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The aerobic treatment of organic wastes and their use in industry

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THE AEROBIC TREATMENT OF ORGANIC WASTES AND THEIR USE IN INDUSTRY

A thesis submitted to Bangor University

by

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ABSTRACT

The production of large amounts of Municipal Solid Waste (MSW) is an inevitable consequence of today's consumer society. Finding safe, sustainable, socially acceptable and cost effective alternatives to the disposal of MSW in landfills represents a major challenge to the waste management industry, and one that was set out in law under the European Landfill Directive in 1999. Composting is seen as an attractive waste management option, providing that there are few negative effects on the environment after undertaking a life cycle assessment. The focus of the research presented in this thesis is on the composting of MSW, both mixed and source-segregated, and the subsequent use of these composts in the remediation, land reclamation and horticultural industries.

Composts were produced in two runs on an industrial scale using the EcoPOD® in-vessel composting system, and changes in key compost quality indicators (e.g. C:N ratio, nutrient and heavy metal availability) were quantified during the composting process (Chapters 3 & 6). Due to UK regulations on wastes containing animal by-products, no field trials were possible using the composts produced in the studies presented in this thesis. Instead, a series of pot trials were carried out over Chapters 3-6, with a mesocosm-scale trial used in Chapters 7 & 8. Of these trials, Chapter 3 investigated potential uses for mixed-waste compost produced using the EcoPOD® system, and found it to be particularly suited to remediation of acidic, heavy metal contaminated soils. This theme of remediation was carried on through Chapter 4 on the pot scale, and Chapters 6 & 7 on a mesocosm scale studying migration of heavy metals down the soil profile over time. Work in Chapter 5 focussed on the difficult subject of ecologically sensitive revegetation of blocky slate waste using composts amended with sulphur and iron hydroxide to make them more suitable for upland restoration purposes. Analysis of soil solution pH and P concentration proved promising with pH being decreased by S^0 , and P being reduced by $Fe(OH)_3$, however the amendments failed to influence above-ground plant diversity trajectories. Finally, nutrient rich composts produced in Chapter 6 was assessed for their potential as a replacement for peat in horticulture, and demonstrated that a 75 % substitution for peat based growing media is possible without affecting plant growth and yield.

In summary, this work has demonstrated that highly contrasting organic wastes can be successfully composted, and has found that even low-quality mixed waste composts may be successfully used in the biostabilisation of acidic, heavy metal contaminated soils. In fact, the high buffering capacity of the MSW compost produced in this study (Appendix 1) lends itself to this role, providing a strong ability to resist pH change from the pyritic nature of the soil used throughout these studies (Chapters 3, 4, 6 & 7). In order to assess the contribution of compost-borne heavy metals to the overall burden, further work using isotopic analysis could be utilised to pinpoint contaminant sources (Appendix 2). The use of chemical amendments to reduce compost pH and P availability showed promise, but further work is required in this area to optimise the amendments. Finally, composts derived from catering wastes were found to provide a real alternative to peat in horticulture, although such wastes are yet to attain full market acceptance.

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TABLE OF CONTENTS

| | |
|---|-----|
| ABSTRACT | ii |
| ACKNOWLEDGEMENTS | iii |
| TABLE OF CONTENTS | iv |
| LIST OF FIGURES | x |
| LIST OF TABLES | xii |
| DECLARATION | xiv |
| | |
| CHAPTER 1: INTRODUCTION | 1 |
| 1.1 The waste problem and the need for research..... | 1 |
| 1.2 Compost uses | 3 |
| 1.3 Thesis outline..... | 4 |
| 1.4 Aims and objectives..... | 6 |
| 1.5 References | 7 |
| | |
| CHAPTER 2: MUNICIPAL SOLID WASTE COMPOSTING AND POTENTIAL COMPOST MARKETS..... | 11 |
| 2.1 Abstract | 11 |
| 2.2 Introduction – The waste problem..... | 11 |
| 2.3 Composting..... | 12 |
| 2.4 Municipal solid waste compost..... | 14 |
| 2.4.1 Mechanical biological treatment (MBT)..... | 14 |
| 2.4.2 Chemical properties of MSW and MBT derived composts | 16 |
| 2.5 Uses of MSW derived composts..... | 25 |
| 2.5.1 Agriculture | 26 |
| 2.5.2 Horticulture | 29 |
| 2.5.3 Remediation | 29 |
| 2.6 Conclusions and recommendations | 34 |
| 2.7 References..... | 35 |

