂O should be an important consideration when estimating the total flux from a composting process. Other studies have highlighted the variation in CH₄ and N₂O emission during composting (discussed earlier in this chapter), therefore the total flux rate estimate for the windrow studied in Chapter 6 should be more accurate than that calculated for the windrow investigated in Chapter 3. Total CH₄ and N₂O flux from the windrow studied in Chapter 6 was calculated as 39 μg CH₄ kg⁻¹ hr⁻¹ and 2.6 μg N₂O kg⁻¹ hr⁻¹ (Table 8.1). These lower fluxes represent mean emissions for the duration of an 85 day windrow composting process after in-vessel pre-treatment. They therefore represent emissions from windrow composting after a mitigation strategy has been employed. The flux of CH₄ and N₂O for the total composting period can be calculated by multiplying these hourly flux rates by 2040 (duration of the compost process in hours). This gives total flux rates of 80 mg CH₄ kg⁻¹ (or g t⁻¹) and 5.3 mg N₂O kg⁻¹ (or g t⁻¹).

Figures calculated for the upper and lower total CH₄ and N₂O flux from composting can be extrapolated to estimate the potential emission from the UK composting sector. At the present rate of composting of 2 Mt year⁻¹ the total estimated emission of CH₄ and N₂O from windrow or pile composting (that accounts for around 80% of composting processes) can be calculated by multiplying the total flux from the windrows studied in Chapters 3 and 6 (calculated above in g t⁻¹) by 2 x 10⁶. This gives a range of 160 – 1540 t CH₄ year⁻¹ and 10.6 – 160 t N₂O year⁻¹ as being the present total emission of CH₄ and N₂O from UK
windrow composting. The UK produces in total around 2,428,000 t CH\(_4\) year\(^{-1}\) and 140,000 t N\(_2\)O year\(^{-1}\) from all sources (Salway et al 2000). Based on the emissions calculated for the total amount of CH\(_4\) and N\(_2\)O produced per year from windrow composting it can be estimated that composting contributes around 0.006 – 0.06 % CH\(_4\) and 0.008 – 0.11 % N\(_2\)O to the total UK CH\(_4\) and N\(_2\)O emission inventory.

With a predicted 16 fold increase in composting (Slater & Frederickson 2001) to enable compliance with the EU landfill directive, emissions would increase to between 2.5 – 24.6 Kt CH\(_4\) year\(^{-1}\) and 0.16 – 2.5 Kt N\(_2\)O year\(^{-1}\) (this range of emissions is calculated multiplying the present estimated total emission of CH\(_4\) and N\(_2\)O from composting by 16). The UK greenhouse gas inventory does not currently include emission of CH\(_4\) and N\(_2\)O from composting. Amounts of CH\(_4\) and N\(_2\)O released from agricultural manure management are recorded as being 105 Kt CH\(_4\) year\(^{-1}\) and 4.6 Kt N\(_2\)O year\(^{-1}\) (Salway et al 2000). Therefore, the significance of the omission of CH\(_4\) and N\(_2\)O emissions from composting is increasing as composting activity in the UK expands.

Jackel et al (2005) state that composting contributes around 0.31 – 0.44 % of the total CH\(_4\) emissions in Germany. The assumptions for this are not made clear. Clemens and Cuhls (2003) speculate that if all of the MSW produced in Germany were treated in MBT processes this contribution may be as high as 3 % and 5 % of the total German annual emission of CH\(_4\) and N\(_2\)O respectively. It is likely that it is the variation and lack of consistency in information regarding CH\(_4\) and N\(_2\)O emissions from composting that have lead to the omission of composting emission data from greenhouse gas inventories. This variation in the flux rate can be seen when comparing total emissions from various composting processes. The MBT process detailed in Clemens and Cuhls (2003) recorded fluxes of 600 – 12000 g t\(^{-1}\) for CH\(_4\) and 1.44 – 378 g t\(^{-1}\) for N\(_2\)O. Fukumoto et al (2003) measured 1900 g t\(^{-1}\) CH\(_4\) during manure composting. The green waste windrow composting examined in Hellebrand (1998) produced 167 g t\(^{-1}\) N\(_2\)O, which was a similar flux rate to that from sewage sludge composting (125 g t\(^{-1}\) N\(_2\)O) (Czepiel et al 1996), and
pig manure (182 g t\(^{-1}\) N\(_2\)O) (Sommer & Moller 2000). Sommer & Moller also recorded a total flux of 254 g t\(^{-1}\) CH\(_4\) from the pig manure composting process.

