THE COMPOSTABILITY AND DIRECT LAND APPLICATION OF PAPER MILL SLUDGE

by

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DEDICATION

To my loving parents, my grandmother and my late grandparents.

PREFACE

I, Bhavna Singh, declare that the research reported in this dissertation, except where otherwise indicated is my original research. This dissertation has not been submitted for any degree or examination at any other university. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons. This dissertation does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then their words have been re-written but the general information attributed to them has been referenced. Where their exact words have been used, then their writing has been placed in italics and inside quotation marks, and referenced. This dissertation does not contain text, graphics or tables copied and pasted from the Internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

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Bhavna Singh Date

As the candidate's Supervisor I agree to the submission of this dissertation.

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Iain Kerr Date

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ABSTRACT

Mpact Ltd strives for the environmentally friendly disposal of waste material generated by 3 mills, Mill A, B and C. Mill C makes use of unbleached bagasse pulp to produce fluting and corrugated packaging paper, producing an effluent sludge stream (PMS_C) and a stream which contains the pith waste (pith). It was in their best interest to investigate the land application of this pith/PMS_C blend as a suitable disposal option. Hence the scope of this study was (i) the preliminary characterisation of the pith/PMS_C blend, (ii) investigate the compostability of pith/PMS_C blend and (iii)to investigate the effects on soil properties when applying raw pith/PMS_C blend to soil.

The nutrient value of this pith/PMS_C blend had not yet been quantified hence Chapter Three covers the preliminary characterisation of all the PMS samples.It was concluded that the moisture content in all samples exceeded the desirable range for composting due to the mill specific dewatering equipment. In addition, an inverse relationship between pH and EC was observed. The nutrient availability was also found to be dependent on the pH.

Chapter Four investigates the compostability of pith/PMS_C on a small and a large scale using porous bags in each case. It was observed that the composting materials in both the small and large scale composting experiments did not rapidly heat up at the beginning. It was concluded that the moisture, air and the volume of the composting material were the key parameters responsible for this. The compostability experiments were, however, successful in producing an end product that was within the desired specifications and limits.

The direct land application of pith/PMS_C (3:1) on soils was investigated by analysing soils treated with pith/PMS_C (3:1). The application was found to be beneficial to soil after seeing an improvement in cation exchange capacity and C/N ratio. It was concluded that more applications of this will be beneficial to the soil and crops in the long run and N immobilisation will be prevented.

A laboratory scale experiment was done to assess the effect of pith/PMS_C (3:1) on soil in a controlled environment using an ASTM standard method. This involved the aerobic degradation of varying ratios of pith/PMS_C (3:1) mixed with soil in bioreactors, with constant monitoring of air flow, CO_2 production and biodegradation rates. This part of the study, however, was inconclusive.The hypotheses of the study were correct as the pith/$PMS_C$was degraded by composting into a stable, environmentally friendly end product and the addition of pith/PMS_C to soil as an amendment was beneficial to the soil.

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CHAPTER ONE

Introduction

The production of pulp and paper is a large industry that generates large quantities of solid waste. This solid waste may include ash, bark and wood and other miscellaneous residues (Beauchamp et al., 2002), however, 87% of this solid waste is paper mill sludge (PMS) (Norrie and Fierro, 1998). The prediction of an increase in global production of PMS between 48 and 86% over current levels, favoured the Asia-Pacific region emerging amongst the major producers of PMS over the next 4 decades (Mabee and Roy, 2003).

One of the most serious issues facing modern industry is the management of wastes in an economically and environmentally acceptable manner, due to the more stringent environmental quality requirements enacted by legislation (Likon and Trebše, 2012).

Some of the integral concerns faced by the pulp and paper industry are energy savings and sustainable energy production. One method that has been recently adopted to utilise the excessive discharge of solid waste by mills is energy recovery. The use of the waste material for bio-gas production is a concept being researched.

Methods of disposal, such as landfilling and incineration, seem to be avoided nowadays. With regard to incineration, burning for energy is not an option due to the high mineral content of PMS (Schut, 2004). Furthermore, the incineration of by-products has become an unfavourable means of disposal (Suriyanarayanan et al., 2010). Degradation of waste in the landfill results in the continuous production of hazardous gases, mainly methane. The rising costs, however, of the aforementioned disposal practices together with the increasingly stringent environmental legislation and a rise in production quantity has resulted in the exploration of alternative uses for PMS, more especially the use of PMS as a soil amendment.

Applications of industrial wastes as fertilisers or soil amendments have become popular in agriculture. Land application is one of the few environmentally friendly methods available to manage solid wastes (Schoof and Houkal, 2005). It is a more economically and ecologically sound option than landfill practice (Zule et al., 2007). According to Nkana et al. (1999) and Foley and Cooperband (2002), PMS contains matter both of organic and nutrient value. This kind of application may correct the organic and nutrient status of poor soil, and improve soil fertility whilst reducing the treatment and disposal costs significantly.

Mpact Ltd. strives for the environmentally friendly disposal of waste material generated by three mills, Mill A, B and C. Mill C makes use of unbleached bagasse pulp to produce fluting and corrugated packaging paper. Two waste streams are produced, an effluent sludge stream (PMS_C) and a stream which contains the pith waste (pith). This study was initially proposed to characterise the pith/PMS_C blend and better understand its functionality. From this, a more complex study was proposed, i.e. the investigation into the compostability of the pith/PMS_C blends as well as understanding the direct land application of this material and its effect on soil properties. The objectives of this study were therefore:

i. The characterisation of the pith/PMS_C blend.
ii. The compostability of the pith/PMS_C blends and the use of the pith/PMS_C blend as quality compost.
iii. The direct land application of the pith/PMS_C blend and its effect on the soil fertility.

The environmentally safe disposal of PMS is a major concern for most paper mills. The hypotheses were thus:

i. Pith/PMS_C can be degraded by composting into a stable, environmentally friendly end product.
ii. The addition of pith/PMS_C to soil as an amendment is beneficial to the soil.

This research began with the project background as well as a general literature review (Chapter Two) which covered the composting processes, the direct land application of PMS as well as alternate uses. Chapters Three to Seven provides the experimental procedure and laboratory methods used to guide any future research together with the results and discussions for each of the experimental methods covered. Chapter Eight provides the conclusions and recommendations. The plan and structure of this study is shown in Figure 1-1.

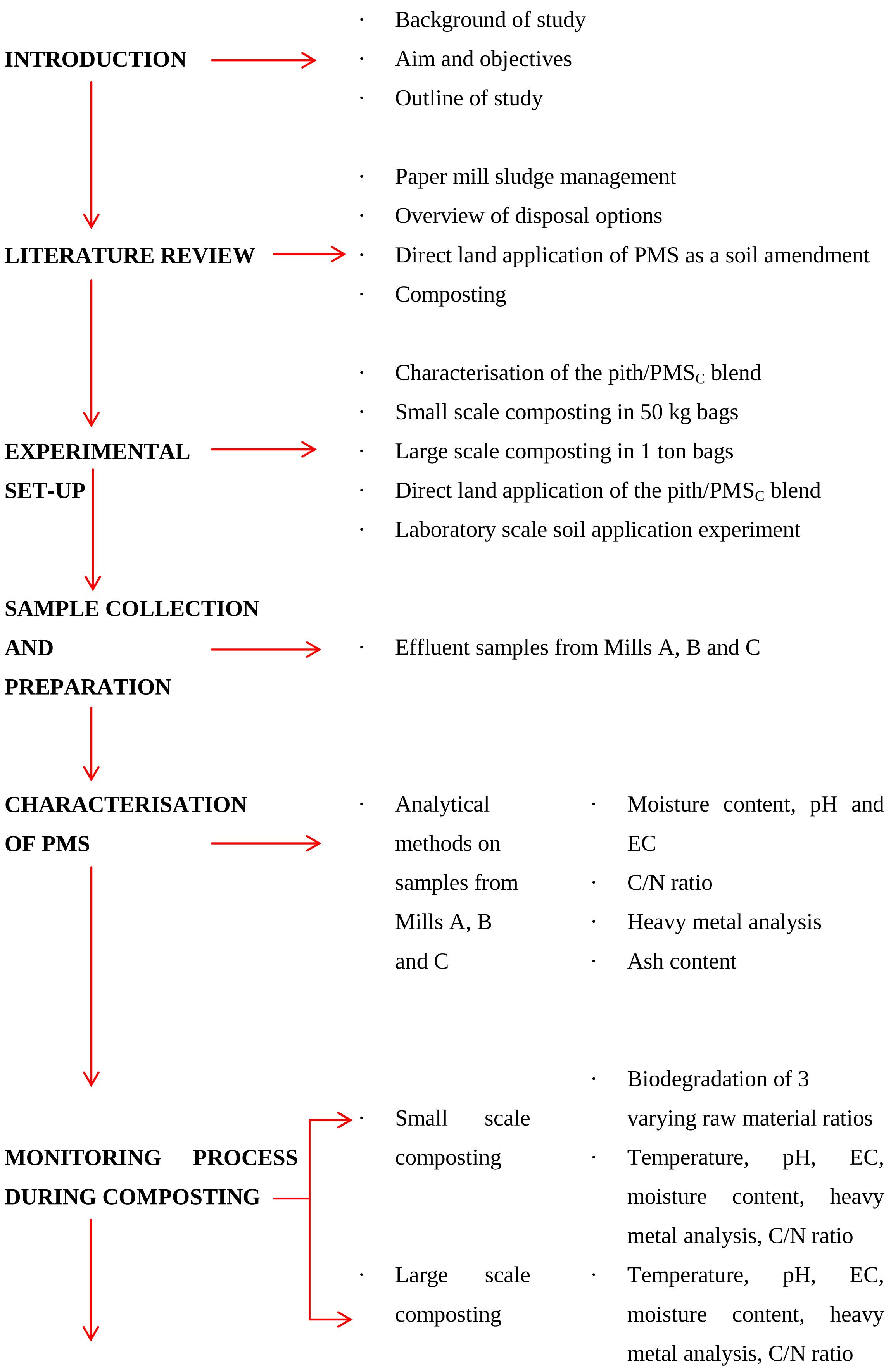

Figure 1-1: *Structure of research work*

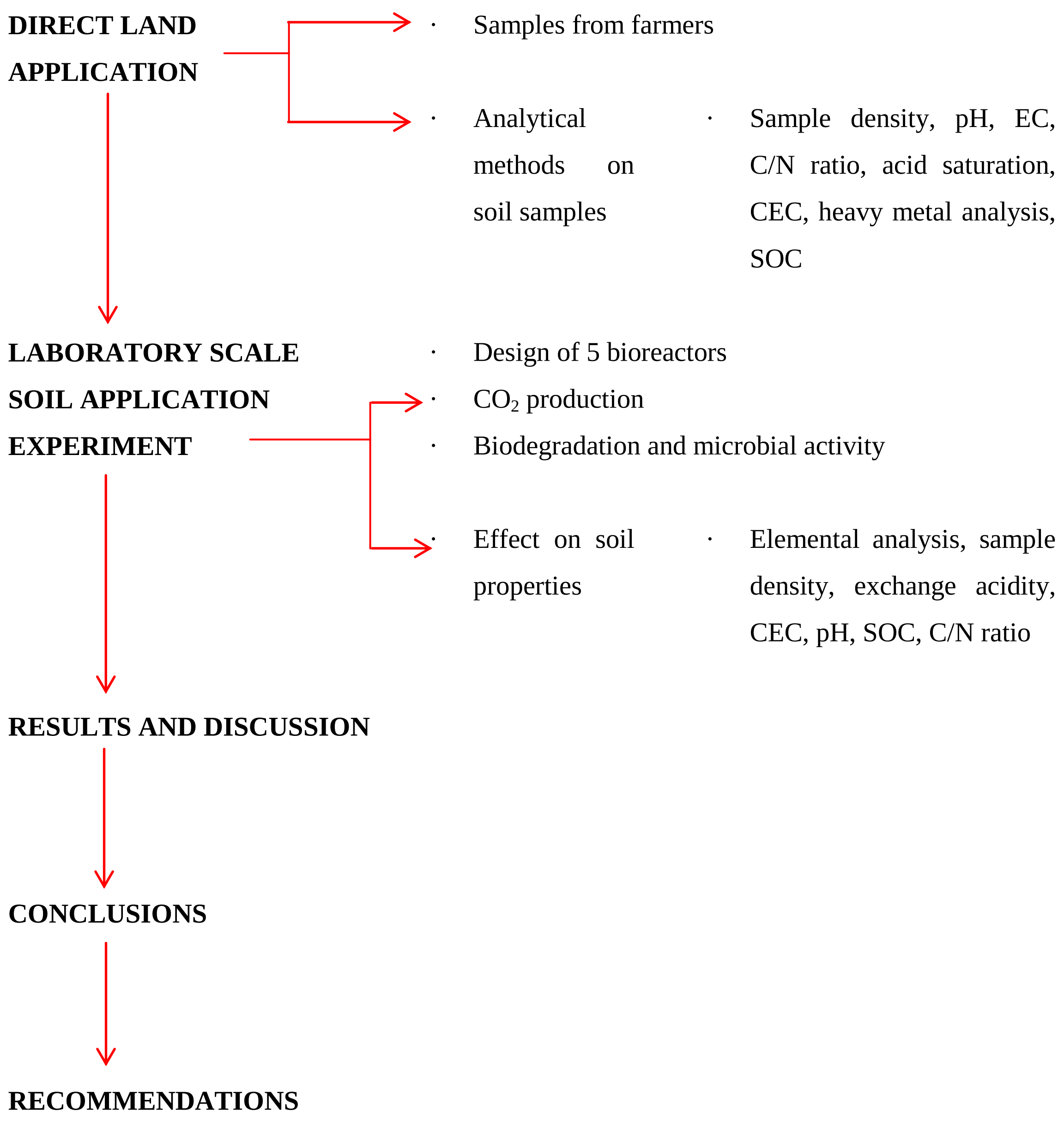

Figure 1-1: *Structure of research work (continued)*

CHAPTER TWO

Theoretical background

2.1 Introduction

The increase in the amount of recycling over the years has increased the amount of material that needs to be disposed of (Scott and Smith, 1995). According to Likon and Trebše (2012), recyclers are producing two to four times more PMS as virgin pulp mills.

In this chapter, an overview of the options available for disposal of the PMS will be discussed. Emphasis will be placed on the land application of PMS as a soil amendment and as compost.

2.2 Overview of the disposal options

According to Mabee and Roy (2003), 45% of PMS is landfilled, 5% is used for land application and approximately 45-50% is incinerated. Using these statistics, three random scenarios for PMS disposal on a global scale were created (Figure 2-1). These scenarios, however, assume that each technique can be a substitute for the other.

In Scenario A, disposal by landfill and incineration are expected to almost double by the year 2050 from the year 2000 (Mabee and Roy, 2003). This means that there will be an increase in the demand on landfills and incinerators. Scenarios B and C show the effect of cutting back on either one of the two leading disposal techniques. By decreasing the quantity permitted for incineration in Scenario B, and the quantity permitted for landfilling in Scenario C, a further 1 000 000 tons of sludge is diverted to each of the other options (Mabee and Roy, 2003). This highlights the need for the third option, which is land application, to be explored more thoroughly to ease the demand on each of the other disposal options.

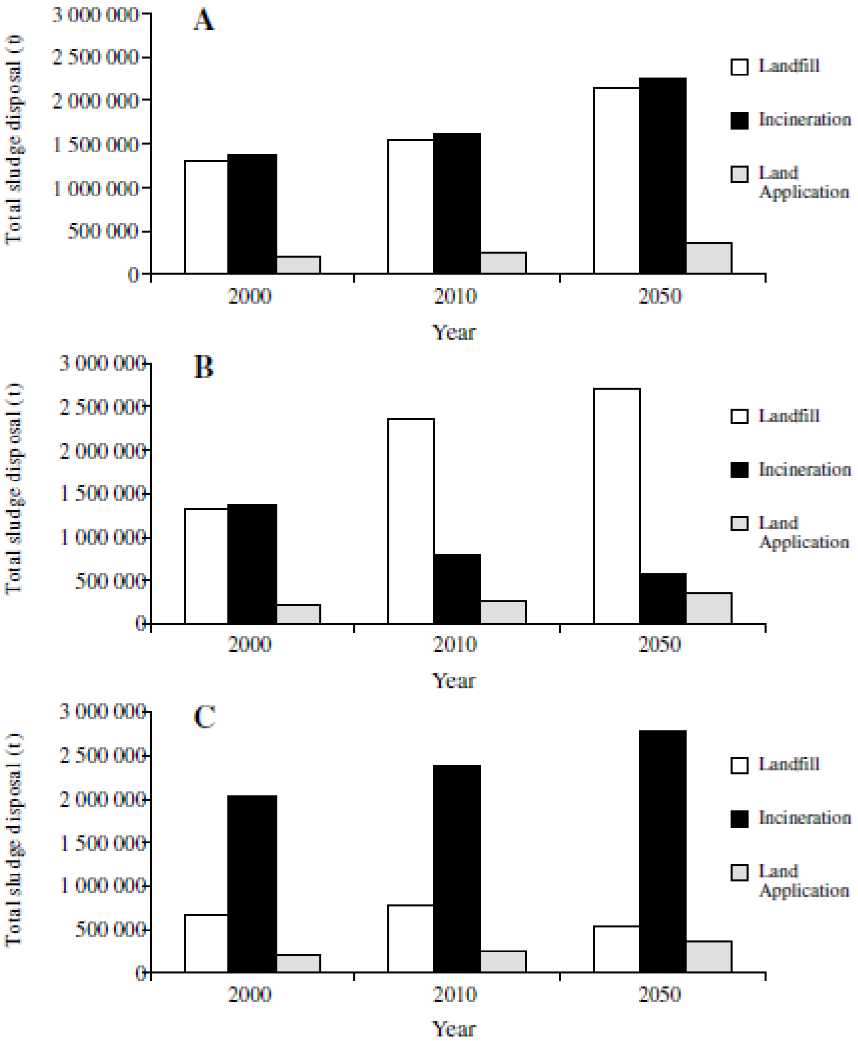

Figure 2-1: *Implications of policy decisions for sludge disposal options over the years 2000-2050. Scenario A illustrates the increase in the demand on landfills and incinerators. Scenario B and C illustrate the effect of diverting the increase in PMS to either landfilling or incinerators respectively (Mabee and Roy, 2003).*

Two global concerns are climate change and the lack of space for potential landfills. This means that there will be an increase in cost for the leading disposal methods. Hence the more sustainable alternative is land application.

2.2.1 Landfilling

Landfill sites can be defined as *"...sites for disposing of solid waste on land engineered for reduction of hazards to public health and safety"* (Deng, 2007). Landfillinghas been the most commonly used method for the disposal of solid wastes since the 1950's (Deng, 2007).

According to the Department of Environmental Affairs (2012), the modelling of available data concluded that of the approximate 108 million tons of waste produced by South Africa in 2011, 97 million tons was disposed to landfill. Waste management in South Africa is therefore still reliant on landfilling as a waste management option.

If landfilling is not carried out in a manner that adheres to satisfactory standards and methods, there can be undesirable effects on the environment. Therefore the design considerations are of vital importance.

A few potential environmental impacts that are worth considering by the landfill designer include the nature and quantity of waste deposited, protection of soil and water, leachate management, gas control and environmental nuisances (Crowley at al., 2003)

2.2.1.1 The environmental effects of landfilling

Landfills are known to be an environmental threat due to the production of landfill gas and contaminated water, wind-blown litter and dust, as well as attracting vermin (Crowley et al., 2003). Landfill gas is known to be produced by the degradation of the waste over four phases (Crowley et al., 2003):

- Over the first few weeks, the O_2 is depleted and CO_2 and H_2O are produced. This is known as aerobic decomposition.
- The CO_2 production peaks and volatile fatty acids and H_2 are produced. No methane is produced hence this phase is called anaerobic and non-methanogenic.
- The anaerobic methanogenic phase is the start of the methane production. H_2 is rapidly used up, and CO_2 production falls to a constant rate. N_2 is produced.
- The gas production rates increaseonly slowly until the nutrient is depleted in the final phase. The methane produced during the anaerobic methanogenic phase contributes to 20% of the total global methane emissions that are caused by humans (Crowley et al., 2003).

For control of landfill gas, landfill gas management systems are installed to prevent any potential risk to the environment. These include the minimisation of the risk of landfill fires, damage to soils and vegetation within the restored landfill area and permit effective control of gas emissions (Crowley et al., 2003).

Another major concern is that of leachate management. Leachate is defined as *"...a contaminated liquid that flows from the waste material"* (Crowley et al., 2003).The volume of the leachate depends on the rainfall.It consists of the penetrating rain or ground water picking up contaminants as it passes through the waste, however, the environmental impact of the leachate is dependent on the nature of the material from which it originates (Crowley et al., 2003).

An effective leachate management system is a prerequisite for all landfill sites. This allows for the removal of the leachate from the landfill by controlling the depth of the leachate above the liner. The leachate management system should include the following (Crowley et al., 2003):

- A drainage layer constructed of granular material.
- Perforated leachate collection pipes within the drainage layer. This allows the leachate to be moved to the sump.
- A protective filter layer over the drainage layer to prevent physical clogging.
- Leachate monitoring points.
- Leachate collection sump.
- A landfill liner to prevent leachate from leaving and groundwater from entering.

Figure 2-2 illustrates an ideal landfill with an effective leachate management system installed.

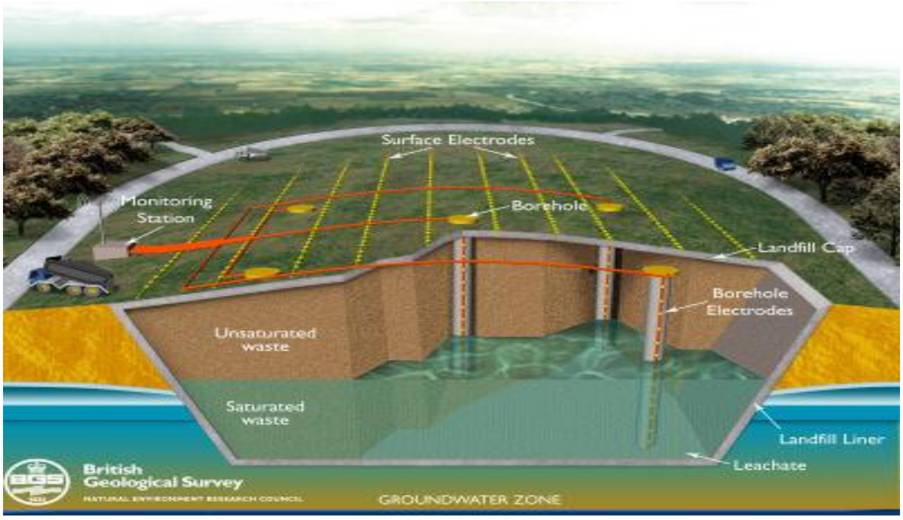

Figure 2-2: *Cross-sectional view of an ideal landfill site (Knotts, 2011)*

2.2.2 Incineration

A large proportion of PMS is disposed of by incineration. According to literature, PMS has high moisture and hence a low heating value (Mabee and Roy, 2003). However, depending on the composition of the PMS, some might have significant calorific values (Sanin et al., 2011). Paper mill sludge also has a high ash content. There is a capital cost involved in using sludge as a heat source resulting from the need for a fluidised bed system rather than a simple grate boiler. Another problem with incineration is the large energy consumption required for the burning of

PMS when the moisture content exceeds the economic moisture range of 28-50% m/m (Mabee and Roy, 2003). PMS can be combusted at a dedicated hazardous waste incineration facility or can be combusted as an auxiliary fuel in combustors of refiners or cement factories (Sanin et al., 2011).

2.2.2.1 PMS ash

Paper mill sludge ash results from the incineration of PMS at 525°C (Tappi, 1993). After incineration, it can be used as a key ingredient in cement production and blended cements due to the presence of calcium, silica and alumina (Mabee and Roy, 2003). Paper mill sludge ash is well suited for use in the construction industry as it is available in large quantities and is an inert material. Currently, PMS ash is also used in waste neutralisation.

2.2.3 Other viable applications of PMS

The critical properties of alternate fuels are (Mabee and Roy, 2003):

- Calorific Value
- Moisture content
- Ash content
- Suspended solid content
- Sulphur content
- Halogen content
- Heavy metal content
- Physical characteristics such as size range

Paper mill sludge is a viscous, sticky material that is difficult to dry. Due to its energy content, PMS can be classified as an alternate fuel, especially in the manufacture of cement.

The application of PMS in the construction field is growing rapidly. Paper mill sludge can be used in the production of plasterboard and alternate fuels for the production of cement and bricks (Mabee and Roy, 2003).

2.3 The direct land application of PMS as a soil amendment

Direct land application, in this context, refers to disposal of sludge onto land in a controlled manner. Because waste management has become a major environmental challenge, applying sludge over large land surfaces is a widely used application as it offers many possible benefits.

These benefits, however, have to be weighed against the potentially harmful effects. These include:

- The risk of excessive nitrate leaching.
- Contamination of the soils and crops with human pathogens and heavy metals.
- Nutritional disorders in crops.
- Increase in soil salinity.
- Contamination of groundwater with pesticides, hormones and pharmaceuticals.
- Decreased stability of native soil organic matter (Robert et al., 2011).

A “soil amendment” can be defined as *“...any material that is added to soil to benefit the soil or plant.”* (Zhang, 2006). Due to the fact that cellulosic pulp is one of the significant components of PMS, it can be categorised as primarily organic in composition. However, in some cases, PMS may contain a higher inorganic content due to an accumulation of fillers such as calcium carbonate.

The use of PMS could prove beneficial in the long run in terms of agricultural productivity as well as long term sustainability. In order to successfully utilise the PMS, however, a thorough understanding of the physical and chemical characteristics of the sludge is required together with the nutrient requirements by the plants and the soil.

2.3.1 Soil fertility

2.3.1.1 Soil pH

Soil pH is an important chemical characteristic for plant growth and directly affects the nutrient availability, nutrient toxicity and microbial activity (Medinski, 2007). Some nutrients bind tightly to soil particles at low pH’s and as a result are unavailable to plants. In addition to this, the chemical structure of some nutrients, particularly phosphorus, change atlow pH and the availability of these nutrients to the plants decreases.

Micronutrients such as boron, chloride, copper, manganese, and zinc are less available at a pH less than 4.5. Macronutrients such as nitrogen, phosphorus, potassium, sulphur, calcium and magnesium are less available at a pH less than5. Therefore, maximum nutrient availability occurs when the pH is optimal for the nutrient (Dinkins and Jones, 2013), as can be seen in Table 2-1.

Table 2-1: *Soil nutrient classes, toxicity levels and optimal pH ranges*

Nutrient	**Low Levels (ppm)**[1]	**Medium Levels (ppm)**[1]	**High Levels (ppm)**[1]	**Toxicity Levels (ppm)**[1]	**pH at which availability is reduced**[2]
N	n/a	n/a	n/a	n/a	< 5 and > 9
P	< 8	8 – 16	> 16	n/a	< 5 and 8.5 – 9.5
K	< 150	150 – 250	> 250	800	< 5
S	n/a	n/a	n/a	n/a	< 5
B	< 0.5	0.5 – 1	> 1	5	< 4.5 and > 7.5 – 8.5
Cl	n/a	n/a	n/a	n/a	< 4.5 and > 8
Cu	< 0.25	0.25 – 0.5	> 0.5	n/a	< 4.5 and > 8
Fe	< 2.5	2.5 – 5	> 5	n/a	>7.5
Mn	< 0.5	0.5 – 1	> 1	n/a	< 4.5 and > 8
Zn	< 0.25	0.25 – 0.5	> 0.5	60	< 4.5 and > 8
Ca	n/a	n/a	n/a	n/a	< 5 and > 9
Mg	n/a	n/a	n/a	n/a	< 5 and > 9
Mo	n/a	n/a	n/a	n/a	< 5.5
Al	n/a	n/a	n/a	n/a	< 5.5

[1] Dinkins and Jones (2013)

[2] Hazelton and Murphy (2007)

Figure 2-3 further illustrates the nutrient availability over a certain pH range. Fungi can survive under all pH ranges, whereas the bacteria/actinomycetes have reduced availability below a pH of 6 (Natural Resources Conservation Service, 2013).

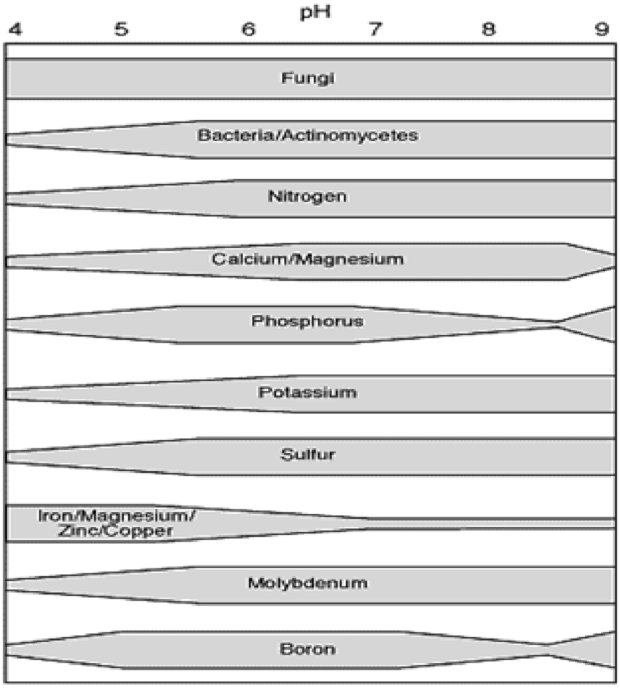

Figure 2-3:*Relationship between soil pH and plant nutrient availability (Natural Resources Conservation Service, 2013)*

2.3.1.2 Soil salinity

Soil salinity affects the yield and the germination rate of plants (Medinski, 2007). These effects can be due to an osmotic effect, specific ion effects orchanges tosoil physical properties (Medinski, 2007). Plants exert an absorptive force greater than that which holds the water to the soil to extract water from the soil by osmosis. The higher the salt concentration in the soil, the more energy required by the plant to extract the water hence high salinity will decrease moisture availability to the plant. This results in dehydration of the plant and diminished nutrient uptake, which restricts plant growth (Medinski, 2007). Generally speaking, the higher the electrical conductivity (EC), the more the plant growth is restricted.

According to Robbins (1993), there exists a relationship between the pH and EC, which he developed to estimate the soil exchangeable sodium percentage (ESP) or soil extract sodium adsorption ratio (SAR) from soil pH and EC.

The model has the form:

$\mathrm{SAR\ or\ ESP} = [(\mathrm{pH} - \mathrm{A})(1 + \mathrm{C} \times \mathrm{EC})/\mathrm{B}]^2$ … (Equation 2.1)

Rearranging Equation 3.5 explicitly shows the relationship between pH and EC:

$\mathrm{pH} = \mathrm{A} + (\mathrm{B} \times \mathrm{SAR}^{1/2})/(1 + \mathrm{C} \times \mathrm{EC})$ … (Equation 2.2)
Where the coefficients A, B and C for a sample are known.

Equation 2.2 shows that pH and EC have an inverse relationship.

Figure 2-4 graphically illustrates the relationship between soils EC (by saturation paste method), SAR, ESP and pH relative to soil classification, as well as plant performance. Using the relationship illustrated in Figure 2-4, together with the guidelines discussed by McCauley (2005), soil can be classified as saline, sodic and saline-sodic based on general EC, SAR, ESP and pH guidelines:

- Saline soils have an EC > 4 dS/m, SAR < 12, ESP < 15 and pH < 8.5
- Sodic soils have an EC < 4 dS/m, SAR > 12, ESP > 15 and pH > 8.5
- Saline-sodic soils have an EC > 4 dS/m, SAR > 12, ESP > 15 and pH < 8.5

The limits for negative impact on survival and growth, acceptable growth and survival are represented by the green, yellow and red curves respectively.

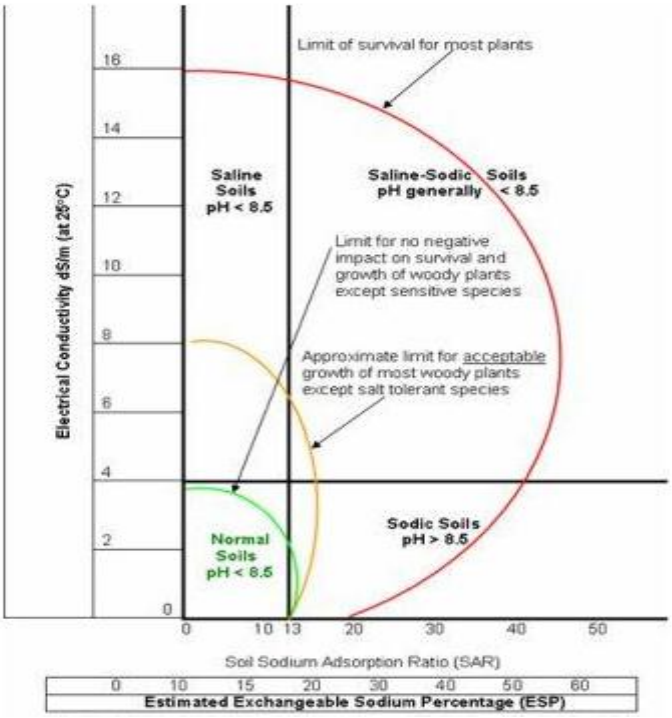

Figure 2-4: *Relationship between soil EC, SAR, ESP and pH (Natural Resources Conservation Service, 2013)*

2.3.1.3 Soil organic matter

Soil organic matter (SOM) affects many soil biological, chemical and physical properties which in turn affect nutrient availability. Some of the roles of organic matter in soil include nutrient storage, energy for microbial activity, an increased water holding capacity as well as buffering pH and EC (Hazelton and Murphy, 2007). Soils rich in SOM will mineralise more N (Dinkins and Jones, 2013).