| | |
|---|----|
| CHAPTER 3: HEAVY METAL CONTAMINATION OF A MIXED WASTE COMPOST: SPECIATION AND FATE | 45 |
| 3.1 Abstract | 45 |
| 3.2 Introduction..... | 46 |
| 3.3 Materials and methods | 48 |
| 3.3.1 In-vessel composting..... | 48 |
| 3.3.2 Compost sampling and analysis | 49 |
| 3.3.3 Growth trial substrates | 50 |
| 3.3.4 Effect of MSW compost application rate and soil type on plant performance | 53 |
| 3.3.5 Use of <i>Thlaspi caerulescens</i> to investigate phytoavailable Cd and Zn | 53 |
| 3.3.6 Statistical analysis..... | 54 |
| 3.4 Results | 54 |
| 3.4.1 Composting of MSW fines..... | 54 |
| 3.4.2 Metal dynamics during composting..... | 56 |
| 3.4.3 Effect of increasing MSWW compost application on plant growth.. | 59 |
| 3.4.4 Effect of soil type on the success of MSW compost at promoting plant growth | 59 |
| 3.4.5 Performance of MSW compost in comparison to other composts | 62 |
| 3.4.6 Comparability of total and EDTA-extractable heavy metals to phytoaccumulated concentrations | 64 |
| 3.5 Discussion | 67 |
| 3.5.1 Composting of MSW..... | 67 |
| 3.5.2 Metal dynamics during composting..... | 68 |
| 3.5.3 Effect of MSW compost on plant growth and metal uptake | 69 |
| 3.5.4 Efficacy of EDTA and total extracts as predictors of phytoaccumulation of heavy metals | 71 |
| 3.5.5 Conclusions..... | 71 |
| 3.6 References..... | 72 |

| | |
|--|-----|
| CHAPTER 4: USE OF COMPOSTS IN REMEDIATION OF A HEAVY METAL CONTAMINATED SOIL..... | 76 |
| 4.1 Abstract | 76 |
| 4.2 Introduction..... | 77 |
| 4.3 Materials and methods | 78 |
| 4.3.1 Substrate characteristics | 78 |
| 4.3.2 Plant growth trials | 80 |
| 4.3.3 Sampling and analysis | 81 |
| 4.3.4 Statistical analysis..... | 82 |
| 4.4 Results | 82 |
| 4.4.1 Substrates and plant growth..... | 82 |
| 4.4.2 Metal uptake and availability..... | 87 |
| 4.4.3 Soil solution metal concentration change over time | 90 |
| 4.5 Discussion | 91 |
| 4.5.1 Metal dynamics in soil..... | 91 |
| 4.5.2 Plant growth and metal accumulation..... | 93 |
| 4.5.3 Use of composts in land restoration | 94 |
| 4.6 References..... | 95 |
| | |
| CHAPTER 5: CHEMICAL MODIFICATION OF COMPOSTS TO ENABLE SUCCESSFUL HABITAT RESTORATION | 99 |
| 5.1 Abstract | 99 |
| 5.2 Introduction..... | 100 |
| 5.3 Materials and methods | 102 |
| 5.3.1 Preliminary studies..... | 102 |
| 5.3.2 Autoecology of <i>Agrostis capillaris</i> and <i>Festuca ovina</i> | 103 |
| 5.3.3 Experimental design | 104 |
| 5.3.4 Substrate characteristics | 104 |
| 5.3.5 Sampling and analysis | 105 |
| 5.3.6 Statistical analysis..... | 107 |
| 5.4 Results | 108 |
| 5.4.1 Substrate properties..... | 108 |