It is clear that considerable variation exists in the flux of CH\(_4\) and N\(_2\)O from composting systems. Up-scaling of the measured emissions from the windrows studied in Chapters 3 and 6 are not only evidence of this variation, but also highlight the importance of accounting for the emission of CH\(_4\) and N\(_2\)O for the entire duration of a composting process. The many different types of composting system that are being used to process increasingly diverse types of organic waste must be studied in greater detail in order to arrive at more accurate estimates of CH\(_4\) and N\(_2\)O emission from the UK composting sector.

8.4 CH\(_4\) and N\(_2\)O emission mitigation options

The generation of CH\(_4\) and N\(_2\)O during composting has been shown to be linked to the degree of anaerobicity of the composting material. Methane is known to be emitted from compost piles when the amount of methane, which is generated under anaerobic conditions, is sufficient to outweigh that which is consumed by oxidising bacteria while in transit through and out of the compost. Therefore good aeration may be regarded as being the best mitigation strategy for reducing CH\(_4\) emission from composting material. The comparatively intensive windrow management practices undertaken in Chapter 6 (i.e. regular turning) appeared not to prevent anaerobic zones developing within the windrow pile as CH\(_4\) was still emitted during composting. It must be considered that some management practices (e.g. infrequent turning) and use of large windrows may further enhance CH\(_4\) emission. Fukumoto et al. (2003) found that the scale of a compost pile was a major factor in gas emission rates with larger windrow piles developing more anaerobic zones and therefore CH\(_4\). Sommer & Moller (2000) found density to be a major factor in CH\(_4\) production with lower densities (after amending material with straw) giving rise to
lower CH$_4$ production. The inhibitory factor of extreme (low and high) temperature and moisture also has an effect on CH$_4$ and N$_2$O but would in turn affect the composting process.

Emission of CH$_4$ and N$_2$O from the mechanically turned windrow (Chapter 6) was considerably lower than those having experienced in-vessel pre-treatment (Chapter 3). During this intensive pre-treatment phase total organic carbon fell by 8%, reducing the amount of microbially available carbon within the material which was subsequently subjected to windrow composting. Microbiological respiration was also greatly reduced (by 75%) after in-vessel treatment also reflecting the loss of available C. This loss in substrate would have the effect of decreasing the amount of carbon available for microbial decomposition thereby reducing the potential of CH$_4$ emission during subsequent composting. Carbon loss during this in-vessel stage will however require further investigation to determine whether it originates from oxidising (CO$_2$ production) or reducing (CH$_4$ production) conditions within the organic matter. This finding was reflected in the reduced CH$_4$ and N$_2$O production from wastes with lower biodegradability observed in Chapter 7. Chapter 7 also showed how method of aeration can affect CH$_4$ or N$_2$O production, with continuous aeration resulting in lower CH$_4$ but increasing N$_2$O production.

Nitrogen transformations throughout the composting process are influenced by either the immobilisation of nitrogen or the suppression of nitrification or denitrification and the emission of N$_2$O can be mediated by the regulation of nitrogen compounds. Nitrogen can be immobilised (in the form of ammonium) by the addition of Mg and P to promote struvite crystal growth (MgNH$_4$PO$_4$) (Jeong & Kim 2001). Increasing the carbon content of the material has also been suggested as a method of immobilising N. Tiquia & Tam (2000) found that the addition of a bulking agent during composting increased C content and reduced the loss of N through NH$_3$ volatilisation and N$_2$O emission. A similar effect was shown by Sommer et al. (2001) on the effects of composting on nutrient loss where increasing the C:N ratio enhanced N immobilisation concurrent with reduced rates of
nitrification and denitrification. N immobilisation can also be induced by the addition of an ammonium absorbent to the composting material. One such material is ‘clinoptilolite’ (a form of zeolite) which is used to remove ammonium from waste water (Witter & Lopez-Real 1988). Nitrification can be inhibited by the addition of dicyandiamide (DCD) or Karajin (tree seed extract) as described in Majumdar (2001). As vermicomposting N$_2$O emissions directly relate to the accumulation of NO$_3$ it would seem logical that periodic removal of this compound throughout vermicomposting would have the effect of reducing N$_2$O release. However nutrients lost in this way would reduce the quality of vermicomposts.