2.3.1.4 Cation exchange capacity and exchange acidity

Cation exchange capacity (CEC) is the capacity of the soil to hold and exchange cations (Hazelton and Murphy, 2007), and buffers the effects of pH changes, nutrient availability, calcium levels and soil structural changes. A high CEC is therefore sought, as it indicates a high capacity for the soil to hold cations (Drinkins and Jones, 2013). The basic cations include Na^+, K^+, Mg^{2+} and Ca^{2+}. The acidic cations are H^+ and Al^{3+} and are represented by the exchange acidity. The more acidic the soil is, the lower the pH, and the closer the acidity number will be to the CEC number. A low CEC means the soil has a low resistance to change in soil chemistry that is caused by land use. Table 2-2 gives the ratings for CEC in soil (Hazelton and Murphy, 2007).

Table 2-2: *Ratings for cation exchange capacity*

Rating	CEC (cmol/kg)
Very low	< 6
Low	6 – 12
Moderate	12 – 25
High	25 – 40
Very high	< 40

Hazelton and Murphy (2007) suggest that proportions of the various cations of the CEC (expressed as a percentage) are more relative to plant performance than the actual levels. Table 2-3 gives the desirable proportions of CEC of cations for most plants (Hazelton and Murphy, 2007).

Table 2-3: *Desirable proportions of CEC of different cations for most plants*

Cations	**Ranges (% CEC)**
Ca	65 – 80
Mg	10 – 15
K	1 – 5
Na	0 – 1
Al	< 5

2.3.2 The effect of PMS on soil fertility

Paper mill sludge has a significant impact on the physical characteristics of soil by:

- Increasing the water holding capacity.
- Increasing the soil temperature by causing a colour change.
- Increasing the soil moisture content.
- Increasing the plant-available water (Cooperband et al., 1998).
- Increased plant growth (Rashid et al., 2006).

In terms of the chemical characteristics of soil, the changes observed are:

- An increase in absorption and cation exchange capacity.
- Increase in the soils total carbon content (Cooperband et al., 1998).
- Increased nutrient retention (Rashid et al., 2006).
- Increase in soil pH (Robert et al., 2011).

And finally, the biological characteristics of soil are influenced as follows:

- There is an increase in the amount and the activity of soil organism metabolism.
- There is an increase in the micro-organism activity in organic decomposition (Cooperband et al., 1998).

The soil properties impact directly on the plant richness and growth, with the soil pH and soil electrical conductivity (EC) playing an important role.

2.3.3 The effect of PMS on heavy metal content

The potential for heavy metal contamination of water and plants is one of the major concerns with regard to the use of PMS on agricultural land. However, the heavy metal content is generally low in PMS, resulting from either the use of chemicals during the processes or originating from the wood itself (Rashid et al., 2006). Soils previously amended with PMS, or plants grown in these soils, have proven to contain concentrations of heavy metals below the established standards (Rashid et al., 2006). Studies by Aitken et al. (1998) observed that increasing the application rate of PMS to agricultural land resulted in a slight increase in concentrations of heavy metals such as zinc, copper and lead. This was further demonstrated by Rashid et al. (2006), who explained that the copper level in soil treated with deinked PMS exceeded the permissible limit. These results suggest that PMS should not be applied in largequantities as a single dose (Rashid et al., 2006) in order to comply withthe annual polluting loading rate limit for Cu and Zn are 75 kg/ha/yr and 140 kg/ha/yr, respectively (Soil Quality Institute, 2000). Therefore the successive application of PMS to agricultural land will always require monitoring in terms of quantity, and methods of application to avoid soil and water pollution.

2.3.4 Nitrogen immobilization

When a nitrogen fertilizer is applied to soil, N is taken up by the microorganisms in the soil. This process is known as nitrogen immobilization (Mulvaney et al., 1993). This immobilized nitrogen is incorporated into the microbes biomass and as these microbes die and decompose, some of the N is released as ammonium (NH_4^+) (Mulvaney et al., 1993). This is the phenomenon of mineralisation. The remaining N is converted into more stable organic compounds which are not readily available to plants. The result of immobilization-mineralisation is a decrease in the N available to plants in the added fertiliser (Mulvaney et al., 1993). Immobilization of N is largely controlled by the C/N ratio. In the case of a C/N ratio of less than 20, mineralisation will exceed immobilization. The opposite is true for a C/N ratio greater than 30. Another important factor is the type of carbon source (Mulvaney et al., 1993). In a simple substrate like glucose, mineral N is rapidly consumed and found to disappear within a few days. In the case of a more complex substrate like cellulose, however, the process is found to be somewhat slower and the mineral N is never really depleted. Studies by King (1984) and Honeycutt et al. (1988) have shown that PMS with a high C/N ratio applied to land caused an initial net immobilisation of N. An extensive study by Bellamy et al. (1995) over a decade concluded that the principle constraint of use of PMS was N immobilisation. Hence to overcome this, it was recommended that necessary quantities of N fertiliser should be added to the soil to compensate for the loss.

2.4 Composting

2.4.1 Understanding the composting process

Composting involves the breaking down of organic matter to produce CO_2, water, heat and humus. Humus is the more stable organic end product (Trautmann and Olynciw, 1996). Figure 2-5illustrates the four phases that are observed during composting over time.

The first phase is known as the mesophilic phase. Over the initial few days, the mesophilic micro-organisms decompose the degradable compounds. Consequently heat is produced which causes the temperature of the compost to quickly rise, as can be seen in Figure 2-5. Mesophiles function at a temperature range of 10 to 45°C. As the temperature increases above 40°C, the activity of the mesophilic micro-organisms decline and the thermophilic micro-organisms become dominant. This gives rise to the second phase. During this thermophilic phase, the high temperature (45 to 70°C) accelerates the breakdown of the proteins, fats and complex carbohydrates (cellulose and hemicelluloses). As the concentration of these deplete, the temperature begins to decline and the mesophilic micro-organisms recolonize for the final phase, the maturation phase. Aeration is often used together with mixing and turning to prevent the temperature from escalating past 65°C. At this point, all microbes might be killed and the rate of decomposition limited (Trautmann and Olynciw, 1996).

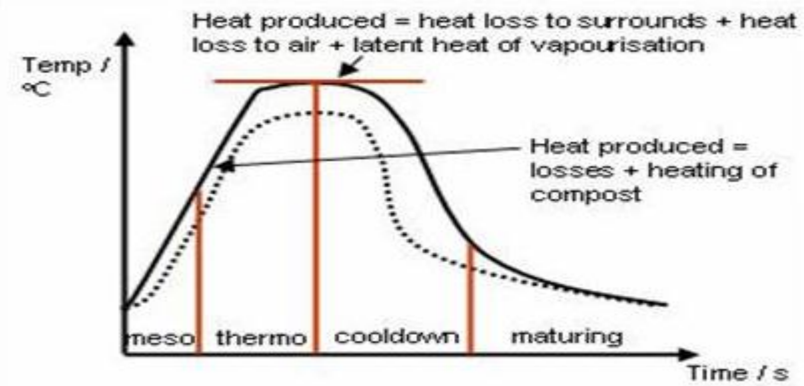

Figure 2-5: *The four phases of composting (Hoang et al., 2012)*

2.4.2 Environmental benefits of composting

The most obvious advantage of composting is the reduction in the waste quantity being landfilled (Ekelund and Nyström, 2007). The advantage doesn't, however, end there. There is not only a reduction in the waste being landfilled, but also a reduction in the environmental impact of the remaining waste already in landfills. By putting less waste into the landfill, the methane production will be reduced (Ekelund and Nyström, 2007). The potential of compost as a fertilizer is also rapidly growing.

Other environmental benefits include economising with limited natural resources, a higher environmental awareness among the population and closing the nutrient loop between the urban and rural areas (Ekelund and Nyström, 2007). Composting is thus a motivating alternative for minimising and recycling waste that inevitably ends up being landfilled.

2.4.3 Chemical characterisation of compost

If the PMS is to be used as compost, the requirements of compost should be met. The key chemical factors and conditions for successful composting are described in the followingsections.

2.4.3.1 pH

During the composting process, the pH varies with time, showing an initial drop due to anoxic conditions and then levels off at about 8 (Sanin et al., 2011). If the pH is greater than 7.5, there is an increased chance of micronutrient deficiencies (Warncke and Krauskopf, 1983). Furthermore, nitrogen escapes as ammonia and causes odour problems (Sanin et al., 2011). A pH that is too low, i.e. less than 6.5, results in calcium and/or magnesium deficiency or manganese toxicity (Warncke and Krauskopf, 1983). At a pH of approximately 8, which is the operational pH of most compost, small losses due to ammonia volatilisation can be expected (Sanin et al., 2011). The pH of the soil is altered once the compost is added resulting from the differences in pH between the soil and the compost. The buffering capacity as well as the quantity of compost utilised may also alter the pH. In addition, the efficiency of the mixing of the soil and compost coupled with the rate at which compost breaks down in the soil may influence the pH value. Consequently, the availability of the nutrients to the plant may be affected (Tester, 1990; Tisdale et al., 1985). The optimum pH range for composting is 6.5-7.5 (Sanin et al., 2011).

During the thermophilic phase of composting, there are changes in pH value due to acetic acid formation and in ammonium content, which is affected by action of the proteolytic bacteria and the temperature (Singh and Kalamdhad, 2012). These changes affect the exchangeable and carbonate fractions.

2.4.3.2 Micronutrients

Micronutrients are essential nutrients required in sludge composting (Sanin et al., 2011). Large concentrations of micronutrients, namely manganese, iron, copper, zinc and boron are toxic to plants. Boron and copper are the most toxic to plants.However, these micronutrients are immobilised by the organic matrix of the compost hence they are not readily available to the plant (Watson, 2007). As the pH increases, there is a noticeable decrease in availability of most micronutrients. Hence it is important to maintain the pH below the maximum (Warncke and Krauskopf, 1983).

2.4.3.3 Macronutrients

The macronutrients, namely nitrogen, potassium, phosphorus, calcium, magnesium and sulphur, are of vital importance to plants. Of these macronutrients, nitrogen availability is most complex. Nitrogen is available in compost in two forms: organic and inorganic nitrogen (Watson, 2007). Inorganic nitrogen is easily obtainable for absorption by plants. The availability of the organic form of nitrogen depends on the rate at which the compost is broken down by microorganisms, which is dependent primarily on temperature and moisture. The remaining macronutrients are readily available to the plant in the first growing season. Their availability, however, depends on the soil type, moisture and temperature (Hue et al., 1994, Wen at al., 1997).

An ample availability of phosphorus is required by plants for the development of the root system, for rapid growth as well as for flower quality in floral plants (Warncke and Krauskopf, 1983). Phosphorus is an important nutrient for photosynthesis. Care should be taken not to over fertilise with phosphate. Excessively high levels may reduce the ability of the plant to take up and utilise several micronutrients.

Potassium is the nutrient that is most often limiting in greenhouse fertility programs (Warncke and Krauskopf, 1983). Potassium demand is the greatest in rapidly growing plants in the vegetative stage.

The availability of calcium for plant uptake is dependent on two factors. Firstly the pH of the growth media and secondly the levels of the remaining cations present, more importantly potassium and magnesium. As the compost becomes more acidic in nature, the availability of calcium is found to plummet. Magnesium is found to have a similar reaction in compost to calcium.

2.4.3.4 Heavy metals

A plants root mechanism functions such that the plant is protected from high heavy metal concentrations. The plant will display toxicity symptoms and possibly die much before the level is high enough to be harmful to the food chain. There are however exceptions to the rule and the heavy metals can be present in toxic concentrations without being detrimental to the plant. Mercury, lead and cadmium may sometimes be present in the raw material (fibre) that is sent to the mill and thus found as trace elements in the PMS. Elements such as copper, molybdenum, cobalt, zinc and in some cases nickel and selenium are micronutrients and are extremely useful to the plant. Cadmium, mercury and lead however have no beneficial value to plants and animals. It must be noted that the constant monitoring of compost applied in large amounts to land is vital so as to ensure that the environment is being protected from any potentially harmful elements found in the compost. Table 2-4 illustrates the heavy metal limits that are enforced in the European countries (Brinton, 2000). European standards are more stringent and often used as guidelines by many researchers, including in South Africa.

Table 2-4: *Heavy metal limits for compost in units of ppm for Europe*

Element	**A**	**B**	**CH**[b]	**DK**	**F**	**D**	**I**	**NL**	**SP**
	Ppm								
Arsenic	-	-	-	25	-	-	10	15	-
Boron	100	-	-	-	-	-	-	-	-
Cadmium	4	5	3	1.2	8	1.5	1.5	1	40
Chromium	150	150	150	-	-	100	100	70	750
Cobalt	-	10	25	-	-	-	-	-	-
Copper	400	100	150	-	-	100	300	90	1750
Lead	500	600	150	120	800	150	140	120	1200
Mercury	4	5	3	1.2	8	1.0	1.5	0.7	25
Nickel	100	50	50	45	200	50	50	20	400
Selenium	-	-	-	-	-	-	-	-	-
Zinc	1000	1000	500	-	-	400	500	280	4000

[a] Country Codes: A-Austria; B-Belgium;CH-Switzerland; DK-Denmark; F-France; D-Germany; I-Italy; NL-Netherlands; SP-Spain;

More concise compost quality limitsare tabulated in Table 2-5 (Watson, 2007), and were used as the reference forcomparison of the different composting trials. This table provides the heavy metal limits used by the United States Environmental Protection Agency, which are different to the European limits expressed in Table 2-4,mostly due to the fact that each country has its own system. This is due to the differences observed in the soils of the different regions of the world.

It is known that regions differ in the nature of the parent material, age of the soil and climate. However, a set of limitations could not be found for South Africa.Furthermore, Mill A uses the European Standards and the United States Environmental Protection Agency Standards as guidelines for characterisation of their sludge stream, and they were therefore considered appropriate for this research purpose.

Table 2-5: *Heavy metal limits required for quality compost*

Heavy Metal	**Limit (ppm)**
Arsenic	41
Cadmium	35
Copper	1500
Lead	300
Mercury	7.8
Nickel	420
Selenium	100
Zinc	2800

According to Singh and Kalamdhad (2012), there is a reduction in heavy metals by physico-chemical methods during composting. This means that during the thermophilic phase, the oxidation process and the formation of organo-metallic complexes could reduce the soluble contents of metals. The humic substances bind with the exchangeable and carbonate fractions of metals (Singh and Kalamdhad, 2012).

2.4.3.5 Soluble salts

Measuring soluble salts provides a general indication of nutrient deficiency or excess. Excess soluble salts in soils is very common and generally results from too much fertilizer in relation to the plants needs, inadequate watering and leaching, or poor drainage (Richard, 1954). An electrical conductivity test is carried out to measure the conductance of electrical current in a solution. All ionic compounds can contribute to the soluble salt content of a growth medium. These soluble ions or nutrients include sodium, nitrate, ammonium, chloride, potassium, calcium, sulphate and magnesium (Warncke and Krauskopf, 1983).

Table 2-6 provides guidelines for interpreting the conductivity readings as discussed by Warncke and Krauskopf (1983) using the 1:5 dilution method of analysis. It can be seen that compost with a conductivity of 0.35 to 0.64 dS/m is most suitable for use. The usefulness of compost is dependent upon the soil to which it is added together with the frequency and quantity of the additions amongst other factors. Some of these factors include the plants tolerance to high salt concentrations as well as the frequency of rainfall or irrigation waters (Watson, 2007). Soluble salts above the normal range of 0.35 to 0.64 dS/m for prolonged periods may cause root injury, leaf chlorosis, marginal burn, and sometimes, wilting. Soluble salts below the normal range may indicate the need for fertilisation.

When the concentration of soluble salts in the soil-compost mix exceeds 0.65dS/m, it shouldbe reduced prior to use. This can be achieved by leaching the compost with water to reduce the soluble salt concentration. Generally it isn't the nutrients themselves that cause the damage; it is their effect on water. Salt in the water reduces its water potential making it less available to the plant (Rhoades et al., 1990). The salt therefore causes water stress on the plant, as discussed in Table 2-6 (Warncke and Krauskopf, 1983). The effect and importance of EC in soil fertility was explained in Section 2.3.1.2.

Table 2-6: *Guidelines for interpretation of the electrical conductivity readings*

Conductivity Meter	**Range (dS/m)**	**Interpretation***
Upper Limit	**Lower Limit**	
0.12	**0**	Low nutrient status. Seeds may germinate.
0.34	**0.13**	Suitable for seedlings and sensitive plants. Plants may grow slowly and may show deficiency.
0.64	**0.35**	Desirable range for most plants. Upper limit may be too high for some plants thus a reduction in growth.
0.89	**0.65**	Higher than desirable for most plants. Loss of vigour in upper limit. Appropriate range for plants that have high nutrient requirements.
1.10	**0.9**	Reduced plant growth and vigour. Wilting and marginal leaf burn.
1.10+		Plant growth severely stunted. Usually result in death.

*A 1:5 (v/v) ratio of compost to distilled water was used to achieve a quantity of solution that could be tested

2.4.3.6 Carbon/Nitrogen ratio

Carbon is an important energy source and N is necessary for cell growth and function, hence the optimum C/N ratio is one of the most critical parameters for composting. Generally at the beginning of composting, a ratio of 30:1 is recommended (Richard and Trautmann, 1996). However, Sanin et al. (2011) suggests that the optimal C/N ratio ranges between 20 and 25:1. This, however, varies depending on the bioavailability of C and N. Nitrogen is readily available, however, C may be bound up in compounds that are highly resistant to biological degradation, particularly lignin. As composting commences, the C is converted into CO_2. Thus the C/N ratio generally drops to approximately 10:1, assuming that there is a negligible loss of N (Richard and Trautmann, 1996). Obtaining a desirable ratio is imperative to achieve quality compost. A lowratio results in the compost becoming too hot due to the excess N. This means that large amounts of N will be lost as ammonia gas thus causing undesirable odours. Should the ratio be too high, the compost heap will not heat up resulting from insufficient N for optimal growth of micro-organisms. The degradation process is thus slow (Richard and Trautmann, 1996).

2.4.3.7 Oxygen

One of the key ingredients for successful composting is oxygen. Some composting systems can maintain ample oxygen by natural diffusion and convection (Richard, 1996b). Other systems require active aeration. This is often achieved in the form of blowers, or physically turning and mixing the compost. An insufficient supply of oxygen results in an anaerobic process resulting in an undesirable odour being produced. Although the concentration of oxygen in the atmosphere is 21%, the aerobic microbes in the compost can survive in an environment with a minimum of 5% oxygen. For aerobic composting, however, a concentration of above 10% is desirable (Cumberland County Solid Waste Authority, 1999). Anoxic conditions causes the pH to drop and thus the availability of oxygen is crucial to keeping the pH up (Sanin et al., 2011). A lack of oxygen can also decrease the composting efficiency (Cumberland County Solid Waste Authority, 1999).

2.4.4 Physical characterisation of compost

2.4.4.1 Moisture content

Moisture content is another vital parameter for composting. Porous spaces are required for air (oxygen) to circulate through the PMS (Sanin et al., 2011). At high levels, water occupies most of the porous space, limiting the available air. High moisture also causes an unwanted odour. To alleviate this problem, the addition of a bulking agent such as bark, dry wood chips, newspaper strips and cardboard pieces is necessary. In the case of low moisture, microbial activity is limited as microbes require a wet environment for survival. Below 10% moisture, all microbial activity ceases (Sanin et al., 2011). Therefore, the desirable moisture content for a quality composting process ranges between 40 and 60% (Cumberland County Solid Waste Authority, 1999).

2.4.4.2 Temperature

Temperature is one of the main indicators during composting. The progress of the process can be gauged simply by monitoring the temperature changes. Temperature probes are important and should be placed at various locations and at different depths to monitor if any temperature gradients are formed with depth. The temperature at each point is dependent on the heat being produced by the micro-organisms together with the loss of heat by surface cooling and aeration (Richard, 1996a). A plot such as Figure 2-5is imperative in tracing the progress of composting over time. The temperature of the system goes hand in hand with the moisture of the system. A dry system will heat and cool off more rapidly than a wet system owing to the higher specific heat of water (Richard, 1996a).

Temperature and time go hand in hand. The best compost is made when temperatures increase from 21°C to about 65°C. Thermophilic bacteria thrive at temperatures between the limits of 45 and 70°C. Above 71°C, the material becomes sterile. Therefore, it is not imperative to achieve high temperatures, unless there is a specific concern about killing diseased organisms and seeds.

2.4.5 Composting methods

There exists a large distinction between conventional composting methods and modern rapid methods. While the more traditional methods can take as long as 8 months to reach completion, as little as 3 weeks is required by the more rapid procedures (Misra and Roy, 2003).

The traditional composting practices are based solely on either anaerobic or aerobic decomposition. Aerobic decomposition is based on passive or static aeration processes. Passive aeration is achieved by turning the heap infrequently. Static aeration eliminates the need for turning by providing aeration through perforated pipes. Traditional methods are extensively used due to the high labour requirements, the lack of need for capital or modern infrastructure (Misra and Roy, 2003). The setbacks, however, are the low turnover and the longer duration.

Rapid composting procedures incorporate various treatments such as shredding and turning more often, the use of worms, forced aeration and mechanical turning, addition of mineral N compounds, and addition of effective micro-organisms and cellulolytic organisms to hasten the composting process (Misra and Roy, 2003).

The Berkley rapid composting and North Dakota State University hot composting methods, which have active periods of approximately 2-3 weeks and 4-6 weeks respectively, are accelerated aerobic decomposition processes (Misra and Roy, 2003). This acceleration is achieved by the chopping of the raw material to a smaller size, the use of ammonium sulphate, chicken manure and urine, and turning the material on a daily basis (Misra and Roy, 2003).

2.4.5.1 Turned windrows

Turned windrows are used mainly by the larger scale operators. This practise involves the composting of material in piles or windrows with the use of a bucket turner or a special turning machine that turns the windrows at regular intervals. This turning operation serves the function of mixing the material thus enhancing the aeration (Misra and Roy, 2003). Aeration is achieved by natural air movement. Porosity is the key factor in determining the size of the windrow that can be effectively aerated. Large windrows create anaerobic zones which release odours when turned. In the case of small windrows, heat is lost rapidly and high temperatures are not achieved. This means that moisture is not evaporated and pathogens are not killed (Misra and Roy, 2003). It is important that regular turning is maintained. The frequency of the turning depends on the rate of decomposition, moisture content and porosity of the materials as well as the desired composting time (Misra and Roy, 2003).

2.4.5.2 Passively aerated windrows

In the case of the passively aerated windrows, the turning requirement is reduced if not eliminated altogether. This is achieved by the use of pipes that act as air ducts to supply air. This procedure can take anywhere between 10 and 12 weeks. The material is usually covered by a layer of compost to act as insulation to the windrow, discourage flies, and help retain the moisture, odour and ammonia (Misra and Roy, 2003).

2.4.5.3 In-vessel composting

In-vessel composting is a method that limits materials to composting within the boundary of a building, container or vessel (Misra and Roy, 2003). This practise relies on forced aeration and mechanical turning techniques that speed up the process.

Bin composting is by far the simplest in-vessel composting process. The bin itself may be a bulk storage building or wooden slatted walls with or without a roof (Misra and Roy, 2003). The advantage of bin composting is that the materials can be stacked much higher and there is a more efficient use of floor space than that of a free standing pile. Furthermore, a more even temperature distribution is achieved, the odour is contained and the weather does not pose a threat of increasing moisture excessively due to rain.

2.4.6 Advantages and disadvantages of composting

Composting as a waste management technique is expanding due to its many benefits, which include:

- A usable end product which is saleable.
- A single facility can handle municipal and industrial organic bio-solids, sludge and waste.
- It decreases the amount of waste to landfill.
- It decomposes and degrades many organic materials.
- A composting facility can be designed and operated to minimise environmental impacts such as odours and bio-aerosols (Pittaway et al., 2001).

However, the disadvantages also need to be considered. Pittaway et al., listedthe disadvantages as:

- The process sometimes requires amendments which are costly.
- A significant land area may be required for the process. The area for storage also needs to be considered.
- There are higher costs involved than direct land application.
- Odour and bio-aerosols can occur during the process, however, these can be mitigated.

2.5 Paper mill sludge management

Paper mill sludge is a composite blend of solid matter. It is produced from the treatment of wastewater that is produced during the pulp and paper manufacturing process. According to Monte et al. (2009), the treated waste undergoes a dewatering process which consequently results in the formation of sludge with high solids content. This process is to facilitate the handling and disposal of the large volumes of sludge.

Mpact Ltd., previously part of the Mondi Group, is a key manufacturer of carton board and other paper products from recycled paper. It is in their best interest to reduce the amount of waste being disposed of to landfill and to find alternative applications for the disposal of this material, as quoted in the 2010 Annual Report: *"...In 2005, we committed to reducing our total waste-to-landfill volumes by 20% by 2010. Through a concerted effort – by increasing the recycling and reuse of materials, and by using more environmentally friendly processes – a 36% reduction to approximately 300,000 tonnes of total waste (hazardous and non-hazardous) to landfill per annum was achieved during this period. Further, we ceased the disposal of process hazardous waste to landfill at the end of 2009."* (Mondi, 2010).

Mondi Lohja, based in Finland, currently produces 7 000 tons of waste water sludge per annum (Mondi, 2011). The predicament faced here was the lack of proper facilities for the incineration of PMS before disposal in a landfill hence PMS wassent to the landfill some 10 km away. In early 2010 a Finnish company, Humuspehtoori Oy, proposed a solution for the use of this PMS (Mondi, 2011). Mixing the PMS with animal manure and applying it to agricultural soil not only improved the long term quality of the soil but also the crop yield. The key to this process is that the paper fibres within the PMS absorb the manure and release fertilising chemical compounds over several years. This process is favoured to the conventional fertilising method as there is a reduced chance of eutrophic compounds being emitted to the environment (Mondi, 2011).

Mpact Ltd. are exploring various disposal methods of the waste materials generated at the three mills, Mill A, B and C. Currently the three mills are disposing of the wastes by the most commonly used applications, namely landfilling, direct land application and composting.

Mill A utilises 95% recycled pulp fibres as well as bleached eucalyptus pulp to produce coated and uncoated carton board for food and industrial packaging. The capacity of each of the two board machines at the mill are 30 000 tons/yr and 107 000 tons/yr, respectively. A successful re-use application that has been adopted by Mill A is the use of the PMS as a litter in the cattle pens at the Beefcor Cattle Feedlot. Once used litter has been recovered, it is composted at the adjoining Conradie Organics Compost Manufacturing Facility. The PMS was previously classified as a high hazard, hazard group 2, which resulted from the leaching of small amounts of Mn (Baldwin, 2009). After an extensive study, however, it was found that the application of the PMS as a litter posed no significant threat to the environment (Baldwin, 2009).

The raw material utilised by Mill B is recycled paper, namely K3 and K4, and a blend of eucalyptus and pine pulp. K3 is a grade of recycled paper containing pure new brown kraft cuttings, new kraft bag waste and clean inner liners of used kraft bags and factory rejects of corrugated kraft offcuts. K4 is a grade of recycled paper containing used corrugated kraft containers and used kraft wrappings. The ratio of virgin to secondary fibre utilised is 60:40. Mill B produces fluting paper and linerboard for food and industrial packaging and has taken the landfill approach to dispose of its PMS. This landfill is located on the site. The mill production capacity is 125 000 tons/yr.

Unbleached bagasse pulp and K4 recycled fibre are the raw materials used by Mill C. This mill produces fluting paper and corrugated packaging paper. Currently this mill supplies the sugar farmers with the pith/PMS_C blend for agricultural use. However, the nutrient value has not yet been quantified.

2.5.1 Direct land application management of PMS from Mill C

Mill C has a paper production capacity of approximately 150 000 tonnes per annum. The main production focus is on fluting paper using a mixture of bagasse fibre and recovered fibre from the recycling plant. Bagasse fibre is a by-product from sugar cane processing, containing approximately 30-40% of parenchymal tissue or "pith" fibre. It is impossible to produce a high quality paper with a poorly depithed bagasse hence the pith is removed before pulping. This pith is the first waste stream produced by the mill, with a second waste stream containing the effluent sludge. These streams are produced in a mass ratio of 3 parts pith to 1 part effluent sludge. The solid wastes from Mill C arrive at the sugar farms in large trucks as can be seen in Plate 2-1, already mixed in this ratio. This mixture of 3 parts pith waste and 1 part effluent sludge will be referred to as pith/PMS_C (3:1) hereafter.

Plate 2-1: *The disposal of pith/PMS_C (3:1) from the paper mill to agricultural lands*

This pith/PMS_C (3:1) is mixed in a ratio of 1:1 with “Smut” or “Milo” obtained from the local sugar mill nearby (see Plate 2-2). This adds the necessary microbial activity and nutrients that are required for good crop growth.

Plate 2-2: *Smut or “milo” obtained from the local sugar mill*

Once the pith/PMS_C (3:1) and smut are mixed, farmers apply the pith/PMS_C (3:1) to their land in application rates of 60–100 tons/ha or until the pith/PMS_C (3:1) is approximately 10 cm thick on the surface of the soil before being turned in. Plate 2-3 shows the land after the pith/PMS_C (3:1) is applied and turned into the soil. Each field receives 150 kg of K/ha and 140 kg N/ha per year as inorganic fertilisers. This makes the soil ideal for planting as it is enriched with readily available nutrients. This application of pith/PMS_C (3:1) and fertilisers to the fields aid in the growth of sugar cane. Sugar cane is best grown in a hot climate, with the temperature ranging between 25 and 30°C, with long periods of sunlight (12 to 14 hours) and high humidity (80 to 85%). Sugar cane grows well in humic soils with good drainage. Sandy loam soil textures with a pH range of 6 to 7 are ideal (Department of Agriculture, Forestry and Fisheries, 2012).

Plate 2-3: *The land post pith/*PMS_C *(3:1) application*

CHAPTER THREE

Characterisation of paper mill sludge

3.1 Materials and methods

3.1.1 Introduction

Some heavy metals contained inPMS may be toxic if they are present in large quantities and could affect the plant growth afterland application. A preliminary elemental analysis of the PMS was therefore of vital importance, particularly from a precautionary point of view. It was expected that each PMS sample would differ significantly from the other depending on various factors such as the nature of the fibre raw material sent to the mill, the chemical treatment processes used during manufacturing as well as the type of waste handling practice in operation within the mill. Samples from Mills A (PMS_A), B (PMS_B) and C (pith/PMS_C (3:1)) were all characterised using the methods discussed in Section 3.1.2.

3.1.2 Analytical methods

3.1.2.1 Moisture content

An empty beaker was weighed. A sample was then placed into the beaker and weighed.Both the beaker and the wet sample (M_w) weighed approximately 190g. The beaker was then placed into an oven and allowed to dry for 24 hours at 110°C. After 24 hours, this sampled was again weighed (M_d).

The moisture content was then calculated usingEquation 3.1:

$$W = \frac{M_w - M_d}{M_w} \times 100 \ldots \text{(Equation 3.1)}$$

Where: W = Moisture content of the sample (%)

M_w = Mass of the wet sample (g)

M_d = Mass of the dry sample (g)

3.1.2.2 pH

A 1:4 (v/v) ratio of suspension of PMS and pith/PMS$_C$ (3:1) was prepared using distilled water. The pH meter (Hanna HI 255) was then calibrated using buffer solutions pH 7 and 10. The electrodes were rinsed between samples to maintain quality of results. Since pH is temperature dependent, it was important to maintain the samples at room temperature.

3.1.2.3 Electrical conductivity

One to five (v/v) ratio samples were prepared by suspendingthe PMS and pith/PMS$_C$ (3:1) in distilled water, and the slurry EC measured (Johnsson et al., 2005). The conductivity meter (Hanna EC 215) was then calibrated using a standard NaCl solution. The electrodes were rinsed between samples to maintain quality of results. Here again, it was important to maintain the samples at room temperature.