| | | |
|---|---|-----|
| 5.4.2 | Vegetation growth, P, Cd and Zn concentration..... | 108 |
| 5.4.3 | Changes in soil solution pH over time..... | 110 |
| 5.4.4 | Changes in soil solution phosphorus over time | 111 |
| 5.5 | Discussion | 113 |
| 5.5.1 | Soil solution chemistry | 113 |
| 5.5.2 | Effect of amendments on <i>Agrostis capillaris</i> and <i>Festuca ovina</i> | 114 |
| 5.6 | References..... | 117 |
| CHAPTER 6: FOOD WASTE COMPOSTING: ITS USE AS PEAT REPLACEMENT..... | | |
| | | 122 |
| 6.1 | Abstract | 122 |
| 6.2 | Introduction..... | 122 |
| 6.3 | Materials and methods | 124 |
| 6.3.1 | In-vessel composting..... | 124 |
| 6.3.2 | Compost analysis..... | 125 |
| 6.3.3 | Growth trial composts..... | 127 |
| 6.3.4 | Plant growth trials | 127 |
| 6.3.5 | Statistical analysis..... | 128 |
| 6.4 | Results | 128 |
| 6.4.1 | Composting of food waste | 128 |
| 6.4.2 | Compost mixture properties | 131 |
| 6.4.3 | Plant growth | 132 |
| 6.5 | Discussion | 134 |
| 6.5.1 | Composting of food waste | 134 |
| 6.5.2 | Use of food waste compost as a peat replacement..... | 135 |
| 6.5.3 | Conclusions..... | 136 |
| 6.6 | References..... | 137 |
| CHAPTER 7: MIGRATION OF HEAVY METALS IN SOIL AS INFLUENCED BY ORGANIC AMENDMENTS | | 140 |
| 7.1 | Abstract | 140 |
| 7.2 | Introduction..... | 141 |

| | | |
|---|--|-----|
| 7.3 | Materials and methods | 143 |
| 7.3.1 | Substrate characteristics | 143 |
| 7.3.2 | Experimental design | 144 |
| 7.3.3 | Sampling and analysis | 145 |
| 7.3.4 | Statistical analysis..... | 146 |
| 7.4 | Results | 147 |
| 7.4.1 | Compost and soil properties | 147 |
| 7.4.2 | Plant growth and metal uptake..... | 147 |
| 7.4.3 | Changes in soil solution chemistry | 150 |
| 7.5 | Discussion | 153 |
| 7.5.1 | Effect of treatments on soil solution chemistry..... | 153 |
| 7.5.2 | Plant growth and metal uptake..... | 156 |
| 7.5.3 | Conclusions..... | 157 |
| 7.6 | References | 158 |
| | | |
| CHAPTER 8: MICROBIAL DIVERSITY AND ACTIVITY ARE INCREASED BY COMPOST AMENDMENT OF METAL CONTAMINATED SOIL... | | 163 |
| 8.1 | Abstract | 163 |
| 8.2 | Introduction..... | 164 |
| 8.3 | Experimental procedures | 166 |
| 8.3.1 | Substrate characteristics | 166 |
| 8.3.2 | Experimental design | 167 |
| 8.3.3 | Sampling and analysis | 168 |
| 8.3.4 | Microbial analyses..... | 168 |
| 8.3.5 | Statistical analyses..... | 170 |
| 8.4 | Results | 170 |
| 8.4.1 | Soil and soil solution chemical properties..... | 170 |
| 8.4.2 | Soil microbial activity..... | 172 |
| 8.4.3 | Correlations between biological activity and chemical properties... | 174 |
| 8.4.4 | TRFLP analysis of bacterial and fungal communities | 174 |
| 8.4.5 | PLFA analysis of fungal communities | 177 |

| | | |
|--|---|-----|
| 8.5 | Discussion | 179 |
| 8.5.1 | Chemical properties and biological activity | 179 |
| 8.5.2 | Microbial community structure | 180 |
| 8.5.3 | Conclusions..... | 183 |
| 8.6 | References | 183 |
| CHAPTER 9: GENERAL DISCUSSION | | 188 |
| 9.1 | Discussion of results | 188 |
| 9.2 | Further work..... | 193 |
| 9.3 | References | 196 |
| APPENDIX 1: pH BUFFERING CAPACITY OF COMPOSTS..... | | 199 |
| APPENDIX 2: USE OF Pb ISOTOPE SIGNATURES TO TRACE SOURCES OF Pb POLLUTION | | 204 |