An interesting method of CH$_4$ and N$_2$O emission abatement during cattle feedlot manure composting was proposed by Hao et al (2001). Emission from the windrows studied was lower when a passive aeration method was employed. For N$_2$O they suggest this was due to NO$_3$ produced in the upper portion of the composting pile leaching down to anaerobic regions where complete denitrification to N$_2$ could occur. A reverse scenario was inferred for CH$_4$ distribution where the products of methanogenesis within the lower anaerobic zones of the pile were oxidised by methanophillic microbes before emission from the pile. Hao et al (2001) concluded that active aeration interrupts the relationships between microbes that produce and consume CH$_4$ and N$_2$O resulting in higher emission. The active aeration system studied did release considerably more CO$_2$ and operated at a higher temperature than the passively aerated system. It may therefore be assumed that active aeration promoted an accelerated compost processing rate, although no data on compost biodegradability or maturity was given to support this. This study highlights that mitigation of CH$_4$ and N$_2$O emission may be achieved by tempering the composting process, and that overall reduction in microbial activity is likely to decrease CH$_4$ and N$_2$O production.

There is a considerable difference (around a factor of 10) between fluxes from windrow composting material that had been pre-treated using an intensive in-vessel phase (Chapter 6) and those that had not (Chapter 3). Such a large potential for mitigation of emission from an individual CH$_4$ source is unprecedented for other anthropogenic sources
and represents the way forward for greenhouse gas emission control. One of the key benefits of emission control during the in-vessel composting stage is the opportunity to contain and treat emissions. Many enclosed composting processes employ biofiltration as a method of reducing emission of NH₃, CH₄, N₂O, and VOCs. Powelson & Chanton (2006) describe the use of biofilters to mitigate the emission of CH₄ from landfill vents. They found that methanotrophic CH₄ oxidation (an aerobic process) within a mature compost biofilter reduced emissions by between 47 and 100%. Biofilter removal of CH₄ and N₂O from the exhaust of an enclosed MBT system was studied by Clemens & Cuhls (2003). The use of a biofilter on this process appears to have been of little benefit in that CH₄ was not removed from the exhaust stream, and N₂O emissions were enhanced by the use of an aerobic biofilter. In this study up to 23% of the NH₃ that was removed by the biofilter was converted to N₂O. It is a possibility that the parameters driving N₂O production and emission during composting discussed earlier in this Chapter are also functional in biofilter media. There is an urgent need for further study into the emission of CH₄ and N₂O from biofilters used in enclosed composting and MBT systems. Waste life cycle analysis (LCA) models such as the Swedish ORWARE model (Organic waste research model) (Bjorklund et al 2000) and the UK Environment Agency WRATE (Waste and Resources Assessment tool for the Environment) model (Environment Agency 2006) provide some estimate of CH₄ and N₂O emissions from organic waste treatment and biofilters. However these estimates are based on data from a very limited number of studies, and are likely to be improved by further investigation.
8.5 Recommendations and future work

- Emissions of CH$_4$ and N$_2$O from large-scale composting need to be further quantified to improve up-scaling estimates of the contribution composting makes to atmospheric CH$_4$ and N$_2$O. Increasing amounts of organic wastes are being diverted away from landfill (where gas collection systems can be used) to open air windrows where all gaseous products are emitted to the atmosphere, therefore quantification of emissions should be undertaken on the wide variety of systems currently in use.

- Practical assessment of methods to mitigate emission of CH$_4$ and N$_2$O from large-scale composting need to be performed, and should take into account the aerobic treatment of other organic wastes.

- Further research is needed to develop protocols and methods of evaluation to determine CH$_4$ and N$_2$O emissions to air for in-vessel systems which incorporate forced air re-circulation systems.

- The inclusion of composting emissions in UK greenhouse gas inventory data is increasingly urgent as the use of composting becomes more widespread. Priority should be given to this as there is a need to produce accurate data on the emission of CH$_4$ and N$_2$O from the many sources in line with the Kyoto protocol.