3.1.2.4 C/N ratio

Samples were sent to the Soil Fertility and Analytical Services Section of the KwaZulu-Natal Department of Agriculture and Environmental Affairs to perform the C/N ratio analysis. Total C and N in the PMS samples were analysed by the Automated Dumas dry combustion method using a LECO CNS 2000 (Manson and Roberts, 2000). Samples were weighed into a ceramic crucible and 0.5g of vanadium pentoxide was added as a combustion catalyst (Manson and Roberts, 2000). The sample was then burned in a horizontal furnace by a stream of oxygen at 1350°C. The gases produced were passed through two infrared cells where the carbon was determined (as CO_2). Nitrogen was determined as N_2in a thermal conductivity cell (Manson and Roberts, 2000).

3.1.2.5 Elemental analysis

An elemental analysis on the samples was carried out using inductively coupled plasma emission spectroscopy (ICPES) at the School of Chemistry atUKZN. The samples were first prepared for this by an acid digestion.

The Perkin Elmer ICP apparatus, model Optima 5300DV ICP-OES uses 3 different wavelengths to detect the presence of each element. Concentration is output in ppm and the RSD (relative standard deviation) of the concentration for each wavelength. The wavelength with the lowest RSD gives the most accurate representation of the concentration of that element in the sample.

Thus for each element investigated the concentration with the lowest RSD was used and the concentration in mg/L was converted to mg/kg dry sample (see Appendix A2).

3.1.2.6 Ash content

The total inorganic solids in each of the samples were determined using the Tappi T211 method (Tappi, 1993). A clean, empty crucible was ignited in a muffle furnace at 525°C for 30-60 minutes. The weight of the crucible was recorded after cooling and placing in a desiccator until the crucible was at room temperature. Approximately 3g of moisture free sample (determined from Section 3.1.1.1) was placed in the crucible and left in the muffle furnace at 100°C. The temperature was slowly raised to 525° to avoid flaming. When the sample was completely combusted (approximately 3 hours), the sample was cooled and then placed in a desiccator and allowed to cool to room temperature. The weight was then recorded.

The ash content was then calculated using Equation 3.4.$\% \text{ Ash} = \frac{\text{A}\times 100}{\text{B}} \ldots$ (Equation 3.4)

Where: A = weight of ash, g

B = weight of test specimen, g moisture-free

3.1.3 Statistical analysis

Samples were analysed in triplicate so as to check for repeatability of results. Error bars were plotted to visually display the deviations from the mean. Mean values were reported and the standard deviation from the mean for each sample was calculated (See Appendix B).

3.2 Results and discussion

3.2.1 Introduction

The results from the preliminary analysis of the waste samples are presented in this section. The raw data obtained during the preliminary testing explained in Section 3.1.2, can be found in Appendix B.

3.2.2 Analytical results

3.2.2.1 Moisture content

Figure3-1 provides the moisture analysis results of the PMS. These sample moistures were 61.22%, 67.21% and 69.24% for PMS_A, PMS_B and pith/PMS_C (3:1), respectively. Moisture content plays a vital role in ensuring that there is sufficient microbial activity. In the event of low moisture content, microbial activity would be limiting during composting. The desirable moisture range for composting is between 40 and 60% (Cumberland County Solid Waste Authority, 1999). The high moisture in the samples could be a result of the dewatering technology adopted by each of the mills. PMS_A falls only slightly out of the desired range. PMS_B and pith/PMS_C (3:1) exceed this range largely and therefore might not perform optimally during a composting process as microbial activity will be inhibited. Furthermore, the water will occupy the porous space leaving very little air availability. Unpleasant odour might also pose a problem during composting.

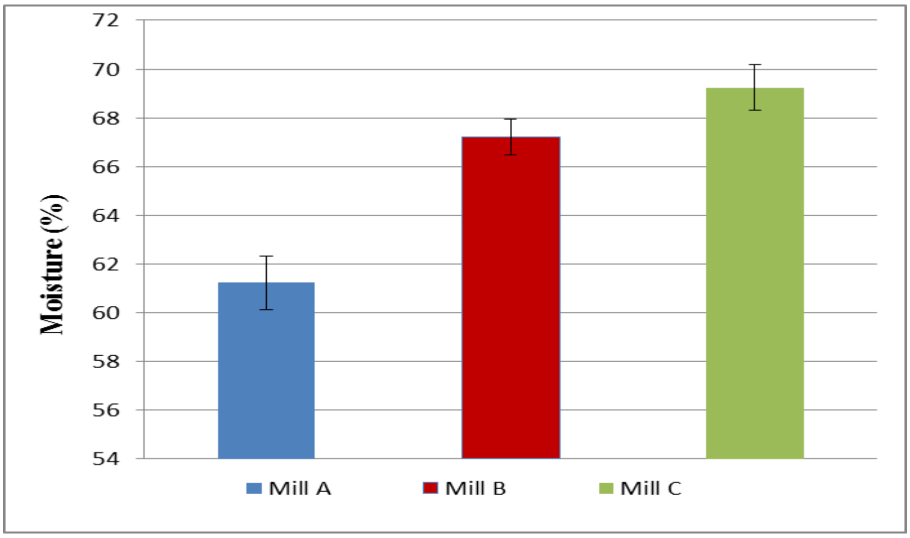

Figure3-1: *Moisture content of the PMS obtained from Mills A, B and C (n = 3)*

3.2.2.2 pH

The mean pH for PMS_A, PMS_B and pith/PMS_C (3:1) were 8.90, 8.30 and 8.24, respectively as illustrated in Figure 3-2. Hence all three mills produce a waste product that is alkaline in nature. The reason for the differences in the pH values are a direct result of the nature of the raw materials used and mill specific chemical usage. The pH was much higher than the optimum range of 6.5-7.5 for composting (Sanin et al., 2011). Since the pH of the samples are above 7.5, there is an increased chance of nitrogen escaping as ammonia thus causing unpleasant odours during composting (Section 2.4.3.1). The highly alkaline nature of these PMS's will cause the availability of phosphorus, boron, chloride, copper, manganese and zinc to decrease (Table 2-1).

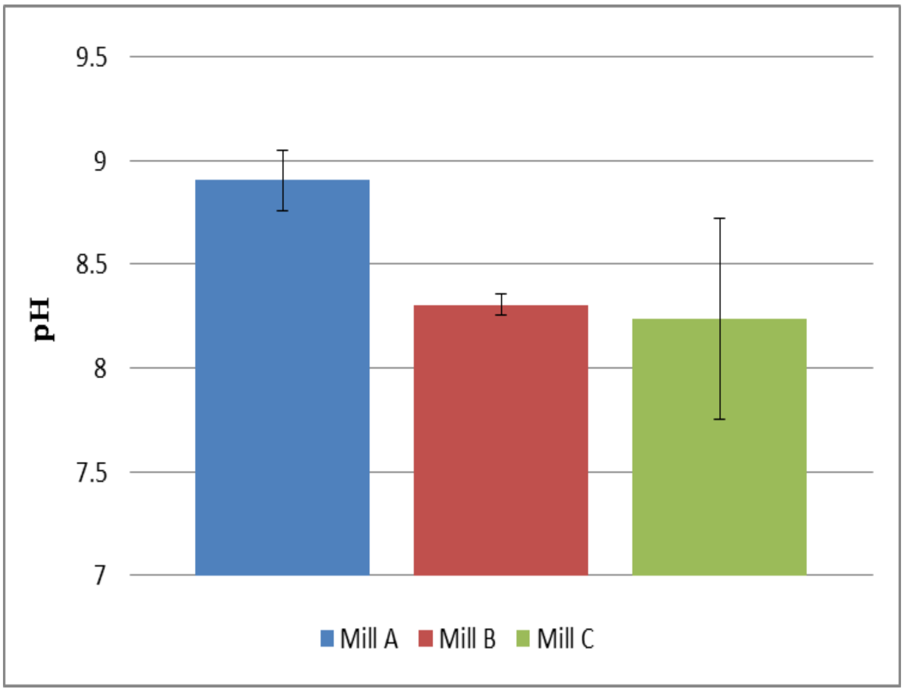

Figure 3-2: *pH of each of the waste samples from Mill A, B and C (n = 3)*

3.2.2.3 Electrical conductivity

In terms of electrical conductivity (EC), all samples fell within the safe range for quality compost. All the samples fell within the range of 0.13 to 0.64 dS/m, confirming their suitability for application to soils (Warncke and Krauskopf, 1983). Reported values of 0.24, 0.40 and 0.34 dS/m for PMS_A, PMS_B and pith/PMS_C (3:1), respectively can be seen in Figure 3-3. Comparing this to literature (see Table 2-6), PMS_A and pith/PMS_C (3:1) would be suitable for seedlings and sensitive plants as the EC was in the range 0.13 to 0.34 dS/m. PMS_B was found to have a more desirable EC. In this case, PMS_B could be suited for most plants and direct land application.

Since the average EC was found to lie close to the upper limit, there is the potential risk of reduction in plant growth.

Equation 2.2 (Section 2.3.1.2) shows that pH and EC are inversely proportional if all other constraints are constant. It was observed that PMS_A had the highest pH (8.90) and the lowest EC (0.24 dS/m), which is supported by Equation 2.2.

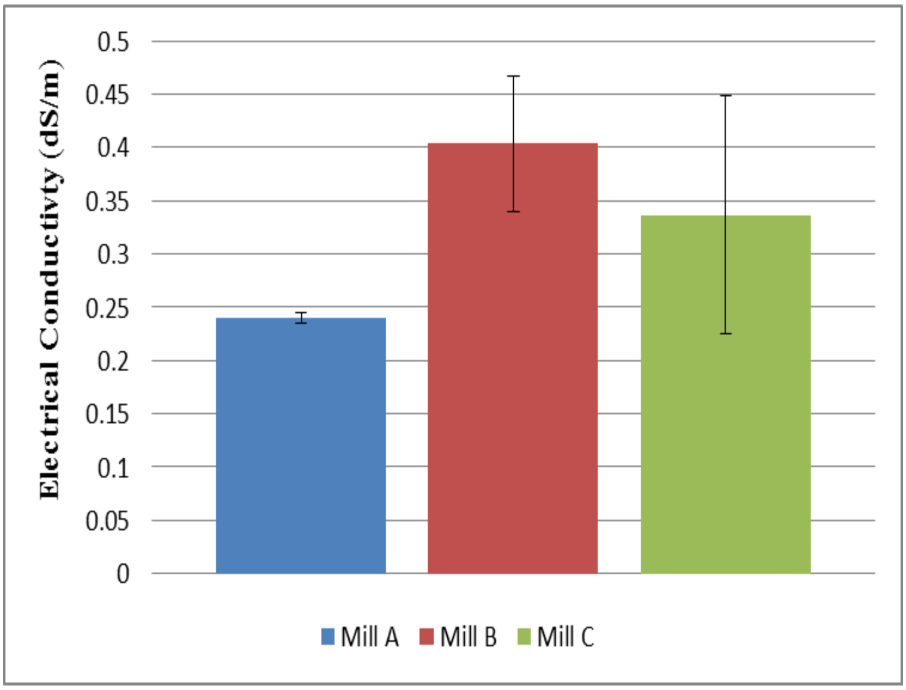

Figure 3-3: *Electrical conductivity of each of the samples from Mill A, B and C (n = 3)*

3.2.2.4 Ash content analysis

The ash content of a sample may consists of various residues from chemicals that are used in the manufacturing process, metallic matter from piping and machinery, mineral matter from the pulp from which the paper was made, and filling, coating and pigmenting or added chemicals (Tappi, 1993). The pith/PMS_C (3:1) blend contained the highest ash content as shown in Figure 3-4. Majority of the ash is known to be Ca which is used in the form of calcium carbonate. Using the Ca concentrations that were determined by ICP analysis, the pith/PMS_C(3:1) blend contained approximately 40696.04 mg/kg of Ca.

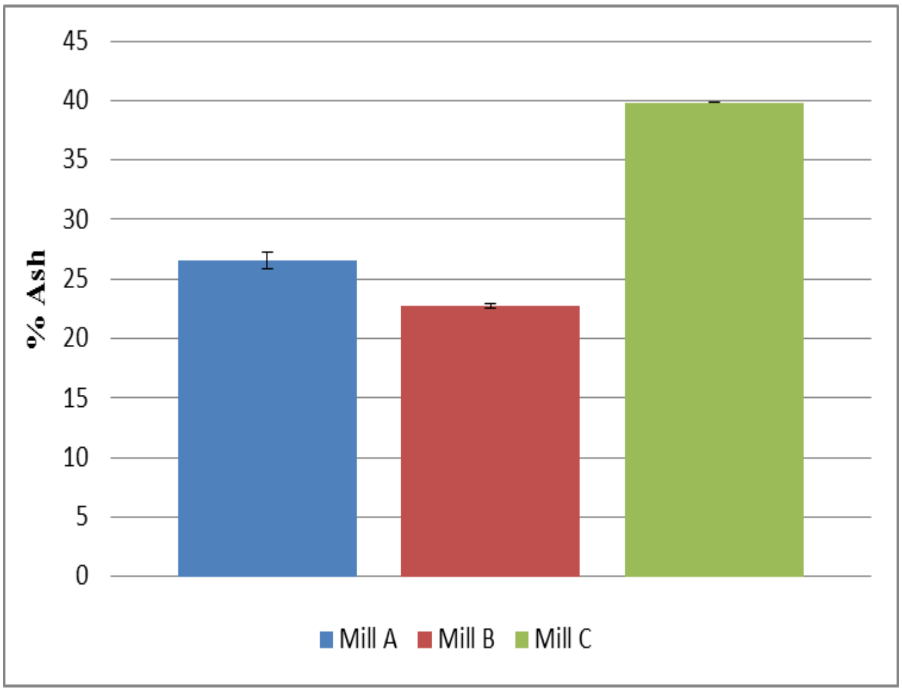

Figure 3-4: *Comparison of ash content from Mill A, B and C (n = 3)*

3.2.2.5 C/ N ratio

The reported results in Table 3-1fall out of the desired range of 20 and 25:1 C/N for rapid composting (Sanin et al., 2011). If these samples were to be used for composting, the high ratio would result in the compost heap not heating up due to the insufficientN. Therefore a desirable ratio at the beginning of the process would be imperative to achieve. A nitrogen source would need to be added to enable composting in all three samples.

Table 3-1: *Carbon and nitrogen in each of the PMS samples (n = 3)*

Sample	**% C**	**% N**	**C/N**
PMS$_A$	35.01±0.14	0.37±0.01	94.40±2.05
PMS$_B$	29.06±0.13	0.56±0.01	52.09±0.81
pith/PMS$_C$ (3:1)	35.03±0.24	0.59±0.01	58.90±0.36
Pith	36.16±0.32	0.60±0.01	59.94±1.30
PMS$_C$	31.63±0.37	0.57±0.06	55.65±5.27

3.2.2.6 Elemental analysis

Figure 3-5 illustrates the concentrations of metals detected during the ICP analysis. Heavy metals such as arsenic, cadmium, lead, mercury, nickel and selenium were below the detectable limit in the samples. Heavy metals can be a major concern. If the concentrations are above the upper limits as reported in literature, phytotoxicity could become an issue depending on the plant. Copper and zinc are notacause for concern in the samples tested as both were detected at well below the environmental limits of 1500 ppm and 2800 ppm for quality composts (Table 2-5). No anionswere analysed.

Potassium is a macronutrient required by plants and was found in high levels in all three samples. The pith/PMS$_C$ (3:1), however, contained approximately 1816 ppm, which is higher than the toxic level of 800 ppm (Table 2-1). PMS$_A$ and PMS$_B$ had reported concentrations of 465.5 ppm and 611.5 ppm, which are classified as high levels since they are more than 250 ppm (Table 2-1). The high levels of potassium could be a result of high amounts of clay in the samples, which could indicate a low amount of leaching (Dinkins and Jones, 2013).

Phosphorus and magnesium were detected to an appreciable degree in all three mill samples. A desirable result since they are macronutrients required by plants. Chromium needs to be monitored to ensure that it does not exceed the limit of 800 mg/kg on commercial or industrial lands. The Cr concentrations in all three samples were well below this limit. Iron was found in large concentrations in all three samples, specifically the pith/PMS$_C$ (3:1). This is a micronutrient that is required by plants and is clearly in excess of the limit.

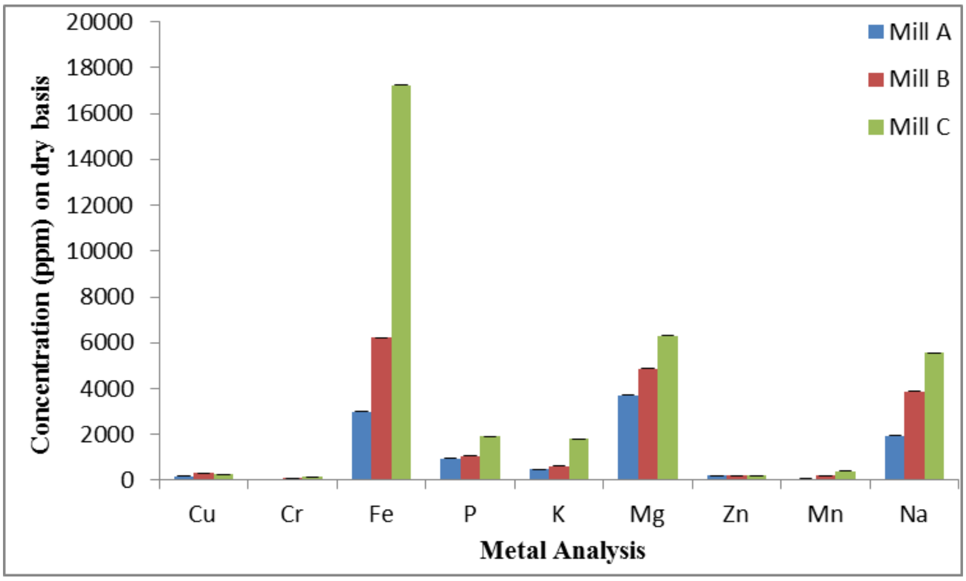

Figure 3-5: *Metal content in a dry sample for Mills A, B and C (n = 3)*

Calcium was found in abundance in all three samples (Figure 3-6) hence it was illustrated on a separate graph. This is desirable as Ca is a macronutrient required by plants.

Using the soil classification guidelines discussed in Section 2.3.1.2 and the relationship highlighted between soils EC, pH, SAR and ESP, all three PMS samples can be classified as saline in nature. This was based on the EC values exceeding 0.34 dS/m, pH values bordering the 8.5 mark and the SAR being less than 12.Another distinguishing characteristic of saline samples from an agricultural standpoint is that soluble salts most commonly present are chlorides and sulphates of sodium, calcium, and magnesium.Salinity could affect the vegetation by causing specific ion effects, such as nutrient deficiencies or toxicities.

The calcium to magnesium ratios were 31, 10 and 16 for Mills A, B and C, respectively. According to Hazelton and Murphy (2007), calcium to magnesium ratios exceeding 10 are representative of magnesium deficiencies.

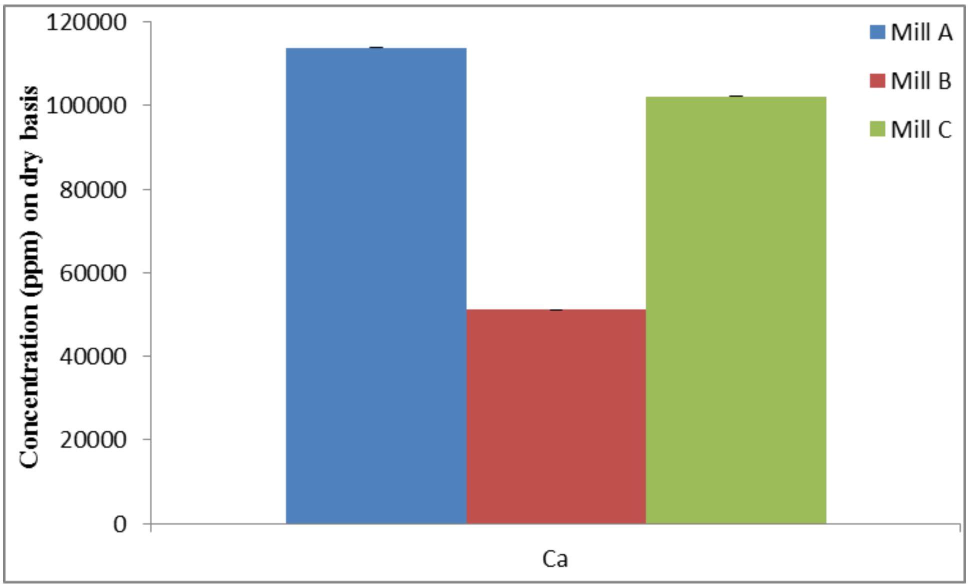

Figure 3-6: *Calcium content in a dry sample for Mills A, B and C (n = 3)*

3.3 Conclusions

Moisture contents were 61.22%, 67.21% and 69.24% for PMS_A, PMS_B and pith/PMS_C (3:1), respectively, which were higher than the desired range of 40 to60% for composting. These could be a result of the dewatering technology usedby each mill. PMS_B and PMS_C exceed this range by more than 10%and therefore might not perform optimally during a composting process as microbial activity will be inhibited.

The mean pH for PMS_A, PMS_B and pith/PMS_C (3:1) were 8.90, 8.30 and 8.24, respectively. Hence all three mills produce a waste product that is alkaline in nature. The reason for the differences in the pH values are a result of mill specific chemical usage. The pH was much higher than the optimum range of 6.5-7.5 for composting (Sanin et al., 2011).

In terms of electrical conductivity all the samples fell within the range of 0.13 to 0.64 dS/m, confirming their suitability for application to soils (Warncke and Krauskopf, 1983). Electrical conductivity values were 0.24, 0.40 and 0.34 dS/m for PMS_A, PMS_B and pith/PMS_C (3:1), respectively. Equation 3.6 shows that pH and EC are inversely proportional if all other parametersare kept constant. It was observed that PMS_A had the highest pH (8.90) and the lowest EC (0.24 dS/m), which is supported by Equation 2.2.

The reported C/N ratios fell above the desired range of 20 and 25:1 for rapid composting. If these samples were to be used for composting, the high ratio would result in the compost not heating up due to the insufficient N. A nitrogen source would need to be added to enable composting in all three samples.

Heavy metals such as arsenic, cadmium, lead, mercury, nickel and selenium were not detectable in the samples. Copper and zinc are no major cause for concern as both were measuredat well below the environmental limits of 1500 ppm and 2800 ppm for quality composts.

The concentration of potassium detected in the pith/PMS_C (3:1) was higher than the toxic level of 800 ppm.Calcium was found in abundance in all three samples, which was expected as it is a macronutrient. The calcium to magnesium ratios all exceeded 10 representing a magnesium deficiency.All three samples of PMS were classified as saline in nature, in accordance with the relationships and guidelines discussed in Section 2.3.1.2.This was based on the EC values exceeding 0.34 dS/m, pH values bordering the 8.5 mark and the SAR being less than 12. Another distinguishing characteristic of saline samples from an agricultural standpoint is that soluble salts most commonly present are chlorides and sulphates of sodium, calcium, and magnesium.Hence the relationship between the pH, EC, SAR and ESP was verified based on soil classification methods.Nutrient availability was not measured; hence the relationship between pH and nutrient availability could not be verified.

CHAPTER FOUR

Small scale compostability of pith/PMS$_C$ blends

4.1 Materials and methods

4.1.1 Introduction

Composting of PMS has been proposed as a method of managing the raw sludge without adversely affecting the environment. Further experimental work was completed on the pith/PMS$_C$ blends from Mill C only. Three small scale composting trials were completed using various ratios of pith to effluent sludge from Mill C to find the mix that would compost into the best quality. The best composting mix from the small scale composting trial was later used in the large scale trials to better understand the degradation process.

4.1.2 Sample collection

Effluent sludge and pith were delivered to the Chemical Engineering Workshop located at the UKZN Howard College campus. Samples were immediately sent to the Soil Fertility and Analytical Services Section of the KwaZulu-Natal Department of Agriculture and Environmental Affairs for C/N ratio testing. The Automated Dumas dry combustion method of testing was used as discussed in Section 3.1.2.4.

4.1.2.1 Method of sampling

Sampling is of equal if not more so important to testing and it is vital that the sampler should use every precaution to obtain samples that are representative of the true nature of the material. The quartering sampling method was used to obtain representative samples for the composting procedure as per the Standard Method of Test for Methods of Reducing Size of Aggregate Sample (South Carolina Department of Transportation, 2008). This method required that thetotal mass of composting material sent by the individual mills be placed on a clean, hard, smooth surface and mixed thoroughly. The material was spread into a circular layer of constant thickness, and then divided into quarters by two lines intersecting at right angles at the centre. The two diagonally opposite quarters were discarded. The remaining quarters were thoroughly mixed and reduced further by quartering until the desired representative masses for each composting bag was achieved. Samples for testing were taken in triplicate for the analytical analyses from 3 random spots in the bag.

4.1.3 Experimental method

The composting systems were to operate as naturally as possible by exposing the entire sample to ambient airand weather conditions. This was achieved using well aerated, porous 50 kg woven polypropylene bags, which provided both aeration and drainage in the event of rain. Moisture and nutrient levels in literature (Sections 2.4.3 and 2.4.4) were used. These were:

- Moisture at approximately 60%.
- C/N ratio of 30:1.

Three trials were initiated concurrently. The volume of a 50 kg woven polypropylene bag was measured, and three such bags were each filled with equal combinedwet masses of PMS_C and pithmixtures. The mass ratios of pith: PMS_Cin each bag was 3:1, 2:1 and 1:1. Each bag also contained wood chips (occupying about one third of the bag volume) to act as a bulking agent and improve aeration. Inoculum was used to provide an initial boost of activity, in the form of mature garden compost. The results of the C/N ratio analyses indicated that extra nitrogen had to be added to all three bags to achieve the 30:1 ratio. The individual volumes of N amendment required by the three mixtures were calculated (see Appendix A4), and urea pellets were added to make up for the nitrogen deficit. Each bag was folded closed.Table 4-1 gives the content breakdowns.

Table 4-1: *Composition of each 50 kg composting bag*

Parameter	Bag 1	Bag 2	Bag 3
Pith: PMS_C	1:1	2:1	3:1
Mass of wet pith	14.56 kg	19.75 kg	22.22 kg
Mass of wet PMS_C	15.07 kg	9.88 kg	7.41 kg
Mass of inoculum	0.5 kg	0.5 kg	0.5 kg
Height of heap	0.60 m	0.60 m	0.60 m
N source and quantity	Urea pellets (0.343 kg)	Urea pellets (0.361 kg)	Urea pellets (0.367 kg)
Period of composting	80 days	80 days	80 days

*Mass of wood chips was not measured but they made up approximately a third of the bag volume.

Each bag was not replicated as this was simply a small scale composting procedure to understand which ratio would compost best. Therefore, repeatability and reproducibility was not a requirement.

Plate 4-1: *The three bags of compost*

4.1.4 Process control

4.1.4.1 Aeration and moisture control

Since the composting bag material was porous, aeration was good hence the bags were closed at the top. However, to provide better air contactto promote microbial activity, speed up the process and prevent any anaerobic pockets from occurring deeper inside the bag, the contents were turned every three days for the first two weeks. Thereafter, the frequency decreased to once a week. The pith/PMS$_C$ blended contents were dropped onto a plastic sheet on the ground and the mixture turned using a shovel. The bags were exposed to all weather conditions hence in the event of rain the bags were opened to allow for extra aeration and evaporation of the increased moisture. This action was taken during week five of the experiment for approximately two days. No additional water was added at any point.

4.1.4.2 Temperature

The temperature was recorded regularly with the use of a digital probe. The frequency of temperature readings was of importance to check that the degradation process was occurring.

Temperatures were measured three times a week (Mondays, Wednesdays and Fridays and recorded at three points in the bag. T_1 was representative of the temperature at the top of the bag; T_2 represented the middle of the bag and T_3, the bottom of the bag. These temperatures were recorded by inserting the temperature probe through the allocated holes in the porous bag (Plate 4-2). A fourth temperature was recorded by inserting the temperature probe down along the y-axis of the bag until reaching the centre (centre T). The ambient temperatures were also recorded at the same time (2pm) as the other temperature readings.

Plate 4-2: *Recording of temperature*

4.1.5 Analytical analysis

Samplesof compost wereremoved by hand from different depths of the bags on a weekly basis analysed in triplicate for pH, moisture content and EC using the analytical methods discussed in Section 3.1.2. Urea and wood chips were not removed from samples and the samples were therefore tested in their entirety.

At the end of the process, asample was sent to the Soil Fertility and Analytical Services Section of the KwaZulu-Natal Department of Agriculture and Environmental Affairs to determine the final C/N ratio and elemental analysis (triplicate tests were completed).

4.1.5.1 C/N ratio

Samples were analysed by the same method discussed in Section 3.1.2.4.

4.1.5.2 Elemental analysis

Phosphorus, zinc and copper were analysed using the same method as that used for soil extracts. This method involvedthe use of the Ambic-2 extracting solution. This solution was adjusted to pH 8 with a concentrated ammonia solution. Twenty five millilitres of this solution was added to 2.5 mL sample, and the suspension was stirred at 400 r.p.m. for 10 minutes using a multiple stirrer. The extracts werefiltered using a Whatman No.1 paper. Phosphorus was determined on a 2 mL aliquot of filtrate using a modification of the molybdenum blue procedure. Zinc and copper were determined by atomic absorption on the remaining undiluted filtrate (Manson and Roberts, 2000). The remaining elements were analysed using ICP analysis (Manson and Roberts, 2000).

4.1.6 Statistical analysis

All analyses were done in triplicate. The pH and moisture content graphs, Figure 4-2 and Figure 4-3, were plotted with error bars to illustrate the deviation from the mean in each sample. Heavy metal results were also reported using the standard deviation for each element.

4.2 Results and discussion

4.2.1 Introduction

The comparison of the results obtained using the selected test methods for the three composting bags are discussed in this section. Raw data and calculations are reported in Appendix C.

4.2.2 Process monitoring parameters

This investigation required monitoring of the change in some parameters, such as temperature, pH and moisture content on a weekly basis. The relevance of these parameters was to indicate the degradation pattern. Other parameters like the C/N ratio and heavy metal analysis required an initial and final characterisation. Comparison of these results would then indicate which mixture of pith/PMS_C blends aerobically decomposed into the best quality compost.

4.2.2.1 Temperature

The initial assumption made with regard to temperature was that the composting bags would experience a non-uniform distribution of heat. It was expected that the centre would experience the highest temperature. Being the most compact, warm and moist the centre would be the most favourable area for rapid metabolic activity. This was based on the assumption that a uniform distribution of oxygen was achieved by the addition of wood chips as a bulking agent for increased aeration. As the distance from the centre increased and the closer the contents were to the surface, the temperature was expected to decrease. For this reason, temperature readings were taken at various points along the height of the bag (T_1, T_2 and T_3) as well as the centre of the bag (centre T).

The temperature at T_2, located at a height closest to the centre, was very similar to the centre T in all three bags. Furthermore, the centre T and the temperature at T_2 were generally higher than the other two temperatures closer to the top and bottom of the bag. Statistically speaking, this was noticed over 85% of the time from weekly readings, indicating that the initial assumption that the centre was most conducive to microorganism activity was true.

Temperatures vs. time plots were found to follow the expected trend to an extent (Figure 4-1). For a long period, excluding the very beginning and very end of the experiment, temperature variations were completely independent of ambient temperature (maximum), which indicated microbiological activity within the bags for that duration of the investigation.

As can be seen in Figure 4-1, all three bags peaked at their maximum temperatures after almost 4 weeks of composting which was much longer than anticipated. There are potentially two reasons for this. The first could be due to the fact that the porous nature of the composting bags was indeed sufficient for aeration and the turning of the contents in the first week actually disrupted the activity. Secondly, the pith/PMS samples contained a high moisture content which possibly inhibited the oxygen flow. This may have limited the activity of the microorganisms. Bag 1 peaked after 20 days of composting to the highest temperature of all three bags, i.e. 36.8°C. Peak temperatures for Bag 2 and 3 were 35.9 °C and 36.7 °C, after 24 and 29 days of composting, respectively. After the peak temperatures were reached, the bags began losing heat rapidly. This did not necessarily imply that composting was over. If the composting process was complete immediately after the temperature peaked, a variety of factors could have been responsible for this:

- Moisture content was always too close to the upper limit of the allowable range (Section 2.4.4.1). Too much moisture could eventually have led to inhibited oxygen flow, limiting or ceasing microorganism activity, forcing the process to end early.
- The process could merely have finished early naturally, i.e. yielding a product having reached maturity to near-completion before expected, without being affected by any outside factors.