LIST OF FIGURES

| | |
|--|-----|
| Figure 2.1: PAHs, PCBs and PCDD/Fs..... | 20 |
| Figure 3.1: Changes in a) temperature at 60 cm depth, b) pH, c) C:N ratio | 55 |
| Figure 3.2: Changes in Cu, Ni, Pb and Zn speciation | 58 |
| Figure 3.3: Yield and metal uptake by <i>L. perenne</i> and <i>T. repens</i> when grown in increasing volumes of MSW compost. | 60 |
| Figure 3.4: Yield and metal uptake by <i>L. perenne</i> and <i>T. repens</i> when grown in 5 different soils with and without a 40% substitution of MSW compost. | 61 |
| Figure 3.5: Yield and metal uptake by <i>L. perenne</i> and <i>T. repens</i> as affected by a 40 % application of seven different composts..... | 63 |
| Figure 3.6: Above-ground biomass and Cd and Zn concentration of <i>T. caerulea</i> grown under the conditions outlined in sections 3.3.2-5. | 66 |
| Figure 3.7: Relationships between EDTA extractable and total Cd and Zn against <i>L. perenne</i> , <i>T. repens</i> , and <i>T. caerulea</i> | 67 |
| Figure 4.1: Influence of compost type and lime application on root and shoot biomass after being grown in a heavy metal contaminated soil for 2 months..... | 83 |
| Figure 4.2: Influence of compost type and lime on the foliar metal content of plants grown in a metal contaminated soil for 2 months..... | 88 |
| Figure 4.3: Influence of compost type and lime on the temporal dynamics of heavy metals in soil solution over a 2 months growth period. | 89 |
| Figure 4.4: Relationship between soil solution pH and heavy metal concentration | 90 |
| Figure 5.1: Langmuir isotherm of P sorption to iron hydroxide sludge used in this study | 103 |
| Figure 5.2: Total above ground biomass g pot ⁻¹ , above ground biomass per species g pot ⁻¹ , and above ground biomass phosphorus content mg after 93 days of growth. | 109 |
| Figure 5.3: Change in soil solution pH over time. | 111 |
| Figure 5.4: Change in soil solution phosphorus (mg l ⁻¹) over time. | 112 |
| Figure 6.1: Changes in compost pH, C:N ratio, nitrate-N and ammonium-N | 130 |
| Figure 6.2: Temperature changes throughout composting. | 131 |

| | |
|---|-----|
| Figure 6.3: Effect of different compost blends on the height gain of sunflowers | 132 |
| Figure 6.4: Effects of different compost blends on key growth parameters for sunflowers at harvest | 133 |
| Figure 7.1: Biomass production of <i>A. capillaris</i> after growth in a contaminated soil. | 148 |
| Figure 7.2: Heavy metal concentration of <i>A. capillaris</i> after growth in a contaminated soil..... | 149 |
| Figure 7.3: Soil solution chemistry over the 112 days of the trial. | 151 |
| Figure 7.4: Soil solution heavy metal concentration..... | 152 |
| Figure 8.1: Influence of remediation strategy and soil depth..... | 173 |
| Figure 8.2: Canonical Correspondence Analysis of bacterial and fungal communities | 175 |
| Figure 8.3: Correspondence Analysis of PLFA data at all four soil depths..... | 176 |
| Figure 8.4: CCA of PLFA variables scores across all four depths as influenced by the environmental data. | 178 |
| Figure 8.5: PCA of all biological and chemical data after 112 days..... | 178 |

LIST OF TABLES

| | |
|---|-----|
| Table 2.1: Typical heavy metal concentrations of MSW, MSW-derived composts and legislative standards. | 17 |
| Table 2.2: Typical nutrient content of MSW and other composts. | 24 |
| Table 3.1: Chemical properties of compost feedstocks and growth trial substrates. .. | 51 |
| Table 3.2: Repeated measures mixed model 3-way ANOVA investigating changes in metal partitioning over time in the two MSW derived composts | 57 |
| Table 3.3: Linear regression analysis results predicting vegetation Cd and Zn concentration from soil EDTA extractable and total soil Cd and Zn concentrations for three plant species | 65 |
| Table 4.1: Chemical properties of the substrates used in the plant growth trials..... | 79 |
| Table 4.2: Chemical properties of the soils and soil solutions from each treatment after 64 days of growth. | 83 |
| Table 5.1: Details of each treatment..... | 105 |
| Table 5.2: Chemical characteristics of composts and soils. | 106 |
| Table 5.3: Fully factorial ANOVA results for total biomass, biomass by species, and P content by species. | 107 |
| Table 6.1: Compost feedstock properties. | 126 |
| Table 6.2: Chemical properties of substrates used for growth trial. | 129 |
| Table 7.1: Chemical properties of the soil and compost (GWC and MSWC) substrates used in the plant growth trials. | 143 |
| Table 7.2: Results from repeated measures ANOVA analysis on changes in soil solution chemistry over time and depth, as affected by soil amendment treatment. | 152 |
| Table 8.1: Effect of an inorganic (lime and fertilizer; Inorganic) or compost (GWC or MSWC) remediation strategy on grass growth and below-ground soil properties versus depth after 4 months of treatment..... | 171 |
| Table 8.2: Pearson’s correlation coefficients between chemical and biological variables across all remediation treatments after 4 months..... | 174 |