- The use of in-vessel composting systems has recently increased on both the large and small scale, and using a wide variety of open and closed systems. Emission limits from these types of systems have not been set in the UK for CH$_4$ and N$_2$O, the only monitoring requirement of in-vessel systems is temperature for animal by-
product order compliance. This legislative delay in response to the growing use of these systems must be addressed as soon as possible.

- Compliance with the EU landfill directive will lead to many diverse organic waste types being biologically stabilised prior to landfill in both open and closed composting systems. The biodegradability of waste has been shown to be one of the most important factors in the production of CH$_4$ and N$_2$O during composting, and therefore monitoring processes that are composting wastes of varying biodegradability is becoming increasingly relevant and should be taken into account when predicting future emission trends.

- The method of assessing how waste biodegradability is measured has an impact on the processing time the diverted organic wastes are subjected to, and the duration of composting time impacts on CH$_4$ and N$_2$O emission. The implementation of biodegradability assessment should take into account greenhouse gas emissions as one of the major purposes of diverting waste away from landfill is to reduce CH$_4$ emissions to atmosphere.

8.6 Summary and conclusions

- CH$_4$ and N$_2$O emissions were observed from all composting systems studied, varying in intensity between composting processes, stage of the composting process, and wastes of differing characteristics. The expansion in the use of composting, in response to Landfill directive and Animal by-product legislation will, increase associated CH$_4$ and N$_2$O emissions.
• The use of respirometry was found to be a powerful test of waste biodegradability, and was used successfully to assess the potential of a waste to produce CH$_4$ and N$_2$O during composting.

• Type of composting process used can dictate the pattern of CH$_4$ and N$_2$O emission. Vermicomposting was shown to be characterised by N$_2$O emission and windrow composting by CH$_4$.

• Emissions of N$_2$O from vermicomposting were shown to be enhanced when the process temperature was raised in order to improve waste processing. The benefits of faster composting time should be balanced against the environmental impact of increased N$_2$O emission.

• In-vessel composting showed the potential to be a significant source of CH$_4$ and N$_2$O production and emission and sampling methods were developed to understand this method of composting.

• Composting was found to be a complex process where simultaneous aerobic and anaerobic microbial processes, during the degradation of wastes of varying substrate content and biodegradability, can produce significant CH$_4$ and N$_2$O emission. These emissions have not as yet been accounted for in inventories of anthropogenic greenhouse gases, an omission which is gaining importance due to the projected increase in the use of composting as a sustainable waste management option.
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Appendix I Individual analysis repetitions

Table A.I.1 Individual measurements of the passive build up of CH₄, N₂O and CO₂ in the headspace of in-vessel composting system 1 at the start of composting (day 0) and after 7 days composting (0–30 minutes)

<table>
<thead>
<tr>
<th>Sample time (minutes)</th>
<th>Day 0 N₂O (ppm) rep1</th>
<th>Day 0 N₂O (ppm) rep2</th>
<th>Day 0 CH₄ (ppm) rep1</th>
<th>Day 0 CH₄ (ppm) rep2</th>
<th>Day 0 CO₂ (%) rep1</th>
<th>Day 0 CO₂ (%) rep2</th>
<th>Day 7 N₂O (ppm) rep1</th>
<th>Day 7 N₂O (ppm) rep2</th>
<th>Day 7 CH₄ (ppm) rep1</th>
<th>Day 7 CH₄ (ppm) rep2</th>
<th>Day 7 CO₂ (%) rep1</th>
<th>Day 7 CO₂ (%) rep2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.4</td>
<td>1.3</td>
<td>2.2</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
<td>0.2</td>
<td>78.2</td>
<td>77.7</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>5</td>
<td>8.0</td>
<td>7.2</td>
<td>2.3</td>
<td>2.4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>151.0</td>
<td>147.6</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>10</td>
<td>10.7</td>
<td>10.9</td>
<td>2.4</td>
<td>2.4</td>
<td>0.6</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
<td>220.4</td>
<td>212.6</td>
<td>0.3</td>
<td>0.3</td>
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<td>15</td>
<td>17.2</td>
<td>16.1</td>
<td>2.6</td>
<td>2.6</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>294.9</td>
<td>274.0</td>
<td>0.4</td>
<td>0.4</td>
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<td>20</td>
<td>22.9</td>
<td>22.8</td>
<td>2.9</td>
<td>2.9</td>
<td>1.1</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
<td>358.6</td>
<td>350.7</td>
<td>0.5</td>
<td>0.5</td>
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<td>25</td>
<td>30.5</td>
<td>30.5</td>
<td>3.0</td>
<td>3.0</td>
<td>1.2</td>
<td>1.2</td>
<td>0.8</td>
<td>0.8</td>
<td>395.4</td>
<td>392.4</td>
<td>0.7</td>
<td>0.8</td>
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<tr>
<td>30</td>
<td>35.5</td>
<td>36.1</td>
<td>3.3</td>
<td>3.4</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
<td>1.0</td>
<td>523.4</td>
<td>510.9</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Day 0: 96.8 - 196.9
Day 4: 73.0 - 126.0
Day 8: 77.5 - 78.2
Day 14: 67.4 - 69.7