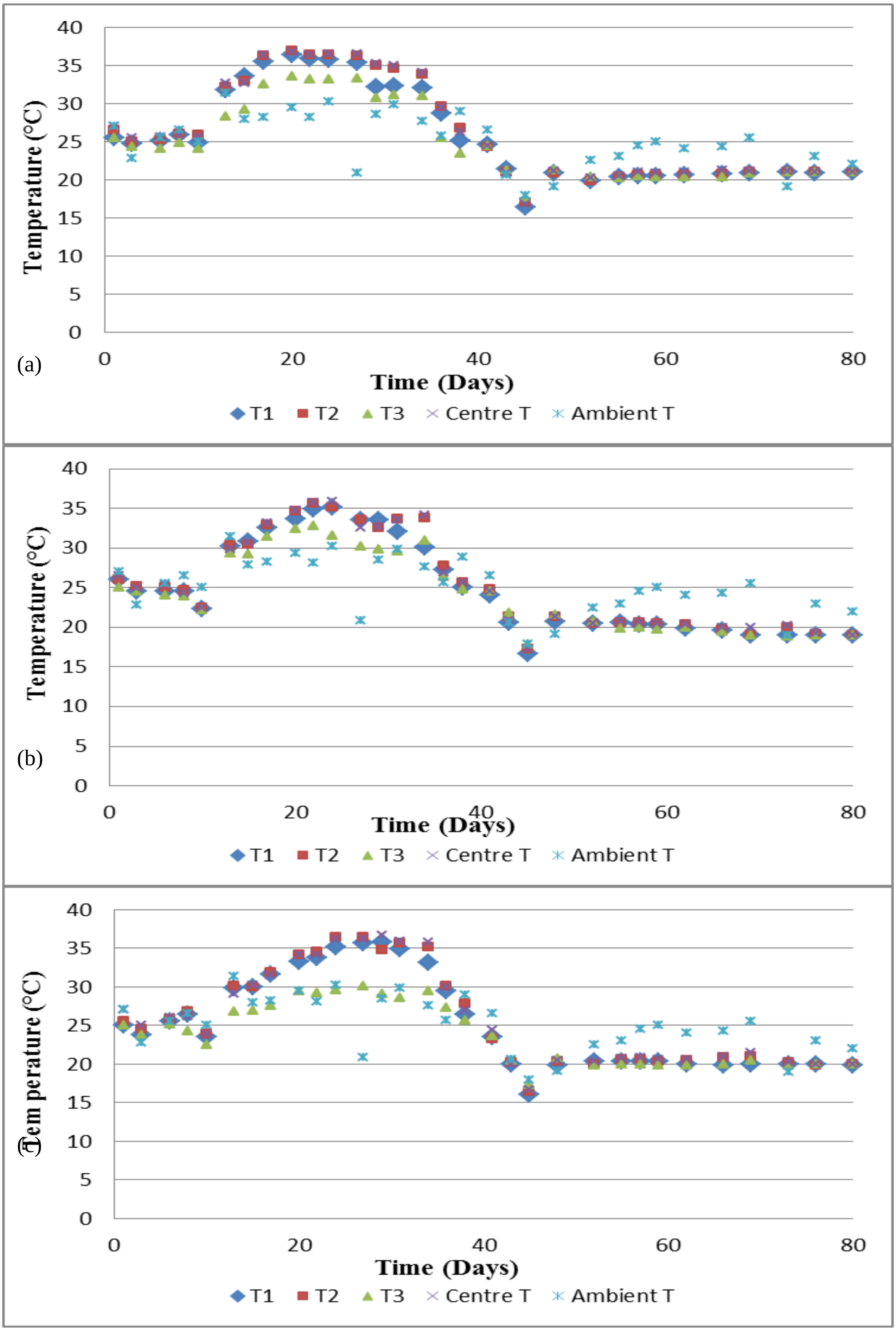

Figure 4-1: *Change in temperature monitored over 12 weeks in (a) Bag1, (b) Bag 2 and (c) Bag 3*

By day 45, all three bag temperatures as well as the ambient temperature had decreased to the lowest recorded of 16.8 °C, 17.3 °C, 16.7 °C and 17.9°C respectively. This was a clear indication that the bags had ceased composting and the temperatures were now largely constrained by ambient temperature.

4.2.2.2 pH

pH trends in Figure 4-2 were as expected. Time zero measurements were almost identical to the week one measurement due to the fact that they were done only a day apart. An initial decrease was indicative of the formation of acetic acid, which are by-products of organism activity (Singh and Kalamdhad, 2012). The urea pellets in the mixture gave off a strong ammonia smell. Approximately one week after the urea pellets were added, they were no longer physically visible in any of the bags. This indicated that they were almost completely dissolved by then.

As the compost matured, pH increased, and reached near-neutral levels. In the final few weeks, some instability in pH readings was noted in all three bags. This may have no real significance, but if the analysis was to continue and a further drop was noted, this could signal a re-establishment of the composting process.

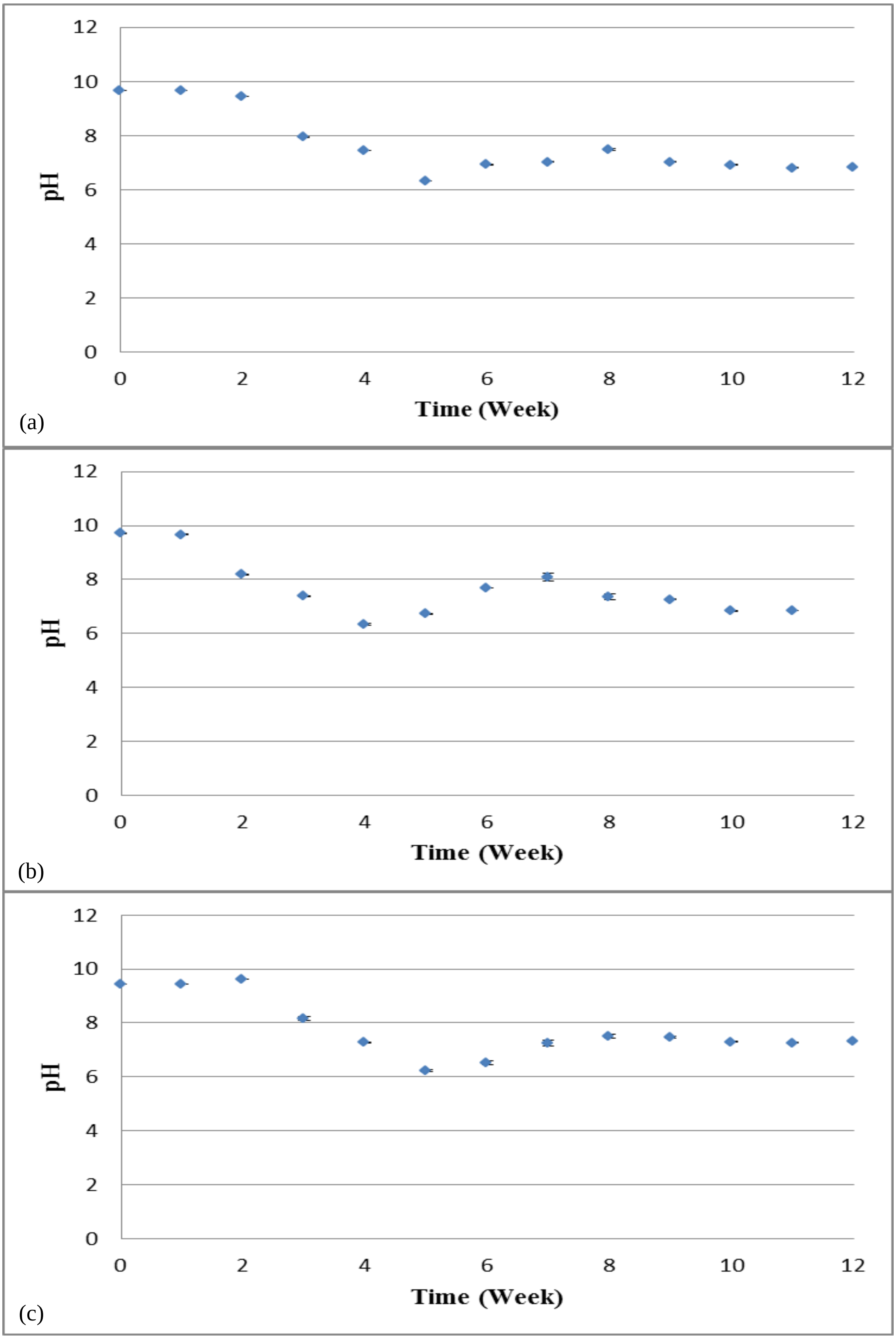

Figure 4-2: *Change in pH for (a) Bag 1, (b) Bag 2 and (c) Bag 3 over the duration of the investigation (n = 3)*

Final pH values after 12 weeks of composting were 6.83, 6.85 and 7.31 for Bag 1, 2 and 3, respectively. Thus all three bags produced composts with the pH within the desired range of 6.5-7.5.

4.2.2.3 Moisture content

The high moisture was an indication that aeration could be the inhibiting parameter, despite the earlier assumptions that the porous bag structure and the weekly compost-turning would lead to adequate conditions. The moisture values continued to stabilise as time progressed, which led to conditions conducive to continued composting. It can be seen that all three bags had an extremely good water holding capacity and maintained excellent moisture of between 50 and 60% throughout most of the investigation. Bag 3 was found to retain water the most whilst Bag 1 retained the least moisture, although both still retained moisture levels that fell within the desired range. Moisture began to decrease when the bags were opened to allow for extra aeration and evaporation which could have been when the biota entered the system.

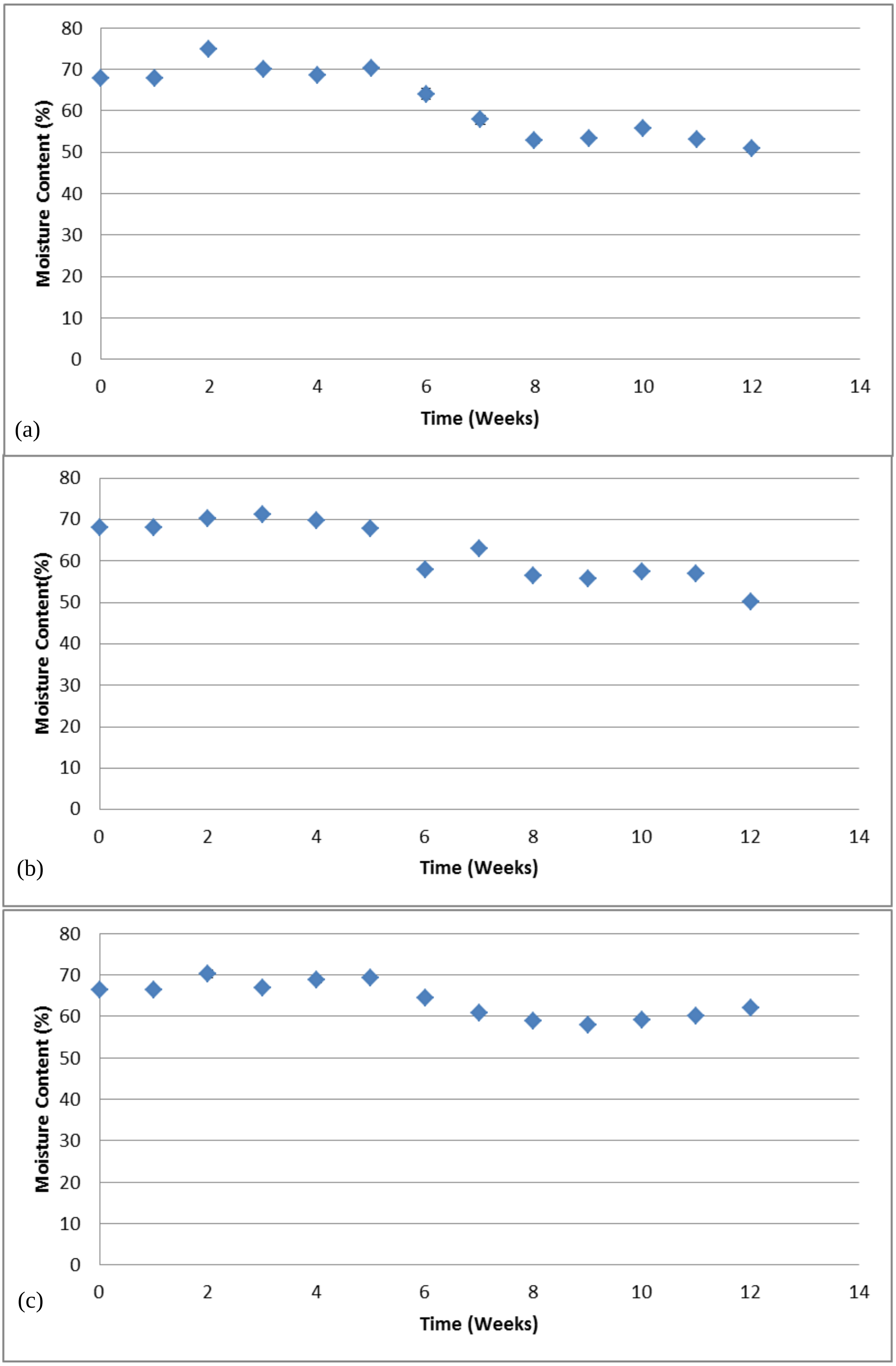

Figure 4-3: *Change in moisture for (a) Bag 1, (b) Bag 2 and (c) Bag 3 over the duration of the investigation (n = 3)*

4.2.2.4 Heavy metal analysis

ICP results showed that the heavy metals found in the final compost were all below the environmental limits for quality compost (Section 2.4.3.4). With reference to Section 3.2.2.6, heavy metals such as arsenic, cadmium, mercury, nickel, lead and selenium were below the detection limits in the raw pith/PMS$_C$. In these samples, only nickel and selenium were not detected. This could mean that the equipment used in the ICP analysis completed in Section 3.1.2.5 was not as sensitive to that used by the Soil Fertility and Analytical Services Section.

As can be seen in Table 4-2, all three bags showed a decrease in copper and zinc. Cadmium, lead and mercury are important trace elements. Concentrations of cadmium and arsenic were almost equal for all three bags. Bag 1 contained the highest concentrations of mercury and lead. According to Singh and Kalamdhad (2012), the thermophilic phase of the composting process affects the exchangeable fraction. Exchangeable Zn was proven to increase by 3.38% during the thermophilic phase but then decrease again by 1.07% in the cooling phase. A decrease tendency was also observed for copper during the thermophilic phase (Singh and Kalamdhad, 2012). Hence the reduction in copper and zinc was due to the physico-chemical method during composting (Singh and Kalamdhad, 2012).As discussed in Section 2.4.3.4 , this means that during the thermophilic phase the oxidation process and the formation of organo-metallic complexes could reduce the soluble contents of metals. The disparity between the results obtained from the raw sludge samples and the compost analysis was also most likely due to a concentrating effect as bulk mass was reduced during the composting process (Norris and Titshall, 2008). Samples were also diluted by the use of wood chips.

Table 4-2: *Heavy metal analysis on each bag*

Heavy Metal	**Limits (mg/L)***	**Initial (mg/L)**	**Bag 1 (mg/L)**	**Bag 2 (mg/L)**	**Bag 3 (mg/L)**
As	41	n.d	0.07±0.006	0.05±0.008	0.04±0.001
Cd	35	n.d	0.10±0.002	0.11±0.003	0.11±0.001
Cu	1500	2.51±0.027	0.76±0.054	0.38±0.005	0.42±0.003
Hg	78	n.d	0.09±0.014	0.002±0.005	n.d
Ni	420	n.d	n.d	n.d	0.12±0.001
Pb	300	n.d	0.25±0.003	0.14±0.002	0.14±0.003
Se	100	n.d	n.d	n.d	0.11±0.01
Zn	2800	2.10±0.014	0.814±0.021	0.46±0.005	0.48±0.002

*(Watson, 2007); n.d = not detectable

4.2.2.5 C/N ratio

C/N ratios of pith and effluent sludge were 59.84 and 54.14, respectively, before the addition of urea and were too high above the ideal value (30:1). This meant too little N was naturally present in these waste products. N is directly responsible for protein and cellular synthesis, and if the insufficiency was not remedied, the population of organisms within the material which are responsible for its decomposition and stabilization would have been inhibited. Urea was added to decrease the C/N ratio to 30:1. Almost halfway through the total composting period, the C/N ratios decreased to just over 20 (Table 4-3). After a total of twelve weeks, Bag 1 and Bag 2 decreased only slightly more to 21.18 and 20.68, respectively. Bag 3 decreased much further to 16.15 indicating that more decomposition took place in this bag than the other two.

Table 4-3: *C/N ratios for the raw PMS and composted samples*

Time	**Bag 1**	**Bag 2**	**Bag 3**
Initial	29.83±0.001	30.08±0.004	30.29±0.001
After 6 weeks	24.19±0.003	22.14±0.003	21.17±0.001
Final compost	21.18±0.002	20.68±0.001	16.15±0.001

4.2.2.6 Final quality analysis

The analyses indicated good compostability of the pith/PMS$_C$ blends. Nonetheless, it was also necessary to compare the results from each pith/PMS$_C$ mixture. The results provided evidence that the pith/PMS$_C$ (1:1), pith/PMS$_C$ (2:1) and pith/PMS$_C$ (3:1) blends were compostable. However, some factors may be important to note.

Plate 4-3 is evidence of the existence of a thriving ecosystem in Bag 3. Other macro organisms present included ants, spiders, praying mantises and beetles.

Plate 4-3: *Macro organism present in Bag 3*

White, long mushrooms grew on several occasions in Bags 2 and 3 (Plate 4-4). The presence of these fungi indicates favourable physical and chemical conditions (Richard, 1996a). Also, more varieties of macro organisms were physically visible in Bag 3, evidenceof a healthy, thriving ecosystem. The source of the macro organisms could be due to the fact that all three bags were opened and allowed to dry up during a period of high moisture.

Plate 4-4: *Fungi in composting bags*

The final height of Bags 1, 2 and 3 were approximately 51.18 cm, 50.22 cm and 49.2 cm, correlating to volume reductions of approximately 14.2%, 16.3% and 18%, respectively.

Although all the bags proved compostable, Bag 3 produced a better quality. Aside from excellent final moisture (62 %), a pH of 7.31, heavy metals all below the environmental limits and a final C/N of 16.15, there was extensive evidence of a thriving ecosystem and the largest volume reduction. These chemical and visible changes represented the best composting result and thus the best quality of the three ratios.

4.3 Conclusions

The centre T and the temperature at T_2 were generally higher than the other two temperatures closer to the top and bottom of the bag. The initial assumption that the centre was most conducive to microorganism activity was true. The highest temperatures at which all three bags peaked were all below 40 °C, much lower than the theoretical expected peak temperature of 70 °C. This was due to the fact that there was high moisture content at the beginning of the process which inhibited microbial activity. The emptying of the bags for aeration also disrupted the process. This was done to ensure that sufficient oxygen was penetrating through the contents and anaerobic conditions were avoided.

The final pH fell within the desired range of 6.5 and 7.5. ICP results showed that the heavy metals found in the final compost were all below the environmental limits for quality compost. All three bags showed a decrease in copper and zinc which were due to physico-chemical methods during composting, meaning that during the thermophilic phase the oxidation process and the formation of organo-metallic complexes could reduce the soluble contents of metals. The C/N ratio in Bag 3 decreased to 16.15 over the twelve weeks indicating that more decomposition took place in this bag than the other two.

Bag 3 produced better quality compost based on the final moisture (62 %), final pH of 7.31, heavy metals all below the environmental limits, a final C/N 16.15 and an 18% reduction in volume.

CHAPTER FIVE

Large scale compostability of paper mill sludge

5.1 Materials and methods

5.1.1 Introduction

The best composting mix from the small scale composting trials, pith/PMS (3:1) blend was used in the large scale trials to better understand the degradation process.

5.1.2 Sample collection

Samples were collected and handled as explained in Chapter Four.

5.1.2.1 Method of sampling

The same method was used to obtain composting masses and representative samples as discussed in Chapter Four.

5.1.3 Experimental method

The composting systems were to operate as naturally as possible by exposing the entire sample to ambient air and pressure. This was achieved using well aerated, porous, 1 ton woven propylene bags, which provided both aeration and drainage in the event of rain.

Moisture and nutrient levels recommended in literature (see Chapter Two, Section 2.4.3 and 2.4.4) were used to control the processes. These were:

- Moisture at approximately 60%
- C/N ratio of 30:1

5.1.3.1 Trial 1

Trial 1 was attempted with the intention of achieving the degradation process of the pith/PMS$_C$ (3:1) with the use of natural ingredients to correct the C/N ratio. This trial was run over a period of 40 days during October and November 2011. The pith/PMS$_C$ (3:1) blend was added to the composting bag. The bag also contained wood chips (occupying about one third of the bag volume) to act as a bulking agent and improve aeration (Plate 5-1). Most readily available composting materials do not fit the ideal 30:1 C/N ratio. The composting mixture was thus created by alternating layers of dry, brown shredded leaves with green grass and green leaves from natural garden surroundings in the pith/PMS (3:1) blend to meet the ratio. According to literature, woody (or brown) material is rich in C, however, green foliage is usually abundant in N (Ministry of Agriculture and Food, 1996). Because the sample was already rich in C (35.23% extracted from Table 3-2), minimal brown material was added to the mixture. These natural ingredients were not analysed for C and N content. Instead, theoretical figures were used as a guideline. Green foliage has a theoretical C/N ratio of approximately 30-80:1, and woody material ranges between 100-500:1 (Ministry of Agriculture and Food, 1996).Each layer was moistened. The pith/PMS$_C$ (3:1) blend used was mixed with an inoculum which consisted of mushroom mycelium and horse manure. This provided the necessary start that was required for organisms to begin with the decomposition process. The bag was folded at the top to ensure a closed environment. Refer to Table 5-1 for the contents of each composting bag. Because this trial was simply to understand if composting could occur naturally without the use of chemicals, the shredded leaves and grass were not analysed.

Plate 5-1: *Freshly mixed pith/PMS$_C$ (3:1) with wood chips for aeration*

5.1.3.2 Trials 2 and 3

Trials 2 and 3 were run with the intention of achieving the degradation process of the pith/PMS_C (3:1) blend by chemical addition to correct the C/N ratio on a larger scale. Both trials were identical, not concurrent, to test for reproducibility. Therefore Trial 2 was run over 95 days between January and April 2012, and Trial 3 between April and July 2012 for 99 days. The volume of a 1 ton woven polypropylene bag was measured, and the bag was filled with masses of PMS_C and pith waste mixtures. The bag also contained wood chips (occupying about one third of the bag volume) to act as a bulking agent and improve aeration. C/N ratios were adjusted to the desired levels of 30:1 by the addition of urea. The quantity of N required by each bag was calculated, as can be seen in Appendix A4. The same inoculum as Trial 1 was used for these runs. Each bag was folded at the top to maintain a closed environment. Table 5-1 shows the contents of each composting bag.

Table 5-1: *Details of each 1 ton composting bag*

Parameter	Trial 1	Trial 2	Trial 3
Mass of sludge	20.68 kg	67.2 kg	68.3 kg
Mass of pith	62.03 kg	201.6 kg	205 kg
Mass of inoculum	7 kg	7 kg	7 kg
Height of heap	0.4 m	0.75 m	0.80 m
N source and quantity	Shredded leaves and grass (2.5 kg)	Urea pellets (2.37 kg)	Urea pellets (2.41 kg)
Period of composting	40 days	95 days	99 days

*Mass of wood chips was not measured but they made up a third of the volume of the bag.

5.1.4 Process control

5.1.4.1 Aeration

In Trial 1, simple turning of the pile in the bag was utilised to provide aeration when temperature increased at the centre. In Trials 2 and 3, however, a method of transferring the contents from one porous composting bag to another while mixing with a shovel was adopted.

5.1.4.2 Temperature

The temperature was recorded regularly with the use of a digital probe during each trial. The frequency of temperature readings was of importance to check that the degradation process was occurring. Maximum ambient temperature readings were recorded at 2pm, the same time as all other temperature readings.

For Trial 1, the temperature was only monitored and recorded at the centre of the bag. For Trials 2 and 3, the temperature was monitored at the centre (T_C) as well as 3 different depths, 10 cm from the base of the compost (T_3), 10 cm from the top of the compost (T_1) and 30 cm from the base of the compost (T_2), all in the middle of the bag (as can be seen in the illustrative figure below, Figure 5-1). Multiple temperature readings were taken so as to obtain a temperature profile through the bag. This gave an idea of the microbial activity at the various measurement locations.

As the volume reduced, the height of the compost in the bag decreased. The points for T_3 and T_2 were fixed as the height did not reduce to this level. The height was measured each time a temperature reading was taken. Thus, the points for T_1 and T_C were measured from the top of the compost level and the readings taken at these new points each time.

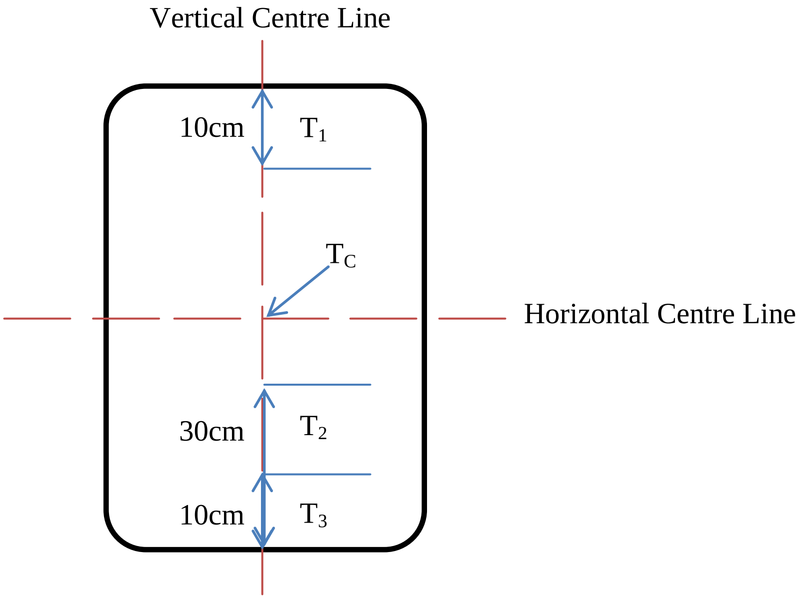

Figure 5-1: *Illustrative figure of the points at which the temperature probe was placed*

5.1.5 Analytical analysis

Compost was removed by hand from different depths of the bags on a weekly basis and used as a representative sample for analysis. Triplicate tests were completed each for pH, moisture content and EC using the analytical methods discussed in Section 3.1.2.

At the end of the process, a sample was sent to the Soil Fertility and Analytical Services Section of the KwaZulu-Natal Department of Agriculture and Environmental Affairs to determine the final C/N ratio and elemental analysis. Triplicate tests were done for each analysis.

5.1.5.1 C/N ratio

Samples were analysed by the same method discussed in Section 3.1.2.4.

5.1.5.2 Elemental analysis

The elemental analysis was completed as explained in Section 4.1.5.2.

5.1.6 Statistical analysis

All analyses were done in triplicate for repeatability reasons. The pH and moisture content graphs, Figure 5-3 and Figure 5-4, were plotted with error bars to illustrate the deviation from the mean in each sample. Heavy metal results were also reported using the standard deviation for each element.

5.2 Results and discussion

5.2.1 Introduction

The results obtained using the selected test methods for the three trials are discussed below. Raw data obtained and calculations are reported in Appendix D.

5.2.2 Process monitoring parameters

The 1 ton bags used for the composting were expected to be highly favourable for the comparative test. Being porous, they were expected to facilitate sufficient aeration and not promote anaerobic conditions that would reduce the ability of the material to be composted. To ensure proper composting conditions, the same approach discussed in Section 4.1.4 was used.

In the case of Trial 1, a more natural, non-synthetic approach was used. The C/N ratio was adjusted to approximately 30:1 by the construction of a layered heap as these C and N sources are the choice for natural composting processes. Additional C provided in the form of dry leaves was not strictly necessary due to the large amount of C already present.

5.2.2.1 Temperature

It was expected that the centre would generate the most heat (microbiological activity) and the temperature would decrease with increasing distance from the centre. Therefore for a better understanding of the heap temperature, readings were taken at 3 different points as well as the centre (See Figure 5.1, Section 5.1.4.2).

Figure 5-2 shows the change in temperature over the period of the investigation.

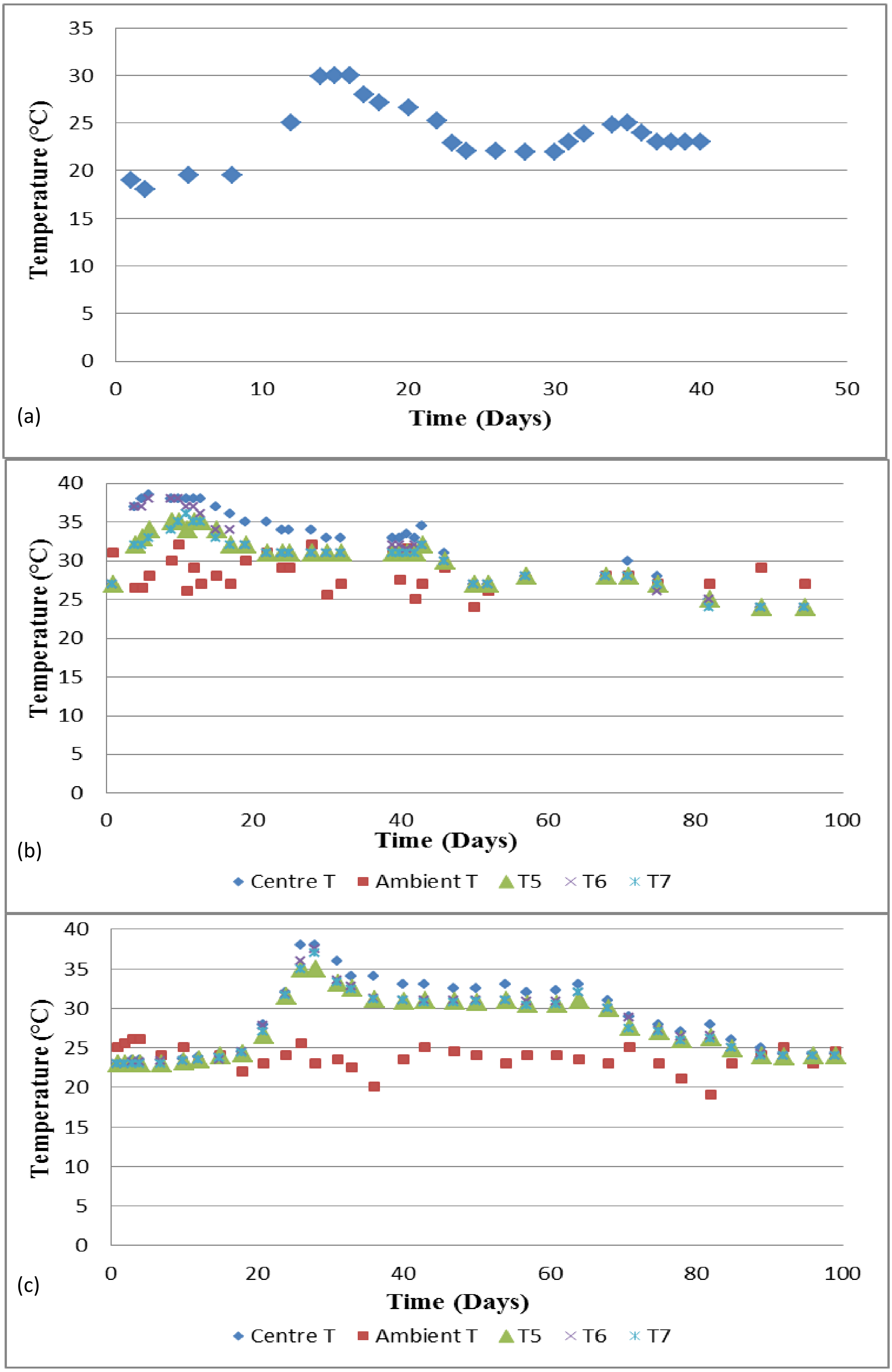

Figure 5-2: *Temperature profiles observed in (a) Trial 1, (b) Trial 2 and (c) Trial 3*

Trial 1 was completed to check if composting would occur in the larger bags using natural, non-synthetic nutrients. Therefore only the centre temperature was recorded. The temperature profile during this trial showed that the three composting phases did in fact occur, even though the peak temperature was only about 30°C.

Trials 2 and 3 were run as discussed above; the temperature was recorded at three different heights as well as the centre so as to obtain a better understanding of the temperature change in the entire bag. These trials composted well. Initially the contents of the bag were turned at least three times a week, and then the frequency of tuning was decreased to once a week after six weeks. Maximum temperatures of 38.5°C and 38°C were recorded for Trial 2 and 3, respectively. Theoretically, temperature should peak between 60°C and 70°C. The reason as to why the temperatures did not peak at theoretical values could be due to the fact that there was unnecessary turning in the first few weeks. This could have hindered the microbial activity.

A well-constructed compost heap generally reaches the thermophilic phase within a short time. The temperature peaked in Trial 2 after nine days. Trial 3 progressed much slower and peaked after twenty six days. The only difference was the ambient temperature. Trial 2 was completed during a much warmer time of the year. This illustrates the effect of the ambient temperature (taken at 2pm) on the composting process due to the relatively small volume of composting material. After 90 days, the compost was considered mature as the temperatures in both trials were more or less stable at 24°C, after this period.