| | |
|--|-----|
| Table 8.3: Effect of inorganic and organic (GWC and MSWC) based remediation treatment on the mean total TRFs and Shannon- <i>H</i> diversity indices from fungal and bacterial TRFLP data..... | 175 |
|--|-----|

CHAPTER 1: INTRODUCTION

1.1 The waste problem and the need for research

Disposal of Municipal Solid Waste (MSW) is a growing problem for the majority of the world's population (Eitzer, 1995). It is caused by social and economic factors linked with growing prosperity and rising household disposable income, and exacerbated by influential advertising encouraging premature disposal of household goods in favour of more recent models. Most goods are also now pre-packaged, greatly adding to the waste problem (WAG, 2002). Within the European Union (EU), there have been many legislative directives covering the management of waste, the first of these being the Waste Framework Directive (EC, 1975), which specified the requirement for governments to categorise wastes and for regulations regarding the treatment of those wastes to be written in to legislation. In 1999, the Landfill Directive (LFD) was passed by the European Commission (EC, 1999). This document above all else set aside the requirement for a major reduction in the amount of biodegradable waste sent to landfill over the coming years and this underpins much of the UK's waste management legislation. In view of this, industrial scale aerobic composting of organic wastes is seen as a promising option for organic waste disposal.

Composting can be defined as the aerobic biological degradation of organic wastes (Williams, 2005). It is thermophilic in nature with temperatures reaching above 45 °C (Dominguez *et al.*, 1997), and it is this factor that makes it particularly useful for waste management as high temperatures denature and destroy potential pathogenic bacteria, as well as weed propagules. It is a relatively fast process, and

depending on feedstock and system used, can take between 4-6 weeks of initial composting, with a further maturation phase to allow the compost to cure and stabilise (Williams, 2005). During the process of composting, a large proportion (50-75 %; Déportes *et al.*, 1995) of the organic matter present is either mineralised to form CO₂ or carbonates, with the remainder being transformed into humic-like substances (García-Gil *et al.*, 2004). Initially, microbes present within the compost feedstocks begin to utilise the easily available nutrients present in the 'biofilm' – the thin liquid phase surrounding the solids of the feedstocks (de Guardia *et al.*, 2002). It is this rapid consumption that causes the large increase in temperatures due to heat generated by microbial respiration, and a shift in the microbial population type to favour thermophilic bacteria. Microbial enzymes are produced that attack the solid phase of the organic matter, replenishing the biofilm with soluble organic matter that the microorganisms can easily utilise. As the quantity of easily degradable organic matter decreases, so too does the metabolic activity of the microbial community. This causes the temperature of the compost to decrease and makes it more suitable to habitation by mesophilic fungi and bacteria (Steger *et al.*, 2005).

Whilst industrial composting of garden trimmings (termed 'green waste') is commonplace throughout the UK, usually taking place in large open windrows, food waste forms a significant proportion of domestic waste that may be currently landfilled. Increasingly, however, food waste is being co-composted with green waste to form a nutrient-rich product that may have added-value and be suitable for the market gardening and horticultural markets. One major barrier to the more widespread composting of food waste (and its acceptance by potential buyers) is the potential risk of transferral of plant, animal or human pathogens from catering waste feedstocks. A major expense over conventional windrow composting of green waste is the legal requirement within the UK under Animal By-Products Regulations (ABPR: DEFRA, 2008) to carry out the first phase of thermophilic composting within a sealed vessel. This added expense has posed a problem for composters, however, increases in landfill tax and the potential fines for failing to comply with Landfill Directive timescales are increasingly making in-vessel systems viable. Whilst the composting of green wastes either on their own (de Guardia *et al.*, 2002) or co-composted with various manure (Sommer *et al.*, 2004) or sewage sludge treatments (Amir *et al.*, 2005)

is well documented, there is much less available information on the effect of catering wastes on the composting process, and whether at high catering waste loadings there is a need to balance the carbon : nitrogen (C:N) ratio with a high C feedstock such as waste paper.