Table A.1.2 Range of dynamic respiration index, volatile solids, total Kjeldahl nitrogen and dry solids content of both the source segregated household waste and residual waste throughout the in-vessel composting process.
Table A.1.3 CH\(_4\) concentration in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.9)

<table>
<thead>
<tr>
<th>Sampling day</th>
<th>CH(_4) ppm (low biodegradability with insufficient aeration)</th>
<th>CH(_4) ppm (high biodegradability with insufficient aeration)</th>
<th>CH(_4) ppm (low biodegradability with sufficient aeration)</th>
<th>CH(_4) ppm (high biodegradability with sufficient aeration)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rep 1  Rep 2  Rep 3  mean</td>
<td>Rep 1  Rep 2  Rep 3  mean</td>
<td>Rep 1  Rep 2  Rep 3  mean</td>
<td>Rep 1  Rep 2  Rep 3  mean</td>
</tr>
<tr>
<td>1</td>
<td>5      5      4      5</td>
<td>5      5      5      5</td>
<td>4.7     4.9     4.9     4.8</td>
<td>4.7     5.4     5.5     5.2</td>
</tr>
<tr>
<td>2</td>
<td>405    458    349    404</td>
<td>383    386    421    397</td>
<td>6.2     6.6     6.5     6.4</td>
<td>123.5   141.8  130.1  131.8</td>
</tr>
<tr>
<td>3</td>
<td>806    903    666    792</td>
<td>1316   1287   1461   1355</td>
<td>7.7     8.6     8.3     8.2</td>
<td>242.4   261.4  265.9  263.2</td>
</tr>
<tr>
<td>4</td>
<td>1160   1345   1107   1204</td>
<td>2253   2224   2629   2369</td>
<td>11.3    12.6    12.4    12.1</td>
<td>338.2   391.0  369.2  366.1</td>
</tr>
<tr>
<td>5</td>
<td>1272   1384   1087   1248</td>
<td>2820   2796   2958   2858</td>
<td>14.8    15.6    16.0    15.5</td>
<td>401.0   410.9  462.1  424.7</td>
</tr>
<tr>
<td>6</td>
<td>1273   1372   1072   1239</td>
<td>2906   2513   3025   2815</td>
<td>18.3    19.9    21.3    19.8</td>
<td>353.0   404.7  387.3  381.7</td>
</tr>
<tr>
<td>7</td>
<td>1244   1401   1151   1265</td>
<td>2885   2517   3443   2948</td>
<td>21.9    25.0    25.7    24.2</td>
<td>330.0   390.6  342.5  354.4</td>
</tr>
<tr>
<td>8</td>
<td>1148   1286   1019   1151</td>
<td>2846   2634   2966   2816</td>
<td>16.1    18.2    17.4    17.2</td>
<td>266.0   310.1  267.0  281.0</td>
</tr>
<tr>
<td>9</td>
<td>1131   1266   952    1116</td>
<td>2811   2369   3387   2856</td>
<td>14.2    15.9    14.6    14.9</td>
<td>237.0   239.2  251.7  242.6</td>
</tr>
<tr>
<td>10</td>
<td>1134   1288   1016   1146</td>
<td>2742   2499   3128   2790</td>
<td>12.4    12.9    13.7    13.0</td>
<td>184.0   215.0  189.9  196.3</td>
</tr>
<tr>
<td>11</td>
<td>1056   1124   912    1030</td>
<td>2678   2533   3049   2753</td>
<td>10.6    12.5    12.5    11.9</td>
<td>163.0   193.4  176.3  177.6</td>
</tr>
<tr>
<td>12</td>
<td>963    1008   801    924</td>
<td>2625   2624   3122   2790</td>
<td>8.5     9.3     10.1    9.3</td>
<td>99.0    101.6  105.7  102.1</td>
</tr>
<tr>
<td>13</td>
<td>876    887    864    876</td>
<td>2550   2245   2942   2579</td>
<td>6.3     7.2     6.5     6.7</td>
<td>65.3    73.5   79.1   72.6</td>
</tr>
<tr>
<td>14</td>
<td>839    923    774    845</td>
<td>2517   2257   2980   2584</td>
<td>5.2     5.4     6.1     5.6</td>
<td>24.8    28.2   27.8   27.0</td>
</tr>
<tr>
<td>15</td>
<td>680    802    693    725</td>
<td>2391   2399   2641   2477</td>
<td>5.5     6.0     5.7     5.7</td>
<td>17.0    11.0   10.2   12.8</td>
</tr>
<tr>
<td>16</td>
<td>656    735    605    665</td>
<td>2355   1929   2801   2361</td>
<td>5.4     5.6     6.6     5.9</td>
<td>11.0    12.1   11.7   11.6</td>
</tr>
<tr>
<td>17</td>
<td>608    702    562    624</td>
<td>2302   2152   2348   2267</td>
<td>5.4     6.6     6.1     6.0</td>
<td>10.0    10.9   11.3   10.7</td>
</tr>
<tr>
<td>18</td>
<td>527    567    464    519</td>
<td>2177   1923   2369   2156</td>
<td>4.4     4.6     4.5     4.5</td>
<td>9.0     9.8    10.6   9.8</td>
</tr>
<tr>
<td>19</td>
<td>526    605    448    527</td>
<td>2130   1864   2491   2162</td>
<td>4.3     4.6     5.0     4.7</td>
<td>11.0    12.8   12.9   12.2</td>
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<tr>
<td>20</td>
<td>490    549    474    504</td>
<td>2105   2047   2331   2161</td>
<td>3.3     4.0     3.9     3.7</td>
<td>9.0     10.5   10.7   10.1</td>
</tr>
<tr>
<td>21</td>
<td>474    512    390    459</td>
<td>2003   1655   2427   2029</td>
<td>2.5     3.0     3.0     2.8</td>
<td>9.0     9.9    9.4    9.5</td>
</tr>
</tbody>
</table>