5.2.2.2 pH

The pH values of all three trials declined and then increased over time. The pH of the composting mix in Trial 1 declined for the first 11 days, in Trial 2 it declined for 47 days and in Trial 3 it declined for 34 days before increasing and stabilising. The presence of the marked increase in pH at the end of the trials confirms the maturity of the final product (Watson, 2007).

Initially during composting, the pH declines as the easily degradable carbon sources are converted into organic acids (Dickson et al., 1991). These easily degradable carbon sources include the monosaccharides and starches present in the raw pith/PMS$_C$. The increase in pH after initially decreasing, results from the ammonia that is liberated due to the depletion of these carbon sources hence the decrease in protein concentrations. It is very important that a further decline in pH be observed after this stage, no matter how small (Dickson et al., 1991). A very slight decline can be seen in Trials 2 and 3 between days 80 and 100. This was representative of the further degradation of the more resistant compounds (cellulose, hemicellulose and lignin) into more stable humus. This final decline was not noted in Trial 1 which further suggests that this bag did not fully compost after 6 weeks into mature compost as Trials 2 and 3 had after approximately 14 weeks (See Table 5-1 for periods of composting).

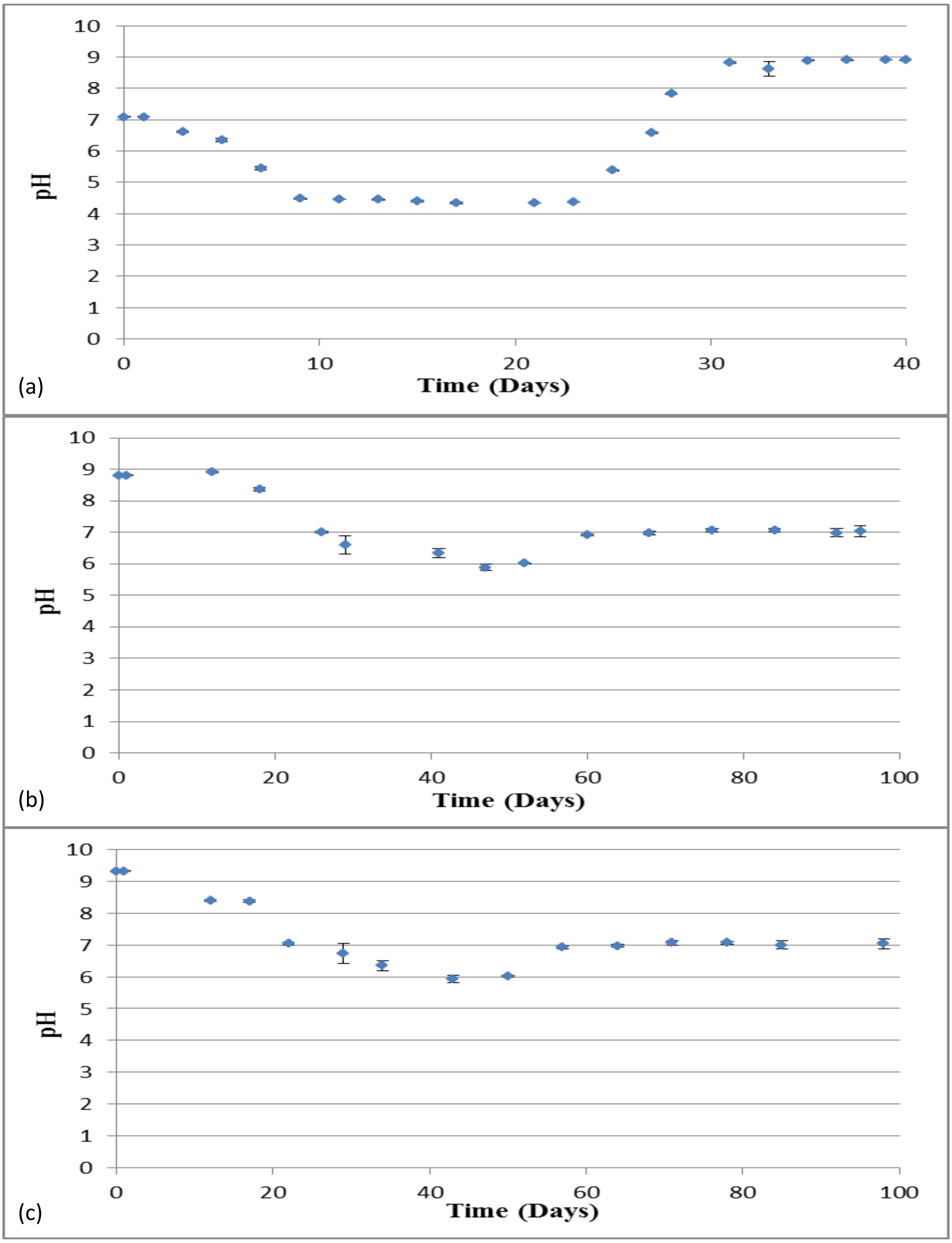

Figure 5-3: *Change in pH over the duration of the experiment for (a) Trial 1, (b) Trial 2 and (c) Trial 3 (n = 3)*

The pH values of the final composts produced were 8.9, 7.04 and 7.03 for Trials 1, 2 and 3, respectively. Trials 2 and 3, which were considered mature, fell within the desired range for quality compost of 6.5–7.5. The extremely high final pH for Trial 1 is not completely understood, especially since this was a natural composting process. As discussed in Section 5.1.3.1, a larger amount of content containing N was added. A possible reason for the high final pH could be due to the production of ammonia from nitrogenous compounds (Ministry of Agriculture and Food, 1996).

5.2.2.3 Moisture content

This investigation further illustrated the sustained water holding capacity of the pith/PMS_C (3:1) blend throughout the duration of the composting process. All three trial compost moistures were close to the desired level of 50% throughout the trial. The use of the larger bags for composting proved to be more favourable in maintaining desirable moisture. In Trials 2 and 3, the moisture levels stabilised resulting in favourable final moisture. Trial 1, although only partially composted, achieved 51.17% final moisture. Trials 2 and 3 were also close to the desirable moisture content at 50.44% and 50.40% moisture respectively.

Looking at Figure 5-4, large deviations in moisture content especially over the first 2 months of the investigation were noted. These deviations could be explained by the fact that in the first 2 months, the pith/PMS_C (3:1) was still clumpy and therefore moisture pockets existed. This implies a poor sampling technique. Over the final 30 days, however, it was noted that the deviations decreased, and the moisture content in the bag was more uniform.

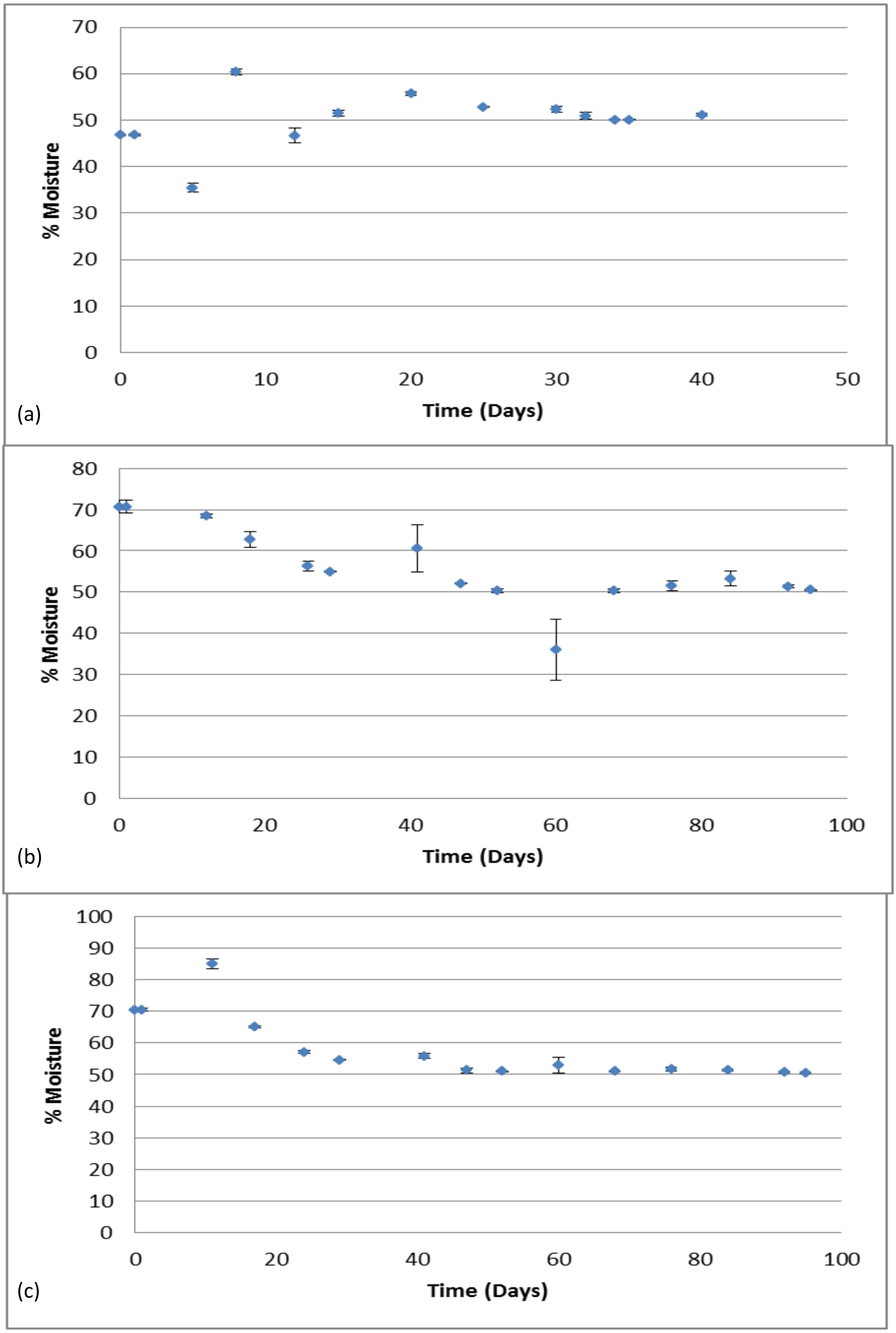

Figure 5-4: *Change in moisture in each trial over the duration of the experiment for (a) Trial 1, (b) Trial 2 and (c) Trial 3(n = 3)*

5.2.2.4 Heavy metal Analysis

Inductively coupled plasma results showed that the heavy metals found in the final compost were all below the environmental limits for quality compost (Section 2.4.3). With reference to Section 3.2.2.6, heavy metals such as arsenic, cadmium, mercury, nickel, lead and selenium were below the detection limits in the raw pith/PMS$_C$ from Mill C. In these samples, only nickel and selenium were non-detectable. As explained in Chapter Four, this could mean that the equipment used in the ICP analysis completed in Section 3.1.2.5 was not as sensitive to that used by the Soil Fertility and Analytical Services Section.

As can be seen in Table 5-2, all three bags showed a decrease in copper and zinc. The reduction in copper and zinc was due to the physico-chemical method during composting (Singh and Kalamdhad, 2012), as discussed in Chapter Four. During the thermophilic phase of composting, the oxidation process and the formation of organo-metallic complexes, could reduce the soluble contents of metals (Singh and Kalamdhad, 2012). Humic substances bind with exchangeable and carbonate fractions of metals. The disparity between the raw PMS analysis and the compost analysis results could also be due to a concentrating effect as bulk mass was reduced during the composting process (Norris and Titshall, 2008). There was also a diluting effect due to the addition of wood chips.

Table 5-2: *Heavy metal analysis of the composts (n = 3)*

Element	**Limits (mg/L)**	**Initial concentration (mg/L)**	**Concentrations (mg/L)**		
			Trial 1	**Trial 2**	**Trial 3**
As	41	n.d	0.08±0.008	0.05±0.006	0.05±0.006
Cd	35	n.d	0.09±0.001	0.09±0.002	0.09±0.001
Cu	1500	2.51±0.027	0.62±0.005	0.42±0.001	0.28±0.002
Hg	78	n.d	0.04±0.002	n.d	n.d
Ni	420	n.d	0.14±0.002	0.11±0.001	0.12±0.005
Pb	300	n.d	0.25±0.005	0.22±0.005	0.23±0.005
Se	100	n.d	n.d	n.d	n.d
Zn	2800	2.10±0.014	0.92±0.008	0.35±0.002	0.36±0.006

n.d = not detectable

5.2.2.5 C/N ratio

Upon completion, the C/N ratios dropped to 17, 13 and 11.5 for Trials 1, 2 and 3, respectively. Trials 2 and 3 resulted in a final C/N ratio closest to the final theoretical optimum value of 10 indicating that there was much more decomposition (carbon removal) occurring in these trials (Richard and Trautmann, 1996).

Table 5-3: *C/N ratios for the raw pith/PMS$_C$ (3:1) and composted samples (n = 3)*

C/N	Trial 1	Trial 2	Trial 3
Raw Blend	30±0.004	30±0.001	30±0.003
Final compost	17±0.003	13±0.001	11.5±0.003

5.2.2.6 Other observed changes

With respect to Trials 2 and 3, after the first month remarkable visible changes were evident. These included the growth of mushrooms, the appearance of worms and an abundance of insect activity. The growth of the mushrooms was, as explained in Section 4.2.2.6, a sign of excellent composting conditions (Richard, 1996a). The aeration was therefore sufficient and the moisture was ideal for the growth of mushrooms and to sustain a thriving microbial population.

Plate 5-2: *Growth of mushrooms after a month of composting in Trial 2*

Once the mushrooms die off, they contribute to the overall quality of the compost (Richard, 1996a). Plate 5-3 depicts what remains of the mushrooms after a week of growth.

Plate 5-3: *The residue of the mushrooms after almost a week of growth in Trial 3*

The appearance of fat white grubs was a sign of mature compost (Richard, 1996a). These were noticed in both Trials 2 and 3 after the first 2 months and their numbers had increased by the third month (Plate 5-4).

Plate 5-4: *Fat white worm present in the mature compost*

The final height of Bags 1, 2 and 3 were approximately 36 cm, 61.05 cm and 64.56 cm, correlating to volume reductions of approximately 10%, 18.6% and 19.3%, respectively.

The thriving biological activity suggests that the composts produced were of a good quality. Physically, the final compostshad reduced from the bulky material to a crumbly, fine textured material, not resembling the structure of the starting material. The composts were high in moisture but not saturated. There was a pleasant, earthy odour that lingered which contrasted with the strong, unpleasant odour of the raw pith/PMS$_C$ (3:1) blend. The pH of the final products was within the range of 6.5 and 7.5, and the C/N ratios were found to drop to almost the theoretical expected value of 10:1 in both Trials 2 and 3.

5.3 Conclusions

The phases of composting were evident for all trials. However, the highest temperatures at which all three bags peaked were all below 40 °C, much lower than the theoretical expected peak temperature of 70 °C. This may be due to the fact that the contents were turned unnecessarily, thus hindering the microbial activity. The fact that the bags did not achieve thermophilic conditions in a short time was due to the relatively small composting volumes.

The final pH fell within the desired range of 6.5 and 7.5. The high final pH observed for Trial 1 was not understood.

The moisture values showed that the composts all displayed good water holding capacities. ICP results showed that the heavy metals found in the final compost were all below the environmental limits for quality compost. All three bags showed a decrease in copper and zinc which were due to physico-chemical methods during composting, where the oxidation process and the formation of organo-metallic complexes, could reduce the soluble contents of metals (Singh and Kalamdhad, 2012). The disparity between the raw PMS analysis and the compost analysis results could also be due to a concentrating effect as bulk mass was reduced during the composting process (Norris and Titshall, 2008). There was also a dilution effect due to the addition of wood chips. The C/N ratio in Trials 2 and 3 decreased to 13 and 11.5 over the composting period indicating that decomposition occurred.

Trials 2 and 3 produced identical quality composts thus proving reproducibility of the process. This was based on the final moisture, final pH, heavy metals all below the environmental limits, a final C/N <10 and an average of 19% reduction in volume. It was therefore concluded that the pith/PMS_C (3:1) is compostable, using this method. The thriving biological activity suggests that the composts produced were of a good quality. Physically, the final composts had reduced from the bulky material to a crumbly, fine textured material, not resembling the structure of the starting material

CHAPTER SIX

Evaluation of the effect of direct land application of pith/PMS_C (3:1)

6.1 Materials and methods

6.1.1 Introduction

The direct application of PMS to agricultural land has become progressively more accepted as a suitable method of sludge disposal. Aside from the popular advantage such as the lower disposal costs, beneficial changes in the physical and chemical condition of the soil may also be induced by the addition of sludge. The sludge contains approximately 50% of organic matter, which is the key ingredient to improving the physical condition of the soil.

The objective of this part of the study was to determine the effects of the direct pith/PMS_C (3:1) application on selected soil physical and chemical properties under natural field conditions.

6.1.2 Sample collection

This study involved the collection of 10 soil samples from various farming plots, each with pith/PMS_C (3:1) applied at different times. Farmers apply the pith/PMS_C (3:1) to their land in large application rates of 60–100 tons/ha or until the pith/PMS_C (3:1) is approximately 10 cm thick on the surface of the soil before being turned in (Section 2.5.1). Each field receives 150 kg of K/ha and 140 kg N/ha per year as inorganic fertilisers.

Each sample was taken from three randomly selected positions on the farms and placed into collection bags. Samples included untreated soils, soils treated pith/PMS_C (3:1) in 2008, 2009 and 2010, respectively. This was necessary as a clear indication of the degradation pattern of the pith/PMS_C (3:1) blend in the soil over time was to be determined as well as the effect of the pith/PMS_C (3:1) on the soil properties over different periods of time. All soil types were of the same sandy loam soil texture.

6.1.2.1 Method of sampling

The quartering sampling method was used to obtain representative samples for analysis, as discussed in Chapter Four. The remaining quarters were thoroughly mixed and reduced further by quartering until the desired masses for each sample was achieved.

6.1.3 Analytical analysis

Triplicate samples were sent to Soil Fertility and Analytical Services Section of the KwaZulu-Natal Department of Agriculture and Environmental Affairs for a soil property analysis. These included the sample density, extractable P, K, Ca, Mg, Zn, Mn and Cu, acid saturation, effective cation exchange capacity, pH, soil organic carbon and total carbon and nitrogen.

6.1.3.1 Sample density

Samples were analysed on a volume rather than mass basis. This was converted to a mass basis. The mass of 10 mL scoop of dried and milled sample was measured and the sample density calculated (Manson and Roberts, 2000).

6.1.3.2 Extractable Ca, Mg and acidity

2.5 mL of soil was scooped into sample cups. 25 mL of 1 M KCl solution was added and the suspension was stirred at 400 r.p.m. for 10 minutes using a multiple stirrer. The extracts were filtered using the Whatman No.1 paper. 5 mL of the filtrate was diluted with 20 mL of 0.0356 M $SrCl_2$.The calcium and magnesium were determined by atomic absorption. To determine extractable acidity, 10 mL of the filtrate was diluted with 10mL of deionised water containing 2-4 drops of phenolphthalein, and titrated with 0.005 M NaOH (Manson and Roberts, 2000).

6.1.3.3 Extractable P, K, Zn, Cu and Mn

This method involved the use of the Ambic-2 extracting solution. This solution was adjusted to pH 8 with a concentrated ammonia solution. 25 mL of this solution was added to 2.5 mL soil, and the suspension was stirred at 400 r.p.m. for 10 minutes using a multiple stirrer. The extracts were filtered using a Whatman No.1 paper. Phosphorus was determined on a 2 mL aliquot of filtrate using a modification of the molybdenum blue procedure. Potassium was determined by atomic absorption on a 5 mL aliquot of the filtrate after dilution with 20 mL deionised water. Zinc, copper and manganese were determined by atomic absorption on the remaining undiluted filtrate (Manson and Roberts, 2000).

6.1.3.4 Effective cation exchange capacity and acid saturation

Effective cation exchange capacity (ECEC) is the sum of the extractable K, Ca, Mg and acidity (Manson and Roberts, 2000).

The percentage acid saturation is calculated as:

$$\%\ \text{acid saturation} = \frac{\text{extractable acidity}}{\text{extractable Ca+Mg+K+extractable acidity}} \times 100 \ldots \text{(Equation 6.1)}$$

6.1.3.5 pH

10 mL of soil was scooped into sample cups. 25 mL of 1 M KCl solution was added the suspension was stirred at 400 r.p.m. for 10 minutes using a multiple stirrer. The suspension was allowed to stand for 30 minutes, and pH measured using a gel-filled combination glass electrode while stirring. (Manson and Roberts, 2000).

6.1.3.6 Soil organic carbon

The readily oxidizable organic carbon was measured using the Walkley-Black procedure. The organic matter was oxidised by potassium dichromate in a sulphuric acid medium. Excess dichromate was determined by titration with a standard ferrous sulphate solution (Manson and Roberts, 2000).

6.1.3.7 Total carbon and nitrogen

The C/N ratio was determined using the same method discussed in Section 3.1.2.4.

6.2 Results and discussion

6.2.1 Introduction

The consideration for the land application of this PMS is based on the ability to improve soils (Barclay, 1991). The results obtained are reported and discussed in this section. Raw data can be found in Appendix E.

6.2.2 Effect on soil properties

Since Farm C provided a full set of results upon analysis of soil treated with pith/PMS$_C$ (3:1) one, two and three years ago, the comparison was based on those reported results (Table 6-1).

A high CEC is sought, as it indicates a high capacity of the soil to hold cations (Drinkins and Jones, 2013). Converting the CEC units to cmol/kg by using the sample densities and comparing the CEC levels to that of Table 2.2 (Chapter Two), the untreated soil was found to have a very low CEC (< 6 cmol/kg). This indicated that the untreated soil was very low in fertility and susceptible to acidification. Soil treated with pith/PMS$_C$ (3:1) two years ago (Sample 2009 of Farm C) was similar to that of untreated soil The low CEC means the soil had a low resistance to change in soil chemistry that is caused by land use. Soils treated with pith/PMS$_C$ (3:1) 1 year and 3 years ago hada moderate CEC (12 – 25 cmol/kg). However, both of these soil samples showed a definite increase in the ability to hold cations. With reference to Table 2-3 (Chapter Two), none of the samples contained the cations in the desired proportions. These very low levels of exchangeable calcium and magnesium (Table 6-2) mean that the soils have been strongly leached and the plant growth may be limited as a result (Hazelton and Murphy, 2007).

In terms of soil changes, Logan and Esmaeilzaden (1985) and Honeycutt et al. (1988), have found an increase in soil pH and organic matter content following the addition of PMS. The pH was found to increase from that of untreated soil after the most recent application of pith/PMS$_C$ (3:1) (Sample 2010 of Farm C). The increase in soil pH was expected considering the alkaline nature of pith/PMS$_C$ (3:1). However, it was noticed that after the pith/PMS$_C$ (3:1) had been in the soil for two years (Sample 2009 of Farm C); there was an almost insignificant decrease in pH, and it was similar to that of untreated soil. The pH was even lower three years after application to the soil (Sample 2008 of Farm C). This decrease brought the pH back down to a value close to that of virgin soil. This indicates that after three years, the pith/PMS$_C$ (3:1) had probably almost completely decomposed and the benefits of this application had decreased. pH of soil affects the availability of the nutrient. It was observed that all samples had a higher pH than that of untreated soil, and fell out of the reduced nutrient availability ranges for phosphorus, potassium, calcium, magnesium, zinc, manganese and copper. Hence, all concentrations were found to increase (Table 6-2).

It was evident that the 2 year old sample (Sample 2009 of Farm C) and the untreated sample had soil properties that were significantly alike. This could conclude that the 2 year old sample was most probably an untreated soil.

Table 6-1: *Soil property changes for the samples obtained from three different farms growing sugar cane*

	Sample	**Years since application**	**Sample Density (g/mL)**	**Exchange acidity (cmol/L)**	**CEC (cmol/L)**	**Acid saturation (%)**	**pH**
	untreated	-	1.34	0.05	2.67	1.87	4.81
Farm A	**2010**	1	1.26	0.82	3.01	27.24	3.89
	2009	-	-	-	-	-	-
	2008	-	-	-	-	-	-
	untreated	-	-	-	-	-	-
Farm B	**2010**	1	1.25	0.06	5.16	1.16	6.4
	2009	2	1.14	0.03	6.21	0.48	6.57
	2008	-	-	-	-	-	-
	untreated	-	1.29	0.02	3.86	0.52	5.94
Farm C	**2010***	1	0.77	0.09	11.82	0.76	7.09
	2009*	2	1.47	-	2.61	-	6.11
	2008*	3	0.98	0.08	11.6	0.69	5.24

*Treated only once in the specified year

There was also a noticeable increase in the soil organic carbon (SOC) (See Table 6-2), which creates a better plant root environment; an improvement in water holding capacity reduces water loss and erosion whilst supplying a variety of micronutrients and macronutrients as well as significant organic matter. Many soil properties and soil qualities are enhanced by soil management practices that promote an accumulation of SOC. After being treated with pith/PMS_C (3:1) in 2008 for the first time and then the third time in 2010, the soil from Farm C showed a positive accumulation of SOC.

There was an increase in the C/N ratio of the soil once pith/PMS_C (3:1) was applied. Studies by King (1984) and Honeycutt et al. (1988) had shown that PMS with a high C/N ratio applied to land would cause an initial net immobilisation of N. Looking at the results for Farm C in Table 6-2, this was observed in the soil treated with pith/PMS_C (3:1) in2010. This phenomenon of immobilisation occurs when the C/N ratio is more than 30. The C/N ratio in this particular soil sample was found to increase from 10 to 48 one year after application. To overcome these losses in N, a fertiliser can be added as an amendment. This explains why the farmers add 140kg N/ha per year to the soils (samples sent for analyses already contained this addition). In the case of a C/N ratio of less than 20 (Farm C 2008 and 2009), mineralisation exceeds immobilization. Hence more applications of PMS are more beneficial to the soil and crops in the long run.From Table 6-2, it can be seen that Sample 2009 (Farm C) and untreated soil have tested the same for % SOC, C/N ratio, and very similar for the remaining nutrients. This further justifies that this sample was most probably an untreated soil.

Table 6-2: *Analysis of soil nutrients, soil organic carbon and C/N ratio for samples obtained from three different farms growing sugar cane*

	Sample	**Years since first application**	**P**	**K**	**Ca**	**Mg**	**Zn**	**Mn**	**Cu**	**SOC (%)**	**C/N (%)**
			(mg/L)								
Farm A	**Untreated**	-	40	60	422	44	1.1	1	1.6	1	20
	2010	1	19	68	276	78	1.1	5	0.7	1.5	18.75
Farm B	**2010**	1	48	191	648	167	1.6	4	2.1	0.5	10
	2009	2	136	170	824	199	5.3	8	2.7	0.7	14
Farm C	**Untreated**	-	31	79	451	169	1.8	1	2.4	0.5	10
	2010	1	350	598	1642	244	9.9	16	4.5	2.4	48
	2009	2	39	43	355	89	2.1	0	2.9	0.5	10
	2008	3	55	409	1691	247	10	7	6.7	4.3	14.33

A study by Bayer et al. (1992) concluded that the addition of PMS to agricultural land did not result in any accumulation of heavy metals in the soil or the plants. These results show that there was a definite increase in copper and zinc concentrations after application. The increase in copper and zinc concentrations is thought to have resulted from the use of recycled paper at the mill, which contains pigments and inks.

Copper and zinc concentrations were very low and well within acceptable limits (Table 2-5). Because prevention is the best method of protecting the environment from contamination by heavy metals, a simple calculation was carried out to find the maximum quantity of pith/PMS_C (3:1) that can be applied to the soils. The annual pollutant loading rate for Cu and Zn is 75 kg/ha/yr and 140 kg/ha/yr respectively (Soil Quality Institute, 2000). The pith/PMS_C (3:1) blend applied to the soils by the farmers currently contains 251.4 mg/kg of Cu and 209.6 mg/kg of Zn respectively (Section 3.1.2.5). Without exceeding the annual pollutant loading rate for Cu, 298.80 tons/ha of pith/PMS_C (3:1) can be applied. In the case of Zn, 667.94 tons/ha of pith/PMS_C (3:1) can be applied (See Appendix A7). Currently the farmers apply a maximum of 100 tons/ha/yr of the pith/PMS_C (3:1) blend which is well below these maximum levels.

It is worth noting that there was a dip in all of the measured values for the 2 year old sample (Farm C 2009). The reasons for this could possibly be due to the fact that this sample was actually an untreated soil. Although much care was taken to obtain representative samples and prevent any confusion between samples by labelling them, this could have affected the results.

6.3 Conclusions

The untreated soil was found to have a very low CEC (< 6 cmol/kg) indicating that the untreated soil was very low in fertility and susceptible to acidification. Soil treated one and three years ago showed a definite increase in the ability to hold cations. However, none of the samples contained the cations in the desired proportions. These very low levels of exchangeable calcium and magnesium meant that the soils had been strongly leached and the plant growth may be limited as a result.

The pH was found to increase from that of untreated soil after most recent application of pith/PMS_C (3:1) (Sample 2010 of Farm C). It was observed that all samples had a higher pH than that of untreated soil, and fell out of the reduced nutrient availability ranges for phosphorus, potassium, calcium, magnesium, zinc, manganese and copper hence the pH of soil affects the availability of the nutrient.

There was an increase in the C/N ratio of the soil once pith/PMS_C (3:1) was applied. Hence, more applications of PMS are expected to be more beneficial to the soil and crops in the long run.

All reported values for the 2 year old sample (Farm C 2009) were in accordance with the results obtained for that of untreated soil. In particular, the results for pH, % SOC and the C/N ratio were identical for both samples. The reason for this was due to the fact that this sample was probably an untreated soil.

CHAPTER SEVEN

Laboratory scale soil application experiment

7.1 Materials and methods

7.1.1 Introduction

Aerobic degradation of the pith/PMS_C in soil was determined using the ASTM standard method designation $D5338 - 98^{\epsilon 1}$, Standard Test Method for Determining Aerobic Biodegradation of Plastic Material Under Controlled Composting Conditions (ASTM International, 1999). Pith/PMS_C (3:1) was applied to the same untreated soil tested in Chapter Six in different ratios and monitored. The aerobic degradation took place in bioreactors constructed from PVC (Figure 7-1), where temperature, aeration and moisture content was closely monitored and controlled.

The test method used was an accelerated laboratory scale method for understanding the degradation of pith/PMS_C (3:1) in soil, its effects and the effect of changing quantity of pith/PMS_C (3:1) applied on soil properties. It was modified and adapted for use in this part of the research as a standard method for biodegradation of paper sludge could not be found. Pure effluent sludge, PMS_C, was also applied so as to understand if this would be more beneficial to soil than varying rates of pith/PMS_C (3:1). This test method was also designed to measure the percentage of carbon in the sample converted to carbon dioxide over time which indicates the rate of biodegradation. The modifications made to this process were:

- Pith/PMS_C (3:1) was mixed with soil rather than inoculum and pure soil was used as a control. This was done so as to observe the breakdown of pith/PMS_C (3:1) in soil and to create a similar environment as the actual degradation occurring on the farms (Chapter Six) in an accelerated period and controlled laboratory conditions.
- Analytical-grade cellulose and polyethylene were suggested as positive and negative controls in the test method. Pure soil was used as a control instead, as the test method was modified to suit the objectives of this study. Reactors contained varying ratios of pith/PMS_C (3:1) in soil to understand the implications of varying application rates on soil.
- Only CO_2 production and pith/PMS_C (3:1) biodegradation was monitored. All other analyses discussed in this method were not completed. Instead, the same analyses on the mixed soil-pith/PMS_C (3:1) samples were carried out as discussed in Chapter Six.

7.1.2 Design of bioreactors

Five bioreactors (R1 – R5) were designed using PVC. A false plate was used and constructed from a metal mesh. It served the purpose of creating a space below for air to enter as well as for any excess water to accumulate. Each bioreactor was installed with a tap at the bottom to release any excess moisture that accumulated. The air inlet pipes were fitted with spargers. The construction of the mini-bioreactor is shown in Figure 7-1.