Another angle of in-vessel composting is the processing of residues from Mechanical Biological Treatment (MBT) plants - a generic term for the treatment and separation of mixed solid wastes into reusable and recyclable fractions. Thermophilic composting can be used to treat the residual organic fraction from the MBT process, to produce a stabilised compost-like substance (Binner and Zach, 1999). Whilst according to EC (1999), this is suitable for landfill, it is desirable to find alternative uses for this mixed waste 'compost'. As soil organic matter levels have declined greatly in recent years (Bellamy *et al.*, 2005) it is advantageous to recycle as much of this 'waste' organic matter as possible, without unduly increasing the loading of contaminants onto uncontaminated soils. Heavy metals such as Cd, Cu, Pb, Ni and Zn are found in potentially high levels in MBT-derived composts, and there are obvious concerns about such toxic elements entering the food chain through food crops to which composts have been applied as fertiliser (Gillett, 1992; Richard and Woodbury, 1992; Déportes *et al.*, 1995; Chung and Poon, 2001). Heavy metals do not degrade throughout the composting process, and can become concentrated due to the loss of carbon and water from the compost due to microbial respiration (Richard, 1992). When properly executed, the aerobic composting of organic wastes has the ability to immobilise the exchangeable pool of heavy metals within an organic waste (Paré *et al.*, 1999), however, there is also little research into the behaviour of heavy metals during the composting of MBT residues, which may contain more point-sources of heavy metals such as batteries, as opposed to the diffuse nature of heavy metal contamination in sewage sludges.

1.2 Compost uses

Composts have a range of uses and may even be tailored for specific purposes (Nason *et al.*, 2006). For agriculture, one of the perceived larger customers for produced composts, nutritional content is the main concern, in order for it to replace or reduce mineral fertilisation requirements. It is especially useful on organic farms

where mineral fertilisation cannot be used. Also, the addition of organic matter in the form of composts to agricultural soils (which can often become deficient in this important property) has been shown to improve the physical aspects of the soil (Ozores-Hampton *et al.*, 2005; Bresson *et al.*, 2001; Aguilar *et al.*, 1997). Compost addition has also been shown to have positive effects on the microbial population of a forest soil after application (Borken *et al.*, 2002a; Borken *et al.*, 2002b). As well as agriculture, the lucrative horticulture industry also requires composts of a high standard, with studies by Cala *et al.* (2005) showing large increases in yield of rosemary, and Castillo *et al.* (2004) stating that it is suitable when blended with peat for use as a potting media for tomato plants. Whilst this does not completely eliminate peat from horticulture, it certainly reduces the amount required, and also reduces the cost for the horticultural business (Ingelmo *et al.*, 1998).

Whilst in the UK, both agriculture and horticulture require composts to have passed the BSI PAS 100 (BSI, 2005) compost quality standard, being free from chemical and physical contaminants, industries such as the landscaping sector require cheaper soil improvers, and are more able to use some of the lower quality composts produced by mixed wastes (Smith, 1992). The landscaping of old landfill sites is a particularly effective use for these poorer quality composts (Hurst *et al.*, in press). The last main use covered here for composts, especially poorer quality products is the restoration of post-industrial sites, either for development (Dickinson *et al.*, 2005) or for ecological restoration. Soil amendments such as composts are inherently rich in organic matter and as such have been shown to act as a sink, stabilising available heavy metals in situ (Bolan *et al.*, 2003). As well as the chemical stabilisation effect caused by the addition of composts to metal-contaminated soils, the addition of high-nitrogen composts can induce vigorous plant growth (Brown *et al.*, 2003; Castaldi *et al.*, 2005), further stabilising the available fraction of the heavy metals.