mean         | 823    911    734    822                                      | 2229   2041   2520   2263                                     | 9.0     9.9    10.0   9.7                                     | 138.5   154.5  150.3  148.0                                   |
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Table A.1.4 N20 concentration (ppm) in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.10)

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Table A.1.5 CO$_2$ concentration (%) in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.11)

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<th>Sampling Day</th>
<th>CO$_2$ % (low biodegradability with insufficient aeration)</th>
<th>CO$_2$ % (high biodegradability with insufficient aeration)</th>
<th>CO$_2$ % (low biodegradability with sufficient aeration)</th>
<th>CO$_2$ % (high biodegradability with sufficient aeration)</th>
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<td>Rep 3</td>
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<td>0.9</td>
<td>0.6</td>
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Table A.16: 0% concentration (%) in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.12)
Table A.1.7 NH₃ concentration (ppm) in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.13)

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<th>NH₃ (ppm) (high biodegradability with insufficient aeration)</th>
<th>NH₃ (ppm) (low biodegradability with sufficient aeration)</th>
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<td>Sampling day (low biodegradability with sufficient aeration)</td>
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<td>FID VOC (ppm)</td>
<td>FID VOC (ppm)</td>
<td>FID VOC (ppm)</td>
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Table A.1.8 Flame ionisation detector (FID) VOC concentration (ppm) in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.14)
Table A.1.9 Photo ionisation detector (PID) VOC concentration (ppm) in the exhaust air from the test chambers (individual repetitions) used in Chapter 7 (Table 7.15)

<table>
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<th>PID VOC (ppm) (high biodegradability with insufficient aeration)</th>
<th>PID VOC (ppm) (low biodegradability with sufficient aeration)</th>
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