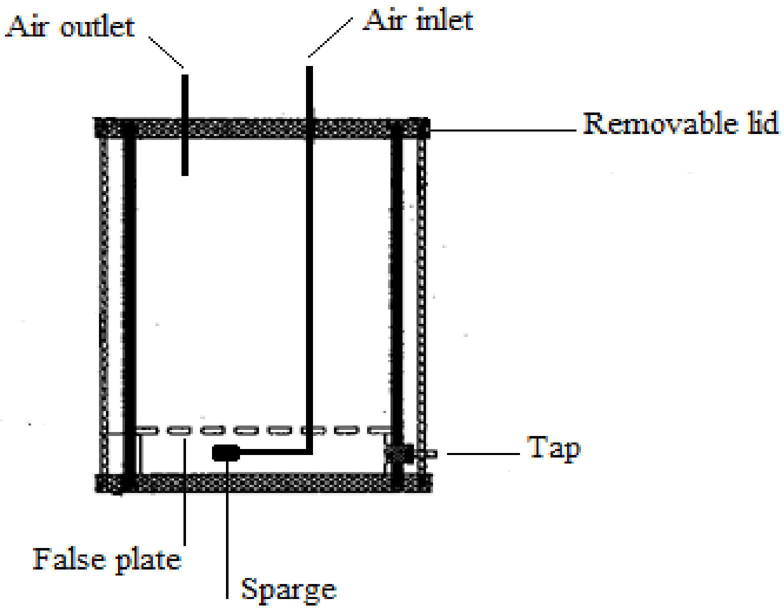

Figure 7-1: *Design of the mini bioreactors*

7.1.3 Experimental set-up

Aeration was provided by a variable speed pump (Plate 7-1). This air flow rate was measured and monitored using soap bubble flow meters constructed from broken burettes. To provide increased moisture in the bioreactors, air was first bubbled through distilled water before entering the bioreactors (humidifiers). The reactors were maintained at 58±2°C with the aid of a water bath. The humidifiers were also maintained at this temperature so as to provide warm saturated air to the reactors. The off gases leaving the reactors were closely monitored. A carbon dioxide trap was constructed by passing the off gas through a carbon dioxide scrubbing solution of barium hydroxide. Flexible tubing that was non-permeable to carbon dioxide was used. The barium hydroxide used to capture the carbon dioxide was titrated using HCl and phenolphthalein as an indicator to quantify the amount of CO_2 produced. The oxygen level in the off gas was monitored with the use of an oxygen detector and maintained within the range of 5-18%.

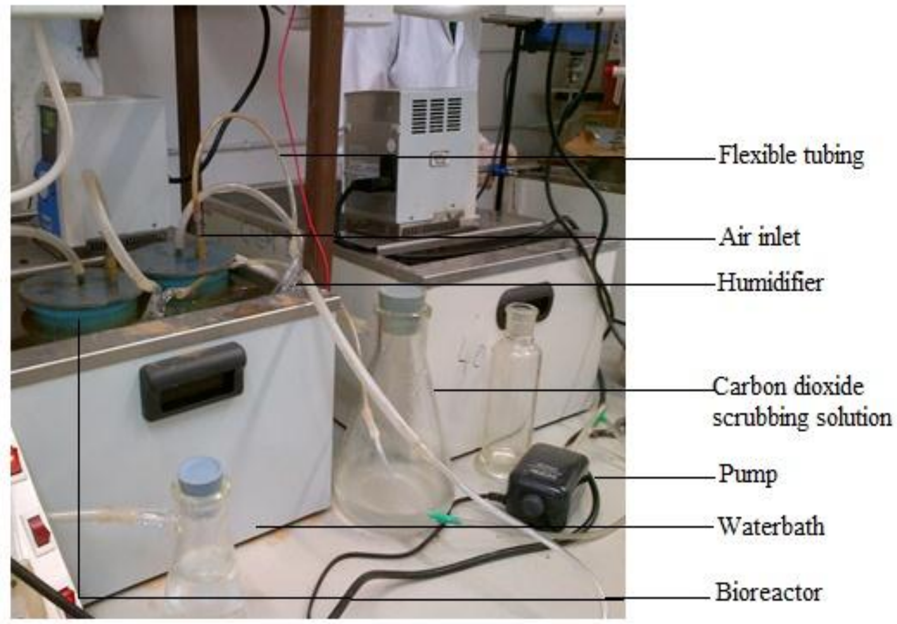

Plate 7-1: *Experimental setup*

7.1.4 Experimental procedure

This experiment was carried out in triplicate over a 45 day period.

7.1.4.1 Sample preparation

Soil and pith/PMS_{C} (3:1) were weighed and mixed together in the ratios listed in Table 7-1 on a dry basis. A handful of inoculum was added to the mixture to provide the initial microbial activity to facilitate composting. The bioreactors were filled to approximately 75% level with the test mixtures to ensure that there was sufficient headspace for manual shaking. The moisture was adjusted to approximately 50% using distilled water. Ammonium chloride was added to obtain a C/N ratio of between 10 and 40. Table 7-1 gives the contents of each reactor.

Table 7-1: *The sample contents of each bioreactor on a dry mass ratio (n = 3)*

	Quantity of organic material	**Quantity of untreated soil**
R1	4.5% pith/PMS (1:3)	95.5%
R2	9% pith/PMS (1:3)	91%
R3	18% pith/PMS (1:3)	82%
R4	Control (0%)	100%
R5	4.5% PMS	95.5%

*Untreated soil samples obtained from Farm C (Section 6.1.2)

7.1.4.2 Start-up procedure

Aeration was initiated such that the air flow rates were sufficiently high enough to ensure that the oxygen levels did not drop below 6% in the exhaust gas.

7.1.4.3 Operating procedure

The temperature was maintained at 58±2°C. The CO_2 and the O_2 concentrations in the outgoing air were recorded daily. Vessels were shaken weekly to prevent excessive channelling and for even moisture distribution. In the event of excessive moisture retention, air flow was increased. In the event of drying, additional moisture was provided. This was recognised by visual inspection. If adjustments were made, the process was monitored closely for the 72 hours that followed. At the weekly shakings and at the end of the test period, all visual observations with respect to colour, moisture content, fungal development, smell of the exhaust air and sample disintegration were recorded.

7.1.5 Analytical analysis

The CO_2 amount in the outgoing air was determined by the difference, in millilitres of titrant, between the test substance and blank $Ba(OH)_2$ traps. The titration was performed using 0.05 N HCl. When CO_2 enters the absorber bottles, it reacts as follows:

$\mathrm{Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O}\ldots$ (Equation 7.1)

The $BaCO_3$ is insoluble and precipitates. The amount of $Ba(OH)_2$ remaining in the solution was determined using end point titration with HCl using phenolphthalein as an indicator according to the equation: $\mathrm{Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O}\ldots$ (Equation 7.2)

Using Equations 7.1 and 7.2, the number of mmoles of CO_2 produced was calculated by the equation:

$\mathrm{mmoles\ of\ CO_2 = mmoles\ of\ Ba(OH)_2\ at\ start} - \frac{\mathrm{mmoles\ HCl}}{2}\ldots$ (Equation 7.3)

The biodegradation of the mixtures were calculated by:

$\%\ \mathrm{biodegradation} = \frac{\mathrm{mean\ C_g(test) - mean\ C_g(blank)}}{\mathrm{C_i}} \times 100\ldots$ (Equation 7.4)

Where: C_g = amount of gaseous carbon produced (g)

C_i = amount of carbon in test compound added (g)

At the end of the experiment, samples were removed from the bioreactors and sent to the Soil Fertility and Analytical Services Section of the KwaZulu-Natal Department of Agriculture and Environmental Affairs for a full analysis. This included the extractable P, K, Ca, Mg, Zn, Mn and Cu, acid saturation, effective cation exchange capacity, pH, soil organic carbon and total carbon and nitrogen as discussed in Chapter Six.

7.1.6 Statistical analysis

The standard error of the percentage of biodegradation was calculated by:

$$s_e = \sqrt{\frac{s_{test}^2}{n_1} + \frac{s_{blank}^2}{n_2}} \times \frac{100}{C_i} \ldots \text{ (Equation 7.5)}$$

Where: n_1 = number of replicate tests

n_2 = number of control digesters

s = standard deviation of the total gaseous carbon produced

The 95% confidence limits were calculated by:

$$95\%\ \mathrm{CL} = \%\ \mathrm{biodegradation} \pm (\mathrm{t} \times \mathrm{s_e}) \ldots \text{ (Equation 7.6)}$$

Where: t = t-distribution value for 95% probability with n = 4

7.2 Results and discussion

7.2.1 Introduction

The results obtained using the selected test methods are discussed below. Raw data obtained and calculations are reported in Appendix F.

7.2.2 Production of CO_2

CO_2 production was recorded daily. From the trends reported in Figure 7-2, it was noted that the CO_2 production by the 4.5% PMS in soil (R5) was comparable with the production by 4.5% pith/PMS_C (3:1) in soil (R1). All three replicates indicated that a larger quantity of pith/PMS_C (3:1) in soil produces CO_2 at a slower rate. Rather than applying a larger amount of pith/PMS_C (3:1) at once, perhaps frequent applications would be more beneficial.

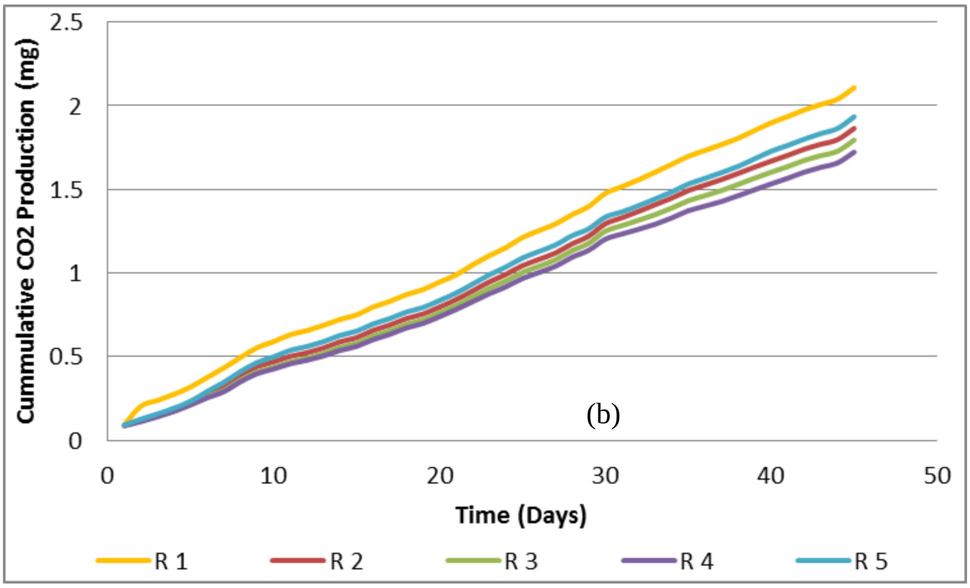

Figure 7-2: *Cumulative CO_2 production over 45 days (n = 3)*

Although replicate 1 showed the same trend, there was a difference between each reactors CO_2 production rates as well as many fluctuations. Comparing the three replicates for each reactor, it was evident that there was not a constant increase in CO_2. A possible reason for this could be due to the fluctuations in air flow rate.

Figure 7-3 displays the fluctuations in air flow rate during the 45 day experimental investigation.

The black dashed line represents the set point (SP) of the air flow rate at 0.25 mL/s. This SP was chosen based on the fact that at this flow rate the O_2 in the off gases were within the 6-18% limit. Maintaining the flow rate at 0.25±0.01 mL/s ensured a steady O_2 level of 16-17% in the off gases as monitored by an oxygen detector. Although the ideal situation would have been to maintain the air flow rate at 0.25 mL/s, this proved difficult to achieve. The method of calculating the flow rate was by using a soap bubble flow meter, which was basic and resulted in a large degree of inaccuracy. This explains the majority of the fluctuations from the SP. To compensate for these variations, multiple readings using the soap bubble flow meter were taken and averages used (n = 3).

The variations and fluctuations in the air flow rate (Figure 7-3) affected the O_2 levels in the off gases, hence probably the microbiological activity.

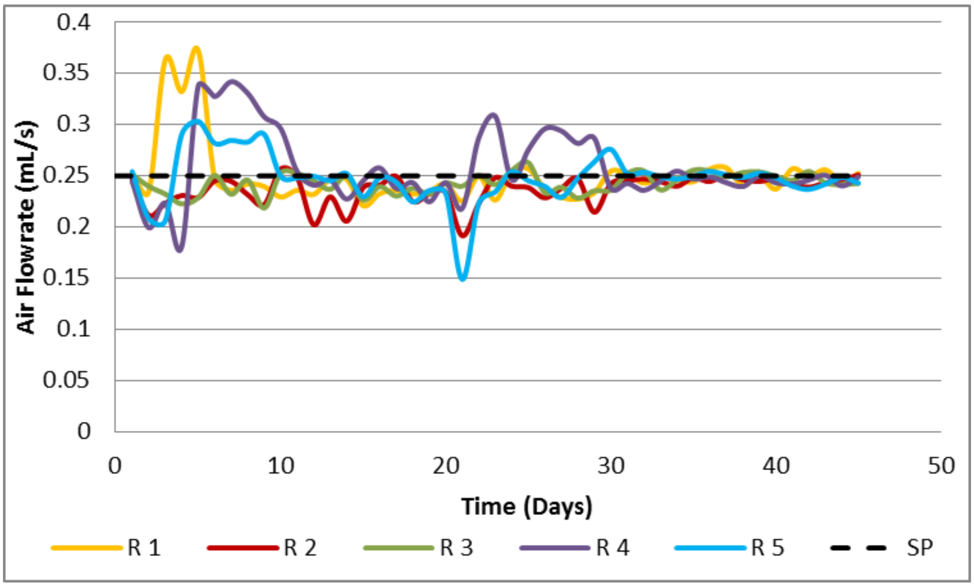

Figure 7-3: *Oscillations observed in air flow rate over 45 days in reactors R1-R5 (n = 3)*

7.2.3 Biodegradation and microbial activity

Over the 45 day period, fungal growth was evident (Plate 7-2). A thick white coating of fungus appeared on the surface of the pith/PMS-soil mixture in each reactor. This was observed to occur to a greater degree in reactors R1 and R5.

Plate 7-2: *Increase in fungal growth over 45 days*

The fact that R1 produced the highest amount of CO_2 over the duration of the experiment suggested that most activity was present in this reactor. This was validated as given in Table 7-2. Reactor R1 had the highest degradation rate, closely followed by reactor R5. The deviations, however, in these two reactors were high and therefore further statistical analysis was required. Aside from this, however, the biodegradation rates of the pith/PMS_C (3:1) in each reactor were extremely low, almost negligible. It was therefore imperative that a statistical analysis be completed to test the validity of these results and the method as a whole. This will be discussed later.

Table 7-2: *Rate of biodegradation of PMS in soil in each reactor (n = 3)*

Reactor	**Average**	**Standard**	**95% Confidence Limits**	
	Biodegradation (%)	**Deviation**	**Upper**	**Lower**
R1	2.73	0.90	2.78	2.68
R2	0.53	0.18	0.64	0.42
R3	0.09	0.09	0.17	0.01
R5	1.75	0.69	1.85	1.64

7.2.4 Effect on soil properties

Although it was found that there was almost negligible degradation in soil, the soil samples in each reactor needed to be analysed for even the slightest change in properties

Analysing the differences in density between each reactor in Table 7-3, and taking into account the confidence intervals on each value, it can be seen that there is negligible difference between the treated soils (R1-R3 and R5) and the control (R4).

There was no increase in exchange acidity that was worth noting however there was an increase in the CEC in R1-R3 and R5. This would indicate an increase in the soils ability to hold and exchange cations (Hazelton and Murphy, 2007). However, converting the CEC units to cmol/kg (using sample densities) and comparing with Table 2-2 (Chapter 2), these samples actually had a very low CEC as all mean values were less than 6 cmol/kg. A low CEC means the soil has a low resistance to change in soil chemistry that is caused by land use. Reactors R1-R3, which contained varying ratios of pith proved to have a greater cation exchange capacity than the reactor, R5, containing pure PMS in soil. The acidic cations are H^+ and Al^{3+} and are represented by the exchange acidity, which were relatively constant in between all reactors. The more acidic a soil is the lower the pH, and the closer the acidity number will be to the CEC number, which was not observed.

Hazelton and Murphy (2007) suggest that proportions of the various cations expressed as a percentage of CEC are more relevant to plant growth performance than the actual levels. Table 2-3 (Chapter 2) gives the desirable proportions of CEC of cations for most plants. Using the results from Table 7-3 and 7-4 to determine the proportion of CEC of calcium, magnesium and potassium, it was found that only potassium was within the range of 1 to 5 % of CEC in each reactor. Calcium was found to range between 39 and 41% of CEC in each reactor, and magnesium ranged between 6.5 to 8.5% of CEC. However, each reactor contained calcium, magnesium and potassium in proportions that deviated only slightly from each other and the control reactor, therefore showing no improvement in CEC.

The pH of all the reactors, including the control was acidic. Considering the alkaline nature of the pith/PMS_C (3:1) an increase was expected, however all the reactors were below the desired pH range of 6.5-7.5 for optimum microbial activity (See Section 2.4.3.1).

Table 7-3: *Post experiment soil analysis in each reactor (n = 3)*

Reactor	Sample Density (g/mL)	Exchange Acidity (cmol/L)	CEC (cmol/L)	pH
R1	1.24 ± 0.06	0.06 ± 0.02	5.56 ± 4.52	5.3 ± 0.41
R 2	1.24 ± 0.02	0.06 ± 0.02	4.68 ± 3.81	5.92 ± 0.07
R 3	1.13 ± 0.03	0.04 ± 0.01	5.03 ± 4.09	6.05 ± 0.05
R 4	1.30 ± 0.05	0.04 ± 0.01	4.11 ± 3.35	5.62 ± 0.05
R 5	1.26 ± 0.09	0.04 ± 0.01	4.32 ± 3.52	6.1 ± 0.24

With regard to the elemental analysis, no conclusions could be drawn. Looking at the upper limits for Cu, the control (R4) contained a higher quantity than the rest of the treated samples. Cu, as explained in Chapter Seven is present in higher quantities in the pith/PMS$_C$ resulting from dyes, inks and pigments. Hence the samples treated with pith/PMS$_C$ (3:1) were expected to contain a greater quantity than the control. The control contained the least amount of Ca. R1 which contained 4.5% pith/PMS$_C$ (3:1) in soil (the least amount of pith/PMS$_C$ (3:1) contained the highest Ca concentration. As the application ratio increased, the Ca quantity decreased. However, R5, which contained pure PMS$_C$ in soil, contained 842.64 g/mL (upper limit) of Ca which was the third highest.

Table 7-4: *Post experiment elemental analysis of soils in each reactor (n = 3)*

		R 1	R 2	R 3	R 4	R 5
P	**(mg/L)**	23.00± 3.46	29.50± 4.03	28.50± 4.03	29.50± 2.88	24.50± 5.18
K	**(mg/L)**	95.50±2.88	86.00± 12.67	73.50± 0.58	78.00± 9.22	65.50± 8.64
Ca	**(mg/L)**	864.00± 67.96	762.50± 154.93	790.50± 37.44	642.50± 74.30	678.50± 164.14
Mg	**(mg/L)**	115.00± 29.95	73.00± 24.19	103.50± 2.88	81.50± 7.49	88.50± 13.25
Zn	**(mg/L)**	2.05± 0.06	1.70± 0.12	3.05± 0.75	1.85± 0.75	1.60± 0.01
Mn	**(mg/L)**	5.00± 0.01	26.00± 25.34	31.50± 25.92	32.00± 3.46	47.00± 4.61
Cu	**(mg/L)**	2.85± 1.09	2.10± 0.12	2.45± 0.06	8.75± 3.63	5.45±4.67
SOC	**(%)**	0.95± 0.52	0.50± 0.03	1.05± 0.21	0.75± 0.35	0.50±0.02
C/N		8.96± 2.09	8.26± 0.09	8.17± 0.19	8.13± 2.16	6.44±2.18

7.2.5 Statistical analysis

With the use of averages, standard deviations and 95% confidence limits, the above results were tested for validity. The standard test method adopted to monitor the CO_2 production was modified which could have affected the reported results. Figure 7-4 plots the average CO_2 produced by R1-5 and the variances observed in each reactor (n = 3). It can be seen that the average CO_2 produced in R1-5 was 2.11 mg, 1.87 mg, 1.80 mg, 1.72 mg and 1.93 mg, respectively. Furthermore, the large variances during the three replicates were plotted using error bars. These large variances show that the results obtained were not significant.

Due to the large variations in CO_2 produced, an ANOVA table was constructed (see Appendix F, Table F-6). The use of an ANOVA table meant that a null hypothesis should be used. This hypothesis (H_0) was that the change in application ratio of pith/PMS_C (3:1) to soil would not affect the amount of CO_2 produced. The ANOVA table was extremely useful in showing that the results obtained from this method were invalid. Because F was calculated as 0.25, which was less than the critical F of 3.48, H_o, was accepted. This was not what the standard method was aimed at proving hence the results obtained were rendered invalid. This was further justified by the extremely low biodegradation rates of the pith/PMS_C (3:1) in the soil as well as the lack of a trend found from analysing the samples after three replicates. The results obtained from this standard method were therefore inconclusive. Perhaps the modifications made to this method were inappropriate. The best way to predict the benefits of applying pith/PMS_C to soil in an accelerated period would be by pot experiments.

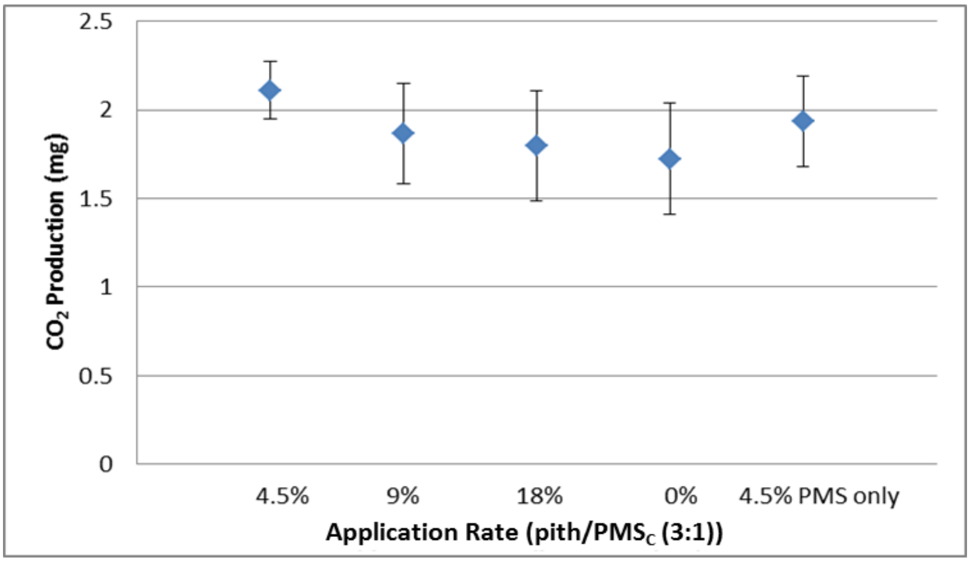

Figure 7-4: *Average CO_2 production in each reactor over the 45 day duration (n = 3)*

7.3 Conclusions

The results produced upon analysis of samples of each reactor showed that there was no significant trend or comparison between the control and the reactors which contained the organic material. Each reactor contained calcium, magnesium and potassium in proportions that deviated only slightly from each other and the control reactor; therefore there was no improvement in CEC. Samples showed no significant change in densities or in elemental concentrations.

It can be concluded that the results obtained from this method were insignificant as proven statistically by the use of the ANOVA table. This was further justified by the extremely low biodegradation rates of the pith/PMS_C (3:1) in the soil as well as the lack of a trend found from analysing the samples after the 45 days period. The results obtained from this standard method were therefore inconclusive. Perhaps the modifications made to this method were inappropriate.

CHAPTER EIGHT

Final conclusions and recommendations

8.1 Conclusions

The characterisation of the waste samples assisted in understanding the composition of each of the mill PMSsamples, as well as the benefits and the shortcoming of its application to land and composting. For instance, it was observed that the PMS_B and the PMS_C exceeded the desirable moisture range for composting. The composting material was found to have a slow degradation at the beginning. One reason for this may have been inhibited microbial activity, due topores being filled with moisture thereby limiting the air flow. The pH and EC were found to be in accordance with the correlation proposed by Robbins (1993), which suggested an inverse relationship between pH and EC. It can therefore be concluded that there exists a relationship between the pH and EC.All three samples had been classified as saline in nature, using the soil classification guidelines thus verifying the relationship discussed in Section 2.3.1.2.

It was observed that the composting materials in both the small and large scale composting experiments did not rapidly heat up at the beginning. It was concluded that the moisture content, air availability and the volume of the composting material were the key parameters responsible for this. As discussed above, the moisture may have inhibited the microbial activity. The turning of the composting material in the first week was not a good decision. This probably disrupted the microbial activity and did not allow the contents to heat up to a peak temperature that was as high as expected from theory. The bags were already of a porous nature and sufficient air should have been allowed in, but diffusion may have been too slow. The bags were not filled to capacity.Thermophilic phase was not achieved rapidly, and as a result there was a reduced heat build-up. The decrease in copper and zinc concentrations were due to physico-chemical methods during the composting process where the heavy metals are decreased during the thermophilic phase. The oxidation process and the formation of organo-metallic complexes, could reduce the soluble contents of metals (Singh and Kalamdhad, 2012). The decrease in heavy metal concetration could also be due to a concentrating effect as bulk mass was reduced during the composting process (Norris and Titshall, 2008).

The direct land application of pith/PMS_C (3:1) was found to be beneficial to soil fertility. It was concluded that more applications of this will be beneficial to the soil and crops in the long run and N immobilisation can be prevented by addition of nitrogen fertilizers. Even though the CEC was very low in the soils, there was an increase after the pith/PMS_C (3:1) applications, which supported theory. It was concluded that the Farm C (2009) sample was actually an untreated soil sample becausemajority of theresults correlated with that of untreated soil.

It can be concluded that the results obtained from the laboratory scale method were insignificant as proven statistically by the use of the ANOVA table. This was further justified by the extremely low biodegradation rates of the pith/PMS_C (3:1) in the soil as well as the lack of any trend found inanalysing the samples after the 45 day period. The results obtained from this standard method were therefore inconclusive.

It was therefore concluded that the hypothesis of the study was correct as the pith/PMS_C was degraded by composting into a stable, environmentally friendly end product. Based on the direct land application study, the second hypothesis was also met hence the addition of pith/PMS_C to soil as an amendment is beneficial to the soil.

8.2 Recommendations

- The EC method used was only an approximation. The saturated paste method should be used in future work. This method involves the diluting of the compost with distilled water to achieve a compost-water paste. The sample is allowed to sit for 4 hours. The paste is then filtered using a highly retentive filter and the filtrate is measured for EC.

- If the standard method, D5338-98$^{\epsilon 1}$ is to be used again, the use of a gas chromatograph should be used as opposed to daily titrations, for accuracy. A problem experienced during the procedure was the fluctuating air flow rate. The use of the soap bubble flow meter to record this flow did not suffice. Better flow monitoring equipment shouldto be used for this purpose.

- During a composting trial, the composting material should not be turned for aeration in the first week or until the material has heated up. This causes the material to lose heat and disturbs the microbial activity thus prolonging the time taken to reach thermophilic conditions.

- If natural ingredients such as green and brown leaves are to be used during composting, it is recommended that they are tested for C and N before use. The production of ammonia from the use of nitrogenous compounds and the effect on final pH should also be reviewed.

- The ash content would not be beneficial in understanding the effect it has on the PMS therefore, further analysis of the ash is recommended to determine the exact constituents.

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APPENDIX A: SAMPLE CALCULATIONS

*All calculations for A1-A3 are based on data from Mill C

A1: Calculation of moisture content

Mass of beaker = 97.7 g

Mass of beaker + Wet sludge sample = 179.9 g

Mass of beaker + Dried sludge sample = 123.6 g

Thus mass of dried sludge = 123.6 g – 97.7 g = 25.9 g

Using Equation 3.1:

$$\% \text{ Moisture} = \frac{(179.9 - 97.7) - (123.6 - 97.7)}{179.9 - 97.7} \times 100 = 68.49\ \%$$

A2: ICP analysis concentration calculation

Data obtained from the ICP program were in units of ppm (mg/L). For a better understanding, conversions to mg/kg were necessary.

Mass of dried sludge = 10 g

Volume of H_2O = 1L(amount used in dilution of sludge samples)

Mill C Dry:

$$\text{Ca concentration} = \frac{1022\text{mg}}{\text{L}} \times \frac{1\text{L}}{10\text{g}} \times \frac{1000\text{g}}{\text{kg}} = 102200\ \frac{\text{mg}}{\text{kg dry sample}}$$

A3: Calculation of % ash

Table A-2: *Ash test results*

Run	Moisture (%)	Wet mass (g)	Dry mass (g)	Crucible mass (g)	Crucible + Ash (g)
1	1.6	3.877	3.814	29.398	30.467

The ash content was calculated using the Equation 3.4:

A = 30.467-29.398 = 1.069 g

B = 3.814 g

$$\% \text{ Ash} = \frac{1.069 \times 100}{3.814} = 28.03\ \%$$

A4: Calculating the quantity of urea required for composting

*Calculation based on data for large scale composting, Trial 2

Mass of wet pith = 201.6 kg

Ratio of pith: sludge = 3 (Mill ratio)

Therefore: Mass of sludge = $\frac{201.6}{3} = 67.2$ kg

Mass of pith + PMS = 201.6 + 67.2 = 268.8 kg

C/N ratio of mixed PMS = 51.79

Carbon content in mixed PMS = 29%

50 kg of urea contains 46% N = $0.46 \times 50 = 23$ kg of N/50 kg of urea

In 268.8 kg of PMS, C content = $0.29 \times 268.8 = 77.95$ kg

For optimum composting, a C/N ratio of 30 is required. To achieve this, the following amount of N is required:

$$\frac{\text{C}}{\text{N}} = \frac{0.29 \times 268.8}{\text{N}} = 30$$

$$\text{N} = \frac{0.29 \times 268.8}{30} = 2.60 \text{ kg}$$

Currently the PMS contains the following amount of N:

$$\frac{\text{C}}{\text{N}} = 51.79$$

$$\frac{\mathrm{C}}{\mathrm{N}} = \frac{0.29 \times 268.8}{\mathrm{N}} = 51.79$$

$\mathrm{N} = 1.51\ \mathrm{kg}$

Hence:

$2.60 - 1.51 = 1.09$ kg of N needs to be added.

50 kg of urea contains 46% N = $0.46 \times 50 = 23$ kg of N/50 kg of urea

The quantity of urea to be added is therefore:

$$\mathrm{Urea} = \frac{1.09}{0.46} = 2.37\mathrm{kg}$$

A5: CO_2 production calculation

*CO_2 production calculation for Phase 1, Day 1, Reactor 1

Table A-3: *Useful data*

Useful Data		
Barium Hydroxide		
Density (ρ)	0.003743	mg/mL
Molecular Weight	0.000189	mg/mmol
HCl		
Density (ρ)	0.00148	mg/mL
Molecular Weight (MW)	3.65E-05	mg/mmol
CO_2		
Molecular Weight (MW)	4.4E-05	mg/mmol

Quantity of CO_2 scrubbing solution, $Ba(OH)_2$ (V) = 250 mL

Mass of $Ba(OH)_2$ (m) = ρV = $0.003743\ {}^{\mathrm{mg}}/_{\mathrm{mL}} \times 250\mathrm{mL} = 0.936\ \mathrm{mg}$

Number of moles of $Ba(OH)_2$ (n) = $\frac{\mathrm{m}}{\mathrm{MW}} = \frac{0.936\mathrm{mg}}{0.000189\frac{\mathrm{mg}}{\mathrm{mmol}}} = 4952.38\ \mathrm{mmol}$

V (HCl) added during titration = 235.60 mL m (HCl) = $\rho V = 0.00148\ ^{\mathrm{mg}}/_{\mathrm{mL}} \times 235.60\mathrm{mL} = 0.35\ \mathrm{mg}$

n (HCl) = $\frac{\mathrm{m}}{\mathrm{MW}} = \frac{0.35\mathrm{mg}}{3.65\times10^{-5}\frac{\mathrm{mg}}{\mathrm{mmol}}} = 9589.04\ \mathrm{mmol}$

n CO_2 produced = n $(Ba(OH)_2)$ - $\frac{\mathrm{n\ (HCl)}}{2}$ = 4952.38$-\frac{9589.04}{2}$ =157.86 mmol

m CO_2 produced = n × MW = 157.86× 4.5 × 10^{-5} = 0.007 mg

A6: Calculation of the % biodegradation of PMS in soil

*Calculation based on results for Reactor 1, Phase 1

Total C produced by control = 1.16 mg

Total C produced by Reactor 1 = 1.70 mg

Initial C content in Reactor 1

= $(\%\ \mathrm{C\ in\ pith} \times \mathrm{mass\ of\ pith}) + (\%\ \mathrm{C\ in\ effluent\ sludge} \times \mathrm{mass\ of\ effluent\ sludge})$

= $(0.365 \times 44.71) + (0.314 \times 14.9)$

= 21.0 g

Initial C content in Reactor 4 (Control) = $\%\ \mathrm{C\ in\ soil} \times \mathrm{mass\ of\ soil} = 0.005 \times 1265.10 = 6.62\ \mathrm{g}$

% biodegradation = $\frac{\mathrm{C\ produced\ by\ Reactor\ 1 - C\ produced\ by\ Control}}{\mathrm{Initial\ C\ in\ Reactor\ 1}} \times 100 = \frac{1.70-1.16}{21.0} = 2.56\%$

A7: Calculation of maximum sludge loading on soil

Concentration of Cu in dry Mill C sample of PMS = 251 mg Cu/kg dry PMS

In units of kg: 251 mg × $\frac{1\ \mathrm{kg}}{1\ 000\ 000\ \mathrm{mg}} = 0.000251\ \mathrm{kg}$

Maximum allowable Cu that can be applied = 75 kg/ha/yr

$$75\ ^{\mathrm{kg}}/_{\mathrm{ha}} \times \frac{\mathrm{kg\ sludge}}{0.000251\ \mathrm{kg\ Cu}} = 298329.40\ ^{\mathrm{kg\ sludge}}/_{\mathrm{ha}} = 298.33\ \mathrm{t/ha}$$

APPENDIX B: CHAPTER THREE RAW DATA

Table B1: *Moisture content of PMS*

Mill	**Sample**	**Wet Sample (g)**	**Dry Sample (g)**	**Moisture Content (%)**	**Average**
A	1	204.7	138.8	61.25	
	2	210.5	142.6	60.09	
	3	190.5	130.8	62.32	61.22 ± 1.11
B	1	159.6	116.4	66.46	
	2	162.1	119.4	67.24	
	3	163.6	116.8	67.92	67.21 ± 0.73
C	1	179.9	123.6	68.49	
	2	180.2	122.5	68.94	
	3	185.3	127.6	70.28	69.24 ± 0.93

Table B2: *pH analysis of PMS*

Mill	**Sample 1**	**Sample 2**	**Sample 3**	**Average**
A	8.57	8.95	9.19	8.90 ± 0.31
B	8.19	8.32	8.4	8.30 ± 0.11
C	7.4	9.38	7.93	8.24 ± 1.03

Table B3: *EC analysis of PMS*

Mill	**Sample 1 (dS/m)**	**Sample 2 (dS/m)**	**Sample 3 (dS/m)**	**Average (dS/m)**
A	0.25	0.24	0.23	0.24 ± 0.01
B	0.5	0.15	0.86	0.50 ± 0.36
C	0.61	0.22	0.18	0.34 ± 0.34

Table B4: *Ash content analysis of PMS*

Mill	Sample	Dry Mass (g)	Ash (g)	Ash (%)	Average (%)
A	1	3.81	1.07	28.03	26.56 ± 1.47
	2	3.62	0.91	25.09	
	3	3.61	0.96	26.55	
B	1	2.00	0.46	23.06	22.75 ± 0.30
	2	1.73	0.39	22.45	
	3	2.01	0.46	22.74	
C	1	2.00	0.80	39.84	39.82 ± 0.03
	2	4.72	1.88	39.79	
	3	2.31	0.92	39.83	

Table B5: *ICP analysis on pure pith (Mill C)*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)
Ca	42.14	43.24	42.45	42.61 ± 1.33
Cu	0.24	0.24	0.24	0.24 ± 0.40
Cr	0.074	0.07	0.072	0.07 ± 1.88
Fe	7.30	7.48	7.34	7.37 ± 1.26
P	1.03	1.02	1.04	1.03 ± 1.06
K	2.21	2.76	2.29	2.42 ± 12.21
Mg	4.12	4.10	4.10	4.11 ± 0.26
Zn	0.43	0.43	0.43	0.43 ± 0.17
Mn	n.d	n.d	n.d	n.d
Na	23.15	22.84	23.12	23.04 ± 0.73

Table B6: *ICP analysis on pure effluent sludge (PMS$_C$)*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)
Ca	8.20	8.11	8.07	8.13 ± 0.86
Cu	0.15	0.15	0.15	0.15 ± 0.45
Cr	0.13	0.13	0.13	0.13 ± 0.71
Fe	31.59	31.21	31.11	31.30 ± 0.81
P	1.73	1.74	1.74	1.74 ± 0.34
K	1.68	1.54	1.54	1.59 ± 5.00
Mg	2.20	2.19	2.20	2.20 ± 0.31
Zn	0.22	0.22	0.22	0.22 ± 0.39
Mn	n.d	n.d	n.d	n.d
Na	8.89	8.31	8.32	8.51 ± 3.90

Table B-7: *ICP analysis of a pith/PMS$_C$ (3:1) on a dry basis*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)	Average Concentration (mg/kg)
Ca	1019.99	1021.52	1025.11	1022	102200 ± 2.63
Cu	2.49	2.54	2.51	2.51	251.40 ± 0.03
Cr	1.56	1.53	1.53	1.54	154 ± 0.01
Fe	171.84	172.20	172.98	172.3	17230 ± 0.58
P	19.38	19.00	18.74	19.04	1904 ± 0.32
K	17.93	18.42	18.13	18.16	1816 ± 0.25
Mg	62.95	63.08	63.40	63.14	6314 ± 0.23
Zn	2.11	2.09	2.10	2.10	209.60 ± 0.01
Mn	3.86	3.93	3.91	3.90	389.90 ± 0.04
Na	56.98	55.64	54.49	55.70	5570 ± 1.25

Table B-8: *ICP analysis of a* PMS_B *on a dry basis*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)	Average Concentration (mg/kg)
Ca	511.72	509.55	513.98	511.70	51170 ± 0.44
Cu	3.23	3.16	3.19	3.20	319.90 ± 0.97
Cr	0.85	0.86	0.87	0.86	85.70 ± 1.23
Fe	62.79	61.65	62.11	62.18	6218 ± 0.92
P	10.33	10.65	10.94	10.64	1064 ± 2.83
K	6.16	6.05	6.13	6.12	611.50 ± 0.92
Mg	47.54	46.60	47.09	47.08	4877 ± 0.99
Zn	2.07	2.04	2.06	2.06	205.80 ± 1.28
Mn	1.90	1.86	1.87	1.87	187.40 ± 1.07
Na	37.87	38.69	39.94	38.83	3883 ± 2.68

Table B-9: *ICP analysis of a* PMS_A *sample on a dry basis*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)	Average Concentration (mg/kg)
Ca	1141.19	1137.08	1138.30	1139	113900 ± 2.11
Cu	1.73	1.72	1.71	1.72	172 ± 0.01
Cr	0.40	0.40	0.39	0.40	39.70 ± 0.003
Fe	29.56	30.45	30.02	30.01	3001 ± 0.44
P	9.45	9.44	9.28	9.39	938.70 ± 0.10
K	4.56	4.72	4.69	4.66	465.50 ± 0.09
Mg	36.36	37.43	37.14	36.97	3697 ± 0.55
Zn	1.90	1.90	1.88	1.89	189.30 ± 0.008
Mn	0.72	0.75	0.74	0.74	73.50 ± 0.01
Na	18.87	19.62	19.36	19.28	1928 ± 0.38

APPENDIX C: CHAPTER FOUR RAW DATA

Bag 1 (Effluent Sludge: Pith waste = 1:1)

Table C1: *Temperature measurements in Bag 1 over the duration of the small scale composting*

		Temperature (˚C)				
		T1	**T2**	**T3**	**Centre**	**Ambient**
Week 1	**Day 1**	25.50	26.50	25.50	27.00	27.00
	Day 3	24.70	25.00	24.30	25.50	22.80
	Day 6	25.10	25.20	24.10	25.60	25.50
Week 2	**Day 8**	25.90	26.00	24.80	25.80	26.50
	Day 10	24.80	25.80	24.10	25.60	25.00
	Day 13	31.80	32.10	28.30	32.60	31.40
Week 3	**Day 15**	33.60	32.90	29.20	32.70	27.90
	Day 17	35.50	36.20	32.50	36.40	28.20
	Day 20	36.30	36.90	33.50	36.80	29.40
Week 4	**Day 22**	35.90	36.30	33.10	36.40	28.10
	Day 24	35.70	36.40	33.20	36.50	30.20
	Day 27	35.30	36.20	33.30	36.50	20.90
Week 5	**Day 29**	32.10	34.90	30.70	35.20	28.50
	Day 31	32.30	34.60	31.10	34.90	29.80
	Day 34	32.00	33.80	31.00	34.10	27.60
Week 6	**Day 36**	28.70	29.60	25.50	29.40	25.70
	Day 38	25.10	26.70	23.40	26.20	28.90
	Day 41	24.60	24.30	24.40	24.40	26.50
Week 7	**Day 43**	21.30	21.00	21.20	20.90	20.60
	Day 45	16.30	17.00	17.70	16.80	17.90
	Day 48	20.90	20.90	21.20	21.10	19.10

Table C1: *Temperature measurements in Bag 1 over the duration of the small scale composting (continued)*

		Temperature (˚C)				
		T1	**T2**	**T3**	**Centre**	**Ambient**
Week 8	**Day 52**	19.80	19.80	20.30	20.20	22.50
	Day 55	20.30	20.40	20.20	20.50	23.00
Week 9	**Day 57**	20.50	20.60	20.50	21.00	24.50
	Day 59	20.50	20.60	20.40	20.90	25.00
	Day 62	20.60	20.60	20.30	21.00	24.00
Week 10	**Day 66**	20.70	20.70	20.40	21.20	24.30
	Day 69	20.90	21.00	20.80	21.10	25.50
Week 11	**Day 73**	21.00	21.00	21.00	21.10	19.00
	Day 76	20.90	21.00	21.00	21.00	23.00
Week 12	**Day 80**	21.00	21.00	21.00	21.00	22.00

Table C2: *pH changes in Bag 1 over the duration of the small scale composting*

	Sample 1	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
Week 1	9.67	9.70	9.65		
	9.65	9.69	9.67		
	9.63	9.64	9.64		
	9.63	9.60	9.62		
	9.65	9.66	9.65	9.65	0.01
Week 2	9.44	9.48	9.46		
	9.42	9.47	9.45		
	9.43	9.46	9.44		
	9.43	9.46	9.44		

Table C2: *pH changes in Bag 1 over the duration of the small scale composting (continued)*

	Sample 1	Sample 2	Sample 3	Average	Standard Deviation
	9.43	9.47	9.45	9.45	0.02
Week 3	8.01	7.89	7.90		
	7.99	7.90	7.93		
	7.98	7.91	7.95		
	7.98	7.91	7.96		
	7.99	7.90	7.95	7.94	0.04
Week 4	7.45	7.47	7.46		
	7.46	7.48	7.47		
	7.47	7.48	7.47		
	7.47	7.46	7.45		
	7.46	7.47	7.45	7.46	0.01
Week 5	6.33	6.31	6.32		
	6.34	6.32	6.33		
	6.35	6.29	6.31		
	6.36	6.32	6.35		
	6.35	6.31	6.33	6.33	0.02
Week 6	6.94	6.93	6.93		
	6.95	6.92	6.94		
	6.93	6.91	6.92		
	6.92	6.91	6.91		
	6.94	6.92	6.93	6.93	0.01
Week 7	7.02	7.03	7.01		
	7.04	7.05	7.03		
	7.03	7.04	7.03		
	7.06	7.02	7.05		
	7.04	7.04	7.03	7.03	$4.00\ x10^{-3}$

Table C2: *pH changes in Bag 1 over the duration of the small scale composting (continued)*

	Sample 1	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
Week 8	7.59	7.43	7.51		
	7.56	7.42	7.48		
	7.57	7.41	7.55		
	7.57	7.41	7.48		
	7.57	7.42	7.45	7.49	0.08
Week 9	7.06	7.04	7.05		
	7.05	7.02	7.03		
	7.07	6.98	7.01		
	7.03	7.03	7.02		
	7.06	6.99	7.02	7.03	0.02
Week 10	6.98	6.88	6.90		
	6.93	6.91	6.92		
	6.97	6.87	6.95		
	6.94	6.90	6.92		
	6.89	6.89	6.90	6.92	0.03
Week 11	6.81	6.84	6.82		
	6.79	6.85	6.81		
	6.82	6.83	6.82		
	6.81	6.80	6.81		
	6.80	6.81	6.82	6.82	0.01
Week 12	6.84	6.84	6.83		
	6.83	6.84	6.82		
	6.83	6.83	6.82		
	6.84	6.80	6.84		
	6.83	6.83	6.82	6.83	3.00×10^{-3}

Table C3: *Change in moisture in Bag 1 over the duration of the small scale composting*

Week	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)	Standard Deviation
1	67.61	68.13	67.88	67.88	0.27
2	75.00	74.60	74.80	74.80	0.21
3	70.00	70.00	69.70	69.90	0.18
4	68.42	68.42	68.40	68.42	0.02
5	69.57	71.05	70.30	70.31	0.75
6	67.00	61.10	64.04	64.05	2.96
7	55.56	60.18	57.90	57.88	2.32
8	51.52	53.96	52.74	52.74	1.22
9	53.94	52.61	53.20	53.25	0.67
10	55.42	56.13	55.73	55.76	0.36
11	53.33	52.94	53.16	53.15	0.20
12	47.47	54.15	51.02	50.88	3.35

Table C4: *ICP analysis on Bag 1 final compost mix of the small scale composting*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)	Standard Deviation
As	0.06	0.07	0.07	0.07	6.00×10^{-3}
Cd	0.10	0.10	0.10	0.10	2.00×10^{-3}
Cu	0.81	0.75	0.70	0.76	5.00×10^{-2}
Hg	0.10	0.09	0.08	0.09	0.01
Ni	b.d	b.d	b.d	b.d	-
Pb	0.25	0.25	0.25	0.25	3.00×10^{-3}
Se	b.d	b.d	b.d	b.d	-
Zn	0.83	0.81	0.79	0.81	0.02

Bag 2 (Effluent Sludge: Pith waste = 2:1)

Table C5: *Temperature measurements in Bag 2 over the duration of the small scale composting*

		Temperature (˚C)				
		T1	**T2**	**T3**	**Centre**	**Ambient**
Week 1	**Day 1**	26.00	26.00	25.00	26.50	27.00
	Day 3	24.60	25.20	24.60	24.90	22.80
	Day 6	24.60	25.00	24.10	25.40	25.50
Week 2	**Day 8**	24.60	24.70	23.90	24.30	26.50
	Day 10	22.30	22.50	22.20	22.40	25.00
	Day 13	30.20	30.40	29.30	29.90	31.40
Week 3	**Day 15**	30.80	30.50	29.20	30.70	27.90
	Day 17	32.60	32.90	31.50	33.20	28.20
	Day 20	33.70	34.60	32.40	34.80	29.40
Week 4	**Day 22**	34.90	35.70	32.80	35.80	28.10
	Day 24	35.10	35.20	31.60	35.90	30.20
	Day 27	33.50	33.50	30.20	32.60	20.90
Week 5	**Day 29**	33.60	32.50	29.90	32.70	28.50
	Day 31	32.10	33.70	29.60	33.50	29.80
	Day 34	30.10	33.80	31.00	34.10	27.60
Week 6	**Day 36**	27.30	27.80	26.40	26.90	25.70
	Day 38	25.10	25.60	24.80	25.70	28.90
	Day 41	24.10	24.80	24.50	24.60	26.50
Week 7	**Day 43**	20.60	21.30	21.80	20.80	20.60
	Day 45	16.60	17.30	17.90	17.30	17.90
	Day 48	20.70	21.30	21.60	21.30	19.10

Table C5: *Temperature measurements in Bag 2 over the duration of the small scale composting (continued)*

		Temperature (˚C)				
		T1	T2	T3	Centre	Ambient
Week 8	**Day 52**	20.50	20.50	20.70	20.50	22.50
	Day 55	20.60	20.60	19.90	20.70	23.00
Week 9	**Day 57**	20.40	20.60	20.00	20.60	24.50
	Day 59	20.30	20.50	19.80	20.50	25.00
	Day 62	19.90	20.30	20.00	20.40	24.00
Week 10	**Day 66**	19.60	19.80	19.50	20.00	24.30
	Day 69	19.00	19.00	19.00	20.00	25.50
Week 11	**Day 73**	19.00	20.00	18.90	20.20	19.00
	Day 76	19.00	19.10	19.00	19.20	23.00
Week 12	**Day 80**	19.00	19.00	19.00	19.00	22.00

Table C6: *pH changes in Bag 2 over the duration of the small scale composting*

	Sample 1	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
Week 1	9.68	9.80	9.70		
	9.69	9.78	9.72		
	9.69	9.71	9.70		
	9.69	9.71	9.71		
	9.69	9.75	9.73	9.72	0.04
Week 2	9.63	9.72	9.68		
	9.61	9.71	9.65		
	9.62	9.71	9.67		
	9.62	9.71	9.65		

Table C6: *pH changes in Bag 2 over the duration of the small scale composting(continued)*

	Sample 1	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
	9.62	9.71	9.68	9.67	0.05
Week 3	8.24	8.16	8.20		
	8.25	8.14	8.19		
	8.23	8.13	8.18		
	8.23	8.12	8.20		
	8.24	8.14	8.19	8.19	0.06
Week 4	7.33	7.45	7.40		
	7.34	7.44	7.38		
	7.32	7.44	7.38		
	7.32	7.44	7.40		
	7.33	7.44	7.41	7.39	0.10
Week 5	6.35	6.31	6.33		
	6.38	6.31	6.35		
	6.39	6.32	6.35		
	6.36	6.32	6.34		
	6.37	6.32	6.35	6.35	0.03
Week 6	6.74	6.68	6.71		
	6.70	6.69	6.69		
	6.76	6.73	6.75		
	6.77	6.75	6.72		
	6.74	6.79	6.75	6.74	0.01
Week 7	7.43	8.01	7.63		
	7.42	7.99	7.65		
	7.42	8.03	7.62		
	7.42	8.05	7.60		
	7.42	8.02	7.60	7.69	0.31

Table C6: *pH changes in Bag 2 over the duration of the small scale composting (continued)*

	Sample 1	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
Week 8	8.35	7.98	7.99		
	8.36	7.95	7.98		
	8.35	7.96	7.98		
	8.35	7.96	7.96		
	8.35	7.96	7.97	8.10	0.23
Week 9	7.42	7.29	7.35		
	7.40	7.31	7.35		
	7.39	7.35	7.37		
	7.39	7.34	7.36		
	7.38	7.34	7.36	7.36	0.04
Week 10	7.28	7.21	7.25		
	7.29	7.23	7.25		
	7.30	7.23	7.27		
	7.29	7.24	7.26		
	7.29	7.27	7.28	7.27	0.03
Week 11	6.81	6.80	6.80		
	6.87	6.87	6.85		
	6.88	6.86	6.85		
	6.80	6.85	6.82		
	6.88	6.86	6.84	6.85	0.01
Week 12	6.84	6.88	6.86		
	6.84	6.87	6.85		
	6.84	6.86	6.85		
	6.84	6.86	6.86		
	6.83	6.85	6.85	6.86	0.02

Table C7: *Change in moisture in Bag 2 over the duration of the small scale composting*

Week	**Sample 1 (%)**	**Sample 2 (%)**	**Sample 3 (%)**	**Average (%)**	**Standard Deviation**
1	67.86	68.32	68.12	68.10	0.24
2	71.20	69.10	70.19	70.17	1.06
3	71.10	71.50	71.30	71.30	0.21
4	70.37	68.97	69.65	69.67	0.71
5	68.09	67.65	67.91	67.89	0.23
6	58.82	57.14	58.01	57.99	0.85
7	62.69	63.24	62.95	62.96	0.28
8	57.54	55.21	56.40	56.39	1.17
9	55.36	56.27	55.80	55.81	0.46
10	57.36	57.25	57.36	57.33	0.07
11	57.56	56.95	56.25	56.92	0.66
12	49.21	51.26	50.21	50.23	1.03

Table C8: *ICP analysis on Bag 2 final compost mix of the small scale composting*

Element	**Sample 1 (mg/L)**	**Sample 2 (mg/L)**	**Sample 3 (mg/L)**	**Average Concentration (mg/L)**	**Standard Deviation**
As	0.05	0.06	0.05	0.05	8.29×10^{-3}
Cd	0.11	0.11	0.11	0.11	2.46×10^{-4}
Cu	0.38	0.37	0.37	0.38	5.49×10^{-3}
Hg	6.25×10^{-3}	2.69×10^{-3}	b.d	1.63×10^{-3}	5.24×10^{-3}
Ni	b.d	b.d	b.d	b.d	-
Pb	0.14	0.14	0.14	0.14	2.32×10^{-3}
Se	b.d	b.d	b.d	b.d	-
Zn	0.45	0.46	0.45	0.46	5.10×10^{-4}

Bag 3 (Effluent Sludge: Pith waste = 3:1)

Table C9: *Temperature measurements in Bag 3 over the duration of the small scale composting*

		Temperature (˚C)				
		T1	**T2**	**T3**	**Centre**	**Ambient**
Week 1	**Day 1**	25.00	25.50	25.00	27.00	27.00
	Day 3	23.70	24.50	23.70	25.00	22.80
	Day 6	25.50	25.80	25.20	26.10	25.50
Week 2	**Day 8**	26.40	26.80	24.30	26.20	26.50
	Day 10	23.50	23.90	22.50	23.90	25.00
	Day 13	29.80	30.10	26.80	29.10	31.40
Week 3	**Day 15**	30.00	30.00	26.90	30.20	27.90
	Day 17	31.60	31.80	27.50	31.50	28.20
	Day 20	33.20	34.10	29.50	34.10	29.40
Week 4	**Day 22**	33.80	34.50	29.20	34.10	28.10
	Day 24	35.20	36.40	29.60	36.20	30.20
	Day 27	35.60	36.40	30.10	36.20	20.90
Week 5	**Day 29**	35.80	34.80	29.10	32.70	28.50
	Day 31	34.90	35.70	28.60	35.90	29.80
	Day 34	33.10	35.20	29.50	35.80	27.60
Week 6	**Day 36**	29.50	30.10	27.30	29.90.	25.70
	Day 38	26.40	27.80	25.60	26.90	28.90
	Day 41	23.50	23.30	23.60	24.40	26.50
Week 7	**Day 43**	20.00	20.20	20.50	20.00	20.60
	Day 45	16.10	16.40	17.30	16.70	17.90
	Day 48	19.90	20.30	20.70	20.50	19.10

Table C9: *Temperature measurements in Bag 3 over the duration of the small scale composting (continued)*

		Temperature (˚C)				
		T1	**T2**	**T3**	**Centre**	**Ambient**
Week 8	**Day 52**	20.30	20.00	19.80	20.40	22.50
	Day 55	20.40	20.60	20.00	20.70	23.00
Week 9	**Day 57**	20.30	20.60	20.00	20.80	24.50
	Day 59	20.30	20.40	19.80	20.60	25.00
	Day 62	20.00	20.50	19.90	20.60	24.00
Week 10	**Day 66**	19.90	20.80	20.00	21.00	24.30
	Day 69	20.00	21.00	20.50	21.50	25.50
Week 11	**Day 73**	20.00	20.20	19.90	20.20	19.00
	Day 76	20.00	19.90	20.00	20.00	23.00
Week 12	**Day 80**	19.90	20.00	20.00	20.00	22.00

Table C10: *pH changes in Bag 3 over the duration of the small scale composting*

	Sample 1	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
Week 1	9.44	9.44	9.45		
	9.43	9.46	9.45		
	9.43	9.45	9.44		
	9.43	9.45	9.46		
	9.43	9.45	9.46	9.45	0.02
Week 2	9.63	9.62	9.61		
	9.62	9.6	9.62		
	9.62	9.61	9.62		
	9.62	9.61	9.61		
	9.62	9.61	9.61	9.62	0.01

Table C10: *pH changes in Bag 3 over the duration of the small scale composting (continued)*

	Sample 1	Sample 2	Sample 3	Average	Standard Deviation
Week 3	8.30	8.01	8.21		
	8.24	8.00	8.23		
	8.29	8.00	8.25		
	8.29	8.00	8.25		
	8.28	8.00	8.24	8.18	0.15
Week 4	7.33	7.23	7.28		
	7.32	7.22	7.29		
	7.30	7.21	7.27		
	7.33	7.21	7.29		
	7.32	7.22	7.28	7.28	0.10
Week 5	6.28	6.17	6.21		
	6.31	6.17	6.27		
	6.29	6.18	6.25		
	6.28	6.18	6.25		
	6.29	6.18	6.26	6.24	0.06
Week 6	6.35	6.68	6.54		
	6.34	6.69	6.55		
	6.38	6.67	6.57		
	6.37	6.67	6.56		
	6.36	6.68	6.6	6.54	0.17
Week 7	7.53	7.01	7.21		
	7.54	7.02	7.18		
	7.55	7.02	7.19		
	7.55	7.03	7.18		
	7.54	7.02	7.20	7.26	0.27
Week 8	7.62	7.35	7.48		
	7.62	7.36	7.52		
	7.63	7.37	7.55		
	7.63	7.37	7.54		
	7.63	7.36	7.55	7.51	0.14

Table C10: *pH changes in Bag 3 over the duration of the small scale composting (continued)*

	Sample 1	Sample 2	Sample 3	Average	Standard Deviation
Week 9	7.58	7.39	7.55		
	7.49	7.41	7.47		
	7.51	7.44	7.50		
	7.48	7.43	7.47		
	7.49	7.41	7.48	7.48	0.06
Week 10	7.28	7.31	7.29		
	7.30	7.33	7.30		
	7.27	7.31	7.29		
	7.27	7.35	7.29		
	7.29	7.32	7.31	7.31	0.03
Week 11	7.29	7.20	7.25		
	7.28	7.22	7.26		
	7.30	7.24	7.26		
	7.31	7.23	7.29		
	7.29	7.24	7.25	7.27	0.04
Week 12	7.31	7.33	7.30		
	7.31	7.34	7.32		
	7.29	7.32	7.31		
	7.30	7.33	7.31		
	7.29	7.32	7.30	7.32	0.02

Table C11: *Change in moisture in Bag 3 over the duration of the small scale composting*

Week	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)	Standard Deviation
1	66.40	65.85	66.67	66.31	0.42
2	68.40	72.40	70.10	70.30	2.01
3	66.90	67.10	66.20	66.74	0.48
4	68.80	67.31	70.27	68.80	1.49
5	70.37	68.24	69.30	69.31	1.07

Table C11: *Change in moisture in Bag 3 over the duration of the small scale composting (continued)*

Week	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average (%)	Standard Deviation
6	64.71	64.50	64.28	64.50	0.22
7	61.29	60.19	60.69	60.73	0.56
8	59.21	58.27	58.80	58.76	0.48
9	57.36	58.21	57.80	57.79	0.43
10	59.03	58.92	59.01	58.99	0.06
11	61.00	59.32	59.99	60.11	0.85
12	62.13	61.85	62.01	62.00	0.15

Table C12: *ICP analysis on Bag 3 final compost mix of the small scale composting*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)	Standard Deviation
As	0.04	0.04	0.04	0.04	5.00×10^{-4}
Cd	0.11	0.11	0.11	0.11	2.00×10^{-4}
Cu	0.42	0.42	0.41	0.42	2.90×10^{-3}
Hg	b.d	b.d	b.d	b.d	-
Ni	0.12	0.12	0.12	0.12	6.00×10^{-4}
Pb	0.14	0.14	0.13	0.14	2.60×10^{-3}
Se	0.12	0.10	0.10	0.11	0.01
Zn	0.47	0.48	0.48	0.48	8.00×10^{-4}

APPENDIX D: CHAPTER FIVE RAW DATA

Composting Trial 1

Table D1: *Temperature measurements at the centre of the heap in Trial 1 over the duration of the large scale composting*

Week	**Day**	**Temperature Readings (°C)**			**Average Temperature (°C)**
1	**1**	19.10	19.00	18.90	19.00
	2	17.90	18.20	18.10	18.07
	5	19.50	19.60	19.50	19.53
2	**8**	19.60	19.50	19.50	19.53
	12	24.80	25.00	25.10	24.97
	14	29.90	29.80	30.00	29.90
3	**15**	30.00	29.90	30.00	29.97
	16	30.00	30.00	30.00	30.00
	17	27.90	28.00	28.00	27.97
	18	27.20	27.00	27.10	27.10
	20	26.70	26.60	26.60	26.63
4	**22**	25.20	25.30	25.20	25.23
	23	23.10	22.80	22.90	22.93
	24	22.00	22.10	22.20	22.10
	26	22.10	22.00	22.20	22.10
	28	22.00	21.90	22.00	21.97
5	**30**	22.00	22.00	22.00	22.00
	31	22.90	23.10	23.00	23.00
	32	23.80	23.90	23.80	23.83
	34	24.80	24.80	24.70	24.77
	35	25.00	25.10	24.90	25.00
6	**36**	23.90	24.10	23.90	23.97
	37	23.10	23.00	23.00	23.03
	38	23.00	23.00	22.90	22.97
	39	23.10	23.00	23.00	23.03
	40	22.90	23.10	23.10	23.03

Table D2: *pH changes in Trial 1 over the duration of the large scale composting*

Week	Day	Sample 1	Sample 2	Sample 3	pH	Standard Deviation
1	**1**	7.10	7.08	7.09	7.09	0.01
	3	6.61	6.60	6.62	6.61	0.02
	5	6.35	6.40	6.30	6.35	0.06
	7	5.40	5.42	5.50	5.44	0.06
2	**9**	4.49	4.47	4.48	4.48	0.02
	11	4.46	4.45	4.46	4.46	0.01
	13	4.45	4.43	4.46	4.45	0.02
3	**15**	4.37	4.42	4.40	4.4	0.03
	17	4.35	4.32	4.33	4.34	0.02
	21	4.33	4.34	4.35	4.34	0.01
4	**23**	4.36	4.38	4.37	4.37	0.01
	25	5.36	5.39	5.38	5.38	0.02
	27	6.55	6.58	6.59	6.58	0.03
	28	7.83	7.80	7.81	7.82	0.02
5	**31**	8.84	8.80	8.85	8.83	0.03
	33	8.40	8.85	8.62	8.63	0.23
	35	8.87	8.90	8.88	8.89	0.02
6	**37**	8.88	8.90	8.90	8.90	0.02
	39	8.92	8.91	8.90	8.91	0.01
	40	8.90	8.92	8.88	8.90	0.02

Table D3: *Changes in moisture in Trial 1 over the large scale composting*

Week	Day	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average Moisture (%)	Standard Deviation
1	**1**	47.10	46.60	46.90	46.87	0.26
	5	35.50	34.50	36.45	35.49	0.98
2	**8**	61.00	59.85	60.30	60.39	0.58
	12	45.00	48.20	46.90	46.70	1.61
3	**15**	50.90	52.00	51.52	51.48	0.56
	20	55.20	56.00	55.80	55.67	0.42
4	**25**	52.70	53.00	52.85	52.85	0.15
	30	51.70	53.00	52.42	52.38	0.66

Table D3: *Changes in moisture in Trial 1 over the duration of the large scale composting (continued)*

Week	Day	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)	Average Moisture (%)	Standard Deviation
5	**32**	51.60	50.10	50.92	50.88	0.76
	34	50.20	49.90	50.12	50.08	0.16
	35	50.10	49.90	50.23	50.08	0.17
6	**40**	50.90	51.40	51.20	51.17	0.26

Table D4: *ICP analysis on Trial 1 final compost mix for large scale composting*

Element	Sample 1 (mg/L)	Sample 2 (mg/L)	Sample 3 (mg/L)	Average Concentration (mg/L)	Standard Deviation
As	0.07	0.07	0.09	0.08	8.00×10^{-3}
Cd	0.09	0.09	0.09	0.09	3.00×10^{-4}
Cu	0.62	0.62	0.62	0.62	5.00×10^{-3}
Hg	0.05	0.04	0.04	0.04	2.00×10^{-3}
Ni	0.14	0.14	0.14	0.14	2.00×10^{-3}
Pb	0.25	0.24	0.25	0.25	5.00×10^{-3}
Se	b.d	b.d	b.d	b.d	-
Zn	0.93	0.92	0.91	0.92	8.00×10^{-3}

Composting Trial 2

Table D5: *Temperature measurements at different points in the heap for Trial 2 and daily ambient temperatures for large scale composting*

Week	**Day**	**T_C (°C)**	**T_3(°C)**	**T_2(°C)**	**T_1(°C)**	**Ambient Temperature (°C)**
1	**1**	27.00	27.00	27.00	27.00	31.00
	4	37.00	32.00	37.00	32.00	26.50
	5	38.00	33.00	37.00	32.00	26.50
	6	38.50	34.00	38.00	33.00	28.00
2	**9**	38.00	35.00	38.00	34.00	30.00
	10	38.00	35.00	38.00	35.00	32.00
	11	38.00	34.00	37.00	36.00	26.00
	12	38.00	35.00	37.00	35.00	29.00
	13	38.00	35.00	36.00	35.00	27.00
3	**15**	37.00	34.00	34.00	33.00	28.00
	17	36.00	32.00	34.00	32.00	27.00
	19	35.00	32.00	32.00	32.00	30.00
4	**22**	35.00	31.00	31.00	31.00	31.00
	24	34.00	31.00	31.00	31.00	29.00
	25	34.00	31.00	31.00	31.00	29.00
	28	34.00	31.00	31.00	31.00	32.00
5	**30**	33.00	31.00	31.00	31.00	25.50
	32	33.00	31.00	31.00	31.00	27.00
6	**39**	33.00	31.00	32.00	31.00	31.00
	40	33.00	31.00	32.00	31.00	27.50
	41	33.50	31.00	31.50	31.00	31.50
	42	33.00	31.00	32.00	31.00	25.00
7	**43**	34.50	32.00	32.00	32.00	27.00
	46	31.00	30.00	30.00	30.00	29.00
8	**50**	27.00	27.00	27.00	27.00	24.00
	52	27.00	27.00	27.00	27.00	26.00
9	**57**	28.00	28.00	28.00	28.00	27.50
10	**68**	28.00	28.00	28.00	28.00	28.00

Table D5: *Temperature measurements at different points in the heap for Trial 2 and daily ambient temperatures for large scale composting (continued)*

Week	**Day**	**T_C (°C)**	**T_3 (°C)**	**T_2 (°C)**	**T_1 (°C)**	**Ambient Temperature (°C)**
11	**71**	30.00	28.00	28.00	28.00	28.00
	75	28.00	27.00	26.00	27.00	27.00
12	**82**	25.00	25.00	25.00	24.00	27.00
13	**89**	24.00	24.00	24.00	24.00	29.00
14	**95**	24.00	24.00	24.00	24.00	27.00

Table D6: *pH changes for Trial 2 over the duration of the large scale composting*

Week	**Day**	**Sample 1**	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
1	**1**	8.81	8.79	8.81	8.81	0.02
2	**12**	8.89	8.94	8.91	8.92	0.03
3	**18**	8.33	8.42	8.35	8.37	0.05
4	**26**	7.02	7.01	6.99	7.01	0.02
5	**29**	6.36	6.92	6.54	6.61	0.29
6	**41**	6.21	6.50	6.32	6.35	0.15
7	**47**	5.98	5.79	5.88	5.89	0.10
8	**52**	5.99	6.01	6.02	6.01	0.02
9	**60**	6.95	6.89	6.91	6.92	0.04
10	**68**	6.92	7.02	6.98	6.98	0.06
11	**76**	7.01	7.12	7.06	7.07	0.06
12	**84**	7.10	7.05	7.02	7.06	0.05
13	**92**	7.12	6.87	6.95	6.98	0.13
14	**95**	7.20	6.86	7.04	7.04	0.17

Table D7: *Changes in moisture for Trial 2 over the duration of the large scale composting*

Week	**Day**	**Sample 1 (%)**	**Sample 2 (%)**	**Sample 3 (%)**	**Average (%)**	**Standard deviation**
1	**1**	69.00	72.13	70.92	70.69	1.58
2	**12**	68.20	69.00	68.35	68.52	0.43
3	**18**	60.58	64.52	63.12	62.74	2.00
4	**26**	55.10	57.40	56.35	56.29	1.16
5	**29**	55.04	54.77	54.93	54.92	0.14
6	**41**	66.55	55.26	59.98	60.60	5.68
7	**47**	51.95	52.13	52.05	52.05	0.10
8	**52**	49.91	50.88	50.23	50.34	0.50
9	**60**	40.52	27.40	39.89	35.94	7.40
10	**68**	49.92	50.90	50.10	50.31	0.53
11	**76**	50.30	52.60	51.35	51.42	1.16
12	**84**	55.20	51.60	52.98	53.26	1.82
13	**92**	51.60	50.90	51.34	51.28	0.36
14	**95**	50.20	50.60	50.50	50.44	0.21

Table D8: *ICP analysis on Trial 2 final compost mix for the large scale composting*

Elements	**Sample 1 (mg/L)**	**Sample 2 (mg/L)**	**Sample 3 (mg/L)**	**Average Concentration (mg/L)**	**Standard Deviation**
As	0.05	0.05	0.04	0.05	6.00×10^{-3}
Cd	0.09	0.09	0.09	0.09	2.00×10^{-4}
Cu	0.42	0.42	0.42	0.42	1.00×10^{-3}
Hg	n.d	n.d	n.d	n.d	-
Ni	0.11	0.11	0.11	0.11	1.00×10^{-3}
Pb	0.22	0.23	0.22	0.22	5.00×10^{-3}
Se	n.d	n.d	n.d	n.d	-
Zn	0.36	0.35	0.35	0.35	2.00×10^{-3}

Composting Trial 3

Table D9: *Temperature measurements at different points in the heap for Trial 3 and daily ambient temperatures for the large scale composting*

Week	**Day**	**T_C(°C)**	**T_3(°C)**	**T_2(°C)**	**T_1(°C)**	**Ambient Temperature (°C)**
1	**1**	23.00	23.00	23.00	23.00	25.00
	2	23.00	23.00	23.00	23.00	25.50
	3	23.50	23.00	23.20	23.00	26.00
	4	23.50	23.00	23.20	23.00	26.00
	7	23.50	23.00	23.40	23.00	24.00
2	**10**	23.60	23.20	23.40	23.30	25.00
	12	23.90	23.50	23.50	23.50	23.00
3	**15**	24.20	24.00	23.50	23.80	24.00
	18	24.50	24.30	24.50	24.40	22.00
	21	28.00	26.50	27.80	27.00	23.00
4	**24**	32.00	31.50	31.80	31.60	24.00
	26	38.00	35.00	36.00	35.00	25.50
	28	38.00	35.00	37.50	37.00	23.00
5	**31**	36.00	33.20	33.50	33.30	23.50
	33	34.00	32.50	32.80	32.40	22.50
6	**36**	34.00	31.10	31.30	31.10	20.00
	40	33.00	30.90	31.00	31.00	25.50
7	**43**	33.00	31.00	31.00	30.80	25.00
	47	32.50	30.90	31.00	30.80	24.50
8	**50**	32.50	30.80	31.00	30.90	24.00
	54	33.00	31.00	31.00	31.00	25.50
9	**57**	32.00	30.50	30.90	30.40	24.00
	61	32.30	30.50	30.90	30.50	24.00
10	**64**	33.00	31.00	32.00	32.00	23.50
	68	31.00	30.00	30.00	30.00	23.00
11	**71**	29.00	27.50	28.80	27.40	25.00
	75	28.00	27.00	27.20	27.00	23.00

Table D9: *Temperature measurements at different points in the heap for Trial 3 and daily ambient temperatures for the large scale composting (continued)*

Week	**Day**	**T_C(°C)**	**T_3(°C)**	**T_2(°C)**	**T_1(°C)**	**Ambient Temperature (°C)**
12	**78**	27.00	26.00	26.40	25.90	21.00
	82	28.00	26.30	26.50	26.20	19.00
13	**85**	26.00	24.90	25.00	25.00	23.00
	89	25.00	24.00	24.30	24.00	24.00
14	**92**	24.30	23.90	24.00	24.00	25.00
	96	24.20	24.00	24.00	24.00	23.00
	99	24.20	24.00	24.00	24.00	24.50

Table D10: *pH changes for Trial 3 over the duration of the large scale composting*

Week	**Day**	**Sample 1**	**Sample 2**	**Sample 3**	**Average**	**Standard Deviation**
1	**1**	9.31	9.31	9.31	9.31	0.01
2	**12**	8.34	8.41	8.40	8.39	0.04
3	**17**	8.32	8.42	8.35	8.37	0.05
4	**22**	7.02	7.01	7.08	7.04	0.04
5	**29**	6.36	6.92	6.89	6.73	0.32
6	**34**	6.21	6.50	6.32	6.35	0.15
7	**43**	5.98	5.79	5.98	5.92	0.11
8	**50**	5.99	6.01	6.02	6.01	0.02
9	**57**	6.95	6.89	6.91	6.92	0.04
10	**64**	6.92	7.02	6.97	6.97	0.05
11	**71**	7.01	7.12	7.05	7.06	0.06
12	**78**	7.10	7.05	7.03	7.06	0.04
13	**85**	7.12	6.87	6.98	6.99	0.13
14	**98**	7.20	6.86	7.02	7.03	0.17

Table D11: *Changes in moisture for Trial 3 over the duration of the large scale composting*

Week	**Day**	**Sample 1 (%)**	**Sample 2 (%)**	**Sample 3 (%)**	**Average (%)**	**Standard Deviation**
1	**1**	70.81	69.98	70.52	70.44	0.43
2	**11**	66.72	84.28	83.98	78.33	10.06
3	**17**	65.23	64.52	65.32	65.03	0.44
4	**24**	57.20	57.40	56.56	57.06	0.44
5	**29**	54.74	54.77	54.30	54.61	0.27
6	**41**	56.59	55.57	55.35	55.84	0.67
7	**47**	50.59	52.15	51.30	51.35	0.79
8	**52**	50.78	50.88	51.05	50.91	0.14
9	**60**	51.02	55.63	51.93	52.86	2.45
10	**68**	50.92	50.90	51.03	50.95	0.08
11	**76**	52.30	51.95	50.90	51.72	0.73
12	**84**	51.50	51.60	50.90	51.34	0.38
13	**92**	50.40	51.00	50.65	50.69	0.31
14	**95**	50.40	50.60	50.20	50.40	0.20

Table D12: *ICP analysis for Trial 3 final compost mix for the large scale composting*

Element	**Sample 1 (mg/L)**	**Sample 2 (mg/L)**	**Sample 3 (mg/L)**	**Average Concentration (mg/L)**	**Standard Deviation**
As	0.06	0.05	0.05	0.05	5.00×10^{-3}
Cd	0.09	0.09	0.09	0.09	1.00×10^{-3}
Cu	0.01	0.39	0.40	0.28	0.20
Hg	n.d	n.d	n.d	n.d	-
Ni	0.12	0.11	0.12	0.12	5.00×10^{-3}
Pb	0.22	0.23	0.22	0.23	5.00×10^{-3}
Se	n.d	n.d	n.d	n.d	6.00×10^{-3}
Zn	0.37	0.36	0.36	0.36	6.00×10^{-3}

n.d = not detectable

APPENDIX E: CHAPTER SIX RAW DATA

Table E1: *Physical and chemical characterisation of soils treated with pith/PMS$_C$ (3:1) at different times*

	Farmland A				**Farmland B**				**Farmland C**			
	Untreated	**2010**	**2009**	**2008**	**Untreated**	**2010**	**2009**	**2008**	**Untreated**	**2010**	**2009**	**2008**
Density (g/ml)	1.34	1.26	-	-	-	1.25	1.14	-	1.29	0.77	1.47	0.98
Exch. Acidity (cmol/L)	0.05	0.82	-	-	-	0.06	0.03	-	0.02	0.09	0.00	0.08
Total cations (cmol/L)	2.67	3.01	-	-	-	5.16	6.21	-	3.86	11.82	2.61	11.60
Acid sat. (%)	2.00	27.00	-	-	-	1.00	0.00	-	1.00	1.00	0.00	1.00
pH	4.81	3.89	-	-	-	6.40	6.57	-	5.94	7.09	6.11	5.24
P (mg/L)	40.00	19.00	-	-	-	48.00	136.00	-	31.00	350.00	39.00	55.00
K (mg/L)	60.00	68.00	-	-	-	191.00	170.00	-	79.00	598.00	43.00	409.00
Ca (mg/L)	422.00	276.00	-	-	-	648.00	824.00	-	451.00	1642.00	355.00	1691.00
Mg (mg/L)	44.00	78.00	-	-	-	167.00	199.00	-	169.00	244.00	89.00	247.00
Zn (mg/L)	1.10	1.10	-	-	-	1.60	5.30	-	1.80	9.90	2.10	10.00
Mn (mg/L)	1.00	5.00	-	-	-	4.00	8.00	-	1.00	16.00	0.00	7.00
Cu (mg/L)	1.60	0.70	-	-	-	2.10	2.70	-	2.40	4.50	2.90	6.70
% Clay	14.00	20.00	-	-	-	13.00	13.00	-	9.00	5.00	6.00	14.00
% C	1.00	1.50	-	-	-	0.50	0.70	-	0.50	2.40	0.50	4.30
% N	0.05	0.08	-	-	-	0.05	0.05	-	0.05	0.05	0.05	0.30

APPENDIX F: CHAPTER SEVEN RAW DATA

Table F-1: *Daily CO_2 production observed by Reactor 1 (n = 3)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**
1	0.24	0.007	**1**	0.26	0.14	**1**	0.26	0.13
2	0.21	0.25	**2**	0.25	0.04	**2**	0.24	0.04
3	0.58	0.006	**3**	0.25	0.05	**3**	0.26	0.05
4	0.49	0.003	**4**	0.25	0.05	**4**	0.26	0.05
5	0.63	0.009	**5**	0.24	0.05	**5**	0.25	0.07
6	0.25	0.04	**6**	0.24	0.05	**6**	0.25	0.08
7	0.22	0.05	**7**	0.25	0.05	**7**	0.24	0.07
8	0.23	0.03	**8**	0.25	0.06	**8**	0.25	0.09
9	0.23	0.05	**9**	0.24	0.08	**9**	0.25	0.04
10	0.22	0.04	**10**	0.23	0.02	**10**	0.25	0.05
11	0.23	0.04	**11**	0.24	0.02	**11**	0.24	0.06
12	0.22	0.04	**12**	0.25	0.03	**12**	0.23	0.01
13	0.25	0.06	**13**	0.25	0.03	**13**	0.24	0.01
14	0.26	0.04	**14**	0.24	0.05	**14**	0.24	0.01
15	0.18	0.02	**15**	0.23	0.05	**15**	0.25	0.01

Table F-1: *Daily CO_2 production observed by Reactor 1 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**
16	0.2	0.02	**16**	0.26	0.11	**16**	0.24	0.01
17	0.19	0.02	**17**	0.27	0.07	**17**	0.25	0.01
18	0.18	0.02	**18**	0.26	0.09	**18**	0.26	0.01
19	0.19	0.02	**19**	0.26	0.05	**19**	0.25	0.02
20	0.21	0.02	**20**	0.26	0.06	**20**	0.26	0.06
21	0.17	1.00×10^{-3}	**21**	0.25	0.06	**21**	0.26	0.06
22	0.27	0.08	**22**	0.23	0.07	**22**	0.25	0.03
23	0.19	0.05	**23**	0.24	0.08	**23**	0.25	0.03
24	0.29	0.04	**24**	0.24	0.07	**24**	0.23	0.03
25	0.28	0.05	**25**	0.25	0.09	**25**	0.24	0.05
26	0.22	0.03	**26**	0.25	0.04	**26**	0.24	0.05
27	0.19	0.02	**27**	0.25	0.05	**27**	0.25	0.05
28	0.18	0.03	**28**	0.25	0.05	**28**	0.25	0.09
29	0.20	0.04	**29**	0.25	0.06	**29**	0.25	0.05
30	0.26	0.12	**30**	0.25	0.07	**30**	0.26	0.05
31	0.25	0.04	**31**	0.25	0.03	**31**	0.25	0.05
32	0.24	0.03	**32**	0.24	0.03	**32**	0.25	0.07

Table F-1: *Daily CO_2 production observed by Reactor 1 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Date	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**CO_2 produced (mg)**
33	0.25	0.04	**33**	0.24	0.03	**33**	0.25	0.07
34	0.25	0.06	**34**	0.25	0.03	**34**	0.24	0.05
35	0.24	0.05	**35**	0.25	0.04	**35**	0.24	0.06
36	0.28	0.01	**36**	0.24	0.06	**36**	0.25	0.03
37	0.27	0.01	**37**	0.25	0.06	**37**	0.25	0.03
38	0.29	0.01	**38**	0.19	0.06	**38**	0.24	0.04
39	0.28	0.01	**39**	0.22	0.07	**39**	0.25	0.06
40	0.28	0.01	**40**	0.20	0.05	**40**	0.23	0.08
41	0.26	0.01	**41**	0.26	0.05	**41**	0.26	0.05
42	0.25	0.01	**42**	0.25	0.05	**42**	0.25	0.05
43	0.26	0.01	**43**	0.25	0.04	**43**	0.25	0.04
44	0.24	0.01	**44**	0.24	0.05	**44**	0.25	0.03
45	0.25	0.14	**45**	0.25	0.05	**45**	0.26	0.02

Table F-2: *Daily CO_2 production observed by Reactor 2 (n = 3)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
1	0.25	3.00×10^{-3}	**1**	0.24	0.13	**1**	0.25	0.13
2	0.14	0.00	**2**	0.24	0.04	**2**	0.25	0.04
3	0.18	3.00×10^{-3}	**3**	0.25	0.04	**3**	0.24	0.04
4	0.21	3.00×10^{-3}	**4**	0.24	0.05	**4**	0.24	0.05
5	0.21	3.00×10^{-3}	**5**	0.24	0.05	**5**	0.24	0.07
6	0.23	0.04	**6**	0.25	0.05	**6**	0.25	0.08
7	0.23	0.04	**7**	0.26	0.05	**7**	0.25	0.06
8	0.22	0.04	**8**	0.23	0.06	**8**	0.25	0.08
9	0.21	0.04	**9**	0.23	0.08	**9**	0.23	0.03
10	0.29	0.03	**10**	0.24	0.02	**10**	0.24	0.04
11	0.27	0.03	**11**	0.24	0.02	**11**	0.24	0.04
12	0.12	0.03	**12**	0.24	0.02	**12**	0.25	0.01
13	0.21	0.05	**13**	0.25	0.03	**13**	0.22	0.01
14	0.20	0.05	**14**	0.21	0.05	**14**	0.21	0.01
15	0.22	0.01	**15**	0.25	0.05	**15**	0.25	0.01
16	0.24	0.01	**16**	0.24	0.10	**16**	0.24	0.01
17	0.25	0.01	**17**	0.24	0.07	**17**	0.26	0.01

Table F-2: *Daily CO_2 production observed by Reactor 2 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
18	0.21	0.01	**18**	0.23	0.09	**18**	0.23	0.01
19	0.20	0.01	**19**	0.25	0.05	**19**	0.25	0.02
20	0.20	0.01	**20**	0.25	0.05	**20**	0.25	0.06
21	0.10	0.01	**21**	0.24	0.06	**21**	0.24	0.06
22	0.16	0.06	**22**	0.26	0.07	**22**	0.25	0.03
23	0.22	0.06	**23**	0.26	0.07	**23**	0.26	0.03
24	0.25	0.03	**24**	0.23	0.07	**24**	0.24	0.03
25	0.24	0.03	**25**	0.24	0.09	**25**	0.24	0.04
26	0.21	0.03	**26**	0.24	0.04	**26**	0.24	0.04
27	0.21	0.03	**27**	0.25	0.04	**27**	0.25	0.04
28	0.22	0.03	**28**	0.26	0.05	**28**	0.26	0.09
29	0.16	0.03	**29**	0.24	0.06	**29**	0.25	0.05
30	0.25	0.10	**30**	0.24	0.07	**30**	0.24	0.05
31	0.26	0.03	**31**	0.24	0.02	**31**	0.24	0.05
32	0.26	0.03	**32**	0.23	0.02	**32**	0.25	0.06
33	0.24	0.04	**33**	0.23	0.02	**33**	0.26	0.06
34	0.23	0.05	**34**	0.25	0.02	**34**	0.24	0.04

Table F-2: *Daily CO_2 production observed by Reactor 2 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
35	0.23	0.05	**35**	0.26	0.03	**35**	0.26	0.05
36	0.23	0.01	**36**	0.25	0.06	**36**	0.25	0.03
37	0.25	0.01	**37**	0.24	0.06	**37**	0.26	0.03
38	0.26	0.01	**38**	0.24	0.06	**38**	0.25	0.03
39	0.25	0.01	**39**	0.24	0.07	**39**	0.24	0.04
40	0.25	0.01	**40**	0.25	0.05	**40**	0.24	0.05
41	0.24	0.01	**41**	0.25	0.05	**41**	0.24	0.04
42	0.22	0.01	**42**	0.25	0.05	**42**	0.25	0.04
43	0.23	0.01	**43**	0.25	0.04	**43**	0.25	0.03
44	0.24	0.01	**44**	0.25	0.04	**44**	0.25	0.03
45	0.25	0.14	**45**	0.25	0.05	**45**	0.25	0.02

Table F-3: *Daily CO_2 production observed by Reactor 3 (n = 3)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
1	0.24	3.00 x10^{-3}	**1**	0.25	0.13	**1**	0.26	0.13
2	0.21	6.00 x10^{-4}	**2**	0.25	0.04	**2**	0.25	0.04
3	0.2	2.00 x10^{-3}	**3**	0.25	0.04	**3**	0.25	0.04
4	0.2	2.00 x10^{-3}	**4**	0.24	0.05	**4**	0.24	0.05
5	0.2	2.00 x10^{-3}	**5**	0.24	0.05	**5**	0.25	0.07
6	0.24	4.00 x10^{-4}	**6**	0.26	0.05	**6**	0.25	0.08
7	0.20	4.00 x10^{-4}	**7**	0.25	0.05	**7**	0.25	0.06
8	0.23	0.04	**8**	0.25	0.06	**8**	0.26	0.08
9	0.13	0.04	**9**	0.26	0.08	**9**	0.26	0.03
10	0.25	0.03	**10**	0.25	0.02	**10**	0.25	0.04
11	0.25	0.03	**11**	0.26	0.02	**11**	0.25	0.04
12	0.24	0.03	**12**	0.24	0.02	**12**	0.26	0.01
13	0.23	0.05	**13**	0.23	0.03	**13**	0.25	0.01
14	0.24	0.05	**14**	0.25	0.05	**14**	0.25	0.01
15	0.19	0.01	**15**	0.25	0.05	**15**	0.24	0.01
16	0.21	0.01	**16**	0.25	0.10	**16**	0.25	0.01
17	0.20	0.01	**17**	0.24	0.07	**17**	0.25	0.01

Table F-3: *Daily CO_2 production observed by Reactor 3 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
18	0.24	0.01	**18**	0.24	0.09	**18**	0.24	0.01
19	0.20	0.01	**19**	0.25	0.05	**19**	0.25	0.02
20	0.25	0.01	**20**	0.24	0.05	**20**	0.24	0.06
21	0.24	0.01	**21**	0.24	0.06	**21**	0.24	0.06
22	0.25	0.05	**22**	0.25	0.07	**22**	0.25	0.03
23	0.22	0.05	**23**	0.25	0.07	**23**	0.25	0.03
24	0.26	0.03	**24**	0.25	0.07	**24**	0.26	0.03
25	0.28	0.03	**25**	0.26	0.09	**25**	0.26	0.04
26	0.24	0.03	**26**	0.25	0.04	**26**	0.21	0.04
27	0.25	0.03	**27**	0.24	0.04	**27**	0.23	0.04
28	0.19	0.03	**28**	0.25	0.05	**28**	0.25	0.09
29	0.23	0.03	**29**	0.24	0.06	**29**	0.24	0.04
30	0.22	0.11	**30**	0.25	0.07	**30**	0.25	0.04
31	0.25	0.03	**31**	0.25	0.02	**31**	0.26	0.05
32	0.26	0.04	**32**	0.25	0.02	**32**	0.26	0.04
33	0.22	0.04	**33**	0.24	0.02	**33**	0.25	0.04
34	0.25	0.05	**34**	0.24	0.02	**34**	0.24	0.04

Table F-3: *Daily CO_2 production observed by Reactor 3 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
35	0.24	0.05	**35**	0.26	0.03	**35**	0.26	0.05
36	0.26	0.01	**36**	0.25	0.05	**36**	0.26	0.03
37	0.25	0.01	**37**	0.25	0.05	**37**	0.25	0.03
38	0.26	0.01	**38**	0.25	0.06	**38**	0.25	0.03
39	0.26	0.01	**39**	0.26	0.06	**39**	0.24	0.04
40	0.25	0.01	**40**	0.25	0.05	**40**	0.25	0.05
41	0.26	0.01	**41**	0.25	0.05	**41**	0.23	0.04
42	0.25	0.01	**42**	0.26	0.05	**42**	0.26	0.05
43	0.22	0.01	**43**	0.26	0.04	**43**	0.25	0.03
44	0.24	0.01	**44**	0.24	0.04	**44**	0.25	0.02
45	0.24	0.14	**45**	0.25	0.05	**45**	0.25	0.02

Table F-4: *Daily CO_2 production observed by Reactor 4 (n = 3)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
1	0.23	2.21 x10^{-5}	**1**	0.25	0.13	**1**	0.25	0.13
2	0.11	6.68 x10^{-5}	**2**	0.24	0.04	**2**	0.25	0.04
3	0.18	8.18 x10-^{5}	**3**	0.25	0.04	**3**	0.24	0.04
4	0.19	8.18x10^{-5}	**4**	0.11	0.05	**4**	0.24	0.05
5	0.51	8.18 x10^{-5}	**5**	0.25	0.05	**5**	0.25	0.07
6	0.48	1.00 x10^{-4}	**6**	0.25	0.05	**6**	0.251	0.08
7	0.53	1.00 x10^{-4}	**7**	0.25	0.05	**7**	0.25	0.06
8	0.49	0.04	**8**	0.26	0.06	**8**	0.24	0.08
9	0.42	0.04	**9**	0.25	0.08	**9**	0.25	0.03
10	0.38	0.03	**10**	0.26	0.02	**10**	0.25	0.03
11	0.25	0.03	**11**	0.25	0.02	**11**	0.26	0.04
12	0.23	0.03	**12**	0.25	0.02	**12**	0.25	0.01
13	0.23	0.04	**13**	0.25	0.02	**13**	0.26	0.01
14	0.17	0.04	**14**	0.26	0.05	**14**	0.25	0.01
15	0.25	0.01	**15**	0.25	0.05	**15**	0.24	0.01
16	0.24	0.01	**16**	0.28	0.1	**16**	0.26	0.01
17	0.22	0.01	**17**	0.24	0.07	**17**	0.25	0.01

Table F-4: *Daily CO_2 production observed by Reactor 4 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
18	0.22	0.01	**18**	0.24	0.09	**18**	0.28	0.01
19	0.18	0.01	**19**	0.25	0.05	**19**	0.24	0.02
20	0.23	0.01	**20**	0.25	0.05	**20**	0.25	0.06
21	0.18	0.01	**21**	0.24	0.06	**21**	0.24	0.06
22	0.35	0.05	**22**	0.26	0.07	**22**	0.25	0.03
23	0.43	0.05	**23**	0.26	0.07	**23**	0.24	0.03
24	0.25	0.03	**24**	0.24	0.07	**24**	0.25	0.03
25	0.32	0.03	**25**	0.24	0.08	**25**	0.26	0.04
26	0.39	0.03	**26**	0.24	0.04	**26**	0.26	0.04
27	0.38	0.03	**27**	0.25	0.04	**27**	0.25	0.04
28	0.36	0.03	**28**	0.24	0.04	**28**	0.24	0.09
29	0.37	0.03	**29**	0.25	0.06	**29**	0.24	0.04
30	0.23	0.09	**30**	0.24	0.07	**30**	0.24	0.04
31	0.25	0.03	**31**	0.25	0.02	**31**	0.23	0.04
32	0.24	0.03	**32**	0.24	0.02	**32**	0.23	0.03
33	0.24	0.04	**33**	0.25	0.02	**33**	0.25	0.03
34	0.25	0.05	**34**	0.26	0.02	**34**	0.25	0.04

Table F-4: *Daily CO_2 production observed by Reactor 4 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
35	0.25	0.05	**35**	0.25	0.03	**35**	0.24	0.05
36	0.25	0.01	**36**	0.25	0.04	**36**	0.25	0.03
37	0.24	0.01	**37**	0.24	0.05	**37**	0.25	0.03
38	0.22	0.01	**38**	0.25	0.06	**38**	0.25	0.03
39	0.25	0.01	**39**	0.26	0.06	**39**	0.24	0.04
40	0.24	0.01	**40**	0.24	0.05	**40**	0.25	0.04
41	0.24	0.01	**41**	0.23	0.05	**41**	0.26	0.04
42	0.24	0.01	**42**	0.25	0.05	**42**	0.25	0.05
43	0.25	0.01	**43**	0.25	0.04	**43**	0.25	0.03
44	0.22	0.01	**44**	0.25	0.04	**44**	0.25	0.02
45	0.24	0.13	**45**	0.26	0.05	**45**	0.26	0.02

Table F-5: *Daily CO_2 production observed by Reactor 5 (n = 3)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
1	0.26	66.14 x10^{-3}	**1**	0.23	0.13	**1**	0.27	0.13
2	0.13	2.85 x10^{-2}	**2**	0.24	0.04	**2**	0.26	0.04
3	0.12	3.33 x10^{-3}	**3**	0.25	0.04	**3**	0.25	0.05
4	0.38	3.33 x10^{-3}	**4**	0.24	0.05	**4**	0.25	0.05
5	0.40	3.33 x10^{-3}	**5**	0.26	0.05	**5**	0.25	0.07
6	0.37	0.04	**6**	0.23	0.05	**6**	0.24	0.08
7	0.35	0.04	**7**	0.26	0.05	**7**	0.24	0.07
8	0.35	0.04	**8**	0.26	0.06	**8**	0.24	9.00 x10^{-3}
9	0.36	0.04	**9**	0.25	0.08	**9**	0.26	0.04
10	0.25	0.03	**10**	0.25	0.02	**10**	0.25	0.05
11	0.25	0.03	**11**	0.25	0.02	**11**	0.25	0.06
12	0.24	0.03	**12**	0.25	0.02	**12**	0.26	0.01
13	0.24	0.05	**13**	0.25	0.03	**13**	0.25	0.01
14	0.23	0.05	**14**	0.26	0.05	**14**	0.26	0.01
15	0.19	0.01	**15**	0.25	0.05	**15**	0.25	0.01
16	0.21	0.01	**16**	0.27	0.10	**16**	0.27	0.01
17	0.25	0.01	**17**	0.23	0.07	**17**	0.25	0.01

Table F-5: *Daily CO_2 production observed by Reactor 5 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
18	0.21	0.01	**18**	0.23	0.09	**18**	0.23	0.01
19	0.20	0.01	**19**	0.26	0.05	**19**	0.25	0.02
20	0.20	0.01	**20**	0.25	0.05	**20**	0.25	0.06
21	0.15	0.01	**21**	0.15	0.06	**21**	0.15	0.06
22	0.17	0.06	**22**	0.25	0.07	**22**	0.25	0.03
23	0.23	0.06	**23**	0.23	0.07	**23**	0.23	0.03
24	0.26	0.03	**24**	0.26	0.07	**24**	0.24	0.03
25	0.26	0.03	**25**	0.24	0.09	**25**	0.24	0.04
26	0.24	0.03	**26**	0.24	0.04	**26**	0.24	0.04
27	0.20	0.03	**27**	0.25	0.05	**27**	0.24	0.04
28	0.20	0.03	**28**	0.27	0.05	**28**	0.27	0.09
29	0.27	0.03	**29**	0.26	0.06	**29**	0.26	0.03
30	0.28	0.11	**30**	0.28	0.07	**30**	0.28	0.03
31	0.25	0.04	**31**	0.25	0.02	**31**	0.25	0.03
32	0.25	0.04	**32**	0.26	0.02	**32**	0.26	0.05
33	0.25	0.04	**33**	0.25	0.02	**33**	0.25	0.06
34	0.23	0.05	**34**	0.26	0.03	**34**	0.25	0.05

Table F-5: *Daily CO_2 production observed by Reactor 5 (n = 3) (continued)*

Replicate 1			**Replicate 2**			**Replicate 3**		
Day	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**	**Day**	**Air Flowrate (mL/min)**	**Mass of CO_2 produced (mg)**
35	0.25	0.05	**35**	0.25	0.03	**35**	0.25	0.06
36	0.26	0.01	**36**	0.25	0.06	**36**	0.25	0.03
37	0.25	0.01	**37**	0.25	0.06	**37**	0.25	0.03
38	0.25	0.01	**38**	0.25	0.06	**38**	0.25	0.03
39	0.27	0.01	**39**	0.24	0.07	**39**	0.24	0.06
40	0.26	0.01	**40**	0.25	0.05	**40**	0.24	0.07
41	0.23	0.01	**41**	0.25	0.05	**41**	0.24	0.04
42	0.22	0.01	**42**	0.24	0.05	**42**	0.24	0.05
43	0.24	0.01	**43**	0.25	0.04	**43**	0.24	0.04
44	0.23	0.01	**44**	0.26	0.05	**44**	0.25	0.03
45	0.23	0.14	**45**	0.25	0.05	**45**	0.25	0.02

Table F-6: *Results from statistical analysis on the* CO_2 *production in each reactor – ANOVA table*

SUMMARY						
Groups	**Count**	**Sum**	**Average**	**Variance**		
Reactor 1	3.00	6.32	2.11	0.16		
Reactor 2	3.00	5.60	1.87	0.28		
Reactor 3	3.00	5.39	1.80	0.31		
Reactor 4	3.00	5.17	1.72	0.32		
Reactor 5	3.00	5.80	1.93	0.25		
ANOVA						
Source of Variation	**SS**	**df**	**MS**	**F**	**P-value**	**F critical**
Between Groups	0.26	4.00	0.07	0.25	0.91	3.48
Within Groups	2.65	10.00	0.26			
Total	2.91	14.00				