1.3 Thesis outline

The first two years of my research were funded by Gwynedd Council, with the remainder by the European Social Fund (ESF) in collaboration with CB Environmental, a waste management company based in Aberystwyth, Wales. The work funded by Gwynedd Council mainly focussed on the production of composts using the EcoPOD®

in-vessel system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA). Two composting sessions were run using the EcoPOD® system, the first of which involved the composting of Municipal Solid Waste (MSW) fines produced in a DANO drum waste pulverisation plant – a feedstock similar to residues from the MBT process. The second run focussed on the co-composting of food waste collected from restaurants and hotels in the region with green waste and shredded paper in three treatments. Various growth trials were carried out using the composts produced in these trials under different scenarios. These then continued under the ESF funding as more in-depth studies into the use of composts for remediation and their effects on soil biochemistry were investigated. Unfortunately, due to the terms set out in our license to compost wastes containing animal by-products from DEFRA, we were unable to carry out any outdoor field-scale trials using the composts, hence all growth trials were carried out on a pot-scale.

This thesis is divided into nine chapters, and is presented as a series of six experimental papers and one review paper. As such, some repetition is unavoidable between chapters due to the need to provide a thorough introduction to each paper. The review paper (Chapter 2) investigates the current state of research into mixed-waste composting, and its uses in various industrial sectors. Chapter 3 investigates the dynamics of heavy metals within MSW during composting, and then looks at the performance of this compost across different soil types, at different application rates, and against different composts in terms of plant growth and metal uptake. Chapter 4 furthered the results of Chapter 3, investigating the ability of different composts with or without a lime amendment to reduce heavy metal availability in an acidic, heavy metal contaminated soil from an old copper mine. In Chapter 5, the use of chemical amendments to reduce the pH and phosphorus availability in composts destined for remediation of blocky waste spoil tips such as those throughout North Wales was studied. The effect of these chemical treatments on the phosphorus uptake and competition between two grassland species was also studied. Chapter 6 investigated the chemical changes that take place during food waste co-composting with green waste and shredded paper. The food waste / green waste compost was then used in a growth trial to assess its suitability for the horticultural / market gardening sectors in replacing peat-based composts. Chapters 7 and 8 returned the focus to the effects of

composts on heavy metal contaminated soils using 40 cm mesocosms to investigate the effect of amendment additions on soil chemistry and microbial structure and function down the soil profile. The Appendix consists of the results from smaller experiments that were not used in the body of the thesis.

1.4 Aims and objectives

The initial objectives of this study were agreed with Gwynedd Council for the first two phases of research, and these are presented in Chapters 3 and 6. The remainder of the research carried on along the broad theme of potential uses for waste-derived composts, most specifically remediation / landscaping. Specific objectives included:

- Assessment of the suitability of the MSW fines generated by the DANO drum waste pulverisation plant for composting, to assess the risk of contamination from heavy metals within the feedstock, and to investigate the resultant compost's suitability across a range of soil types, at different application rates, in comparison to other composts (Chapter 3).
- Investigate nutrient fluxes during co-composting food waste and green waste, and to assess its suitability to replace high fertility peat-based composts in the market gardening / horticultural sectors (Chapter 6).
- As a follow on from the growth trials in Chapter 3, I assessed the potential use of composts in the remediation / stabilisation of acidic, heavy metal contaminated sites. Changes over time in acidity, nutrient status and heavy metal availability were monitored in the soil solution, and heavy metal uptake and growth of plants after compost application were studied (Chapter 4).
- This work was furthered in Chapters 7 and 8, by assessing the effects on nutrient status, acidity and heavy metal availability down the soil profile to assess whether dissolved organic carbon (DOC) released from the incorporation of composts into the soil would increase heavy metal leaching.
- To assess the effect of compost addition to heavy metal contaminated soil on the soil microbial community to determine whether function can be restored to degraded soils (Chapter 8).

- In addition to contaminated land, I assessed the use of composts to revegetate extremely porous blocky waste spoil. Previous work under the *Life-Environment TWIRLS* project had investigated the effects of acidifying compost on the pH and phosphorus availability to improve the suitability of composts for upland restoration. The effect of using iron hydroxide to reduce P availability and its effect on the competition between *Agrostis capillaris* and *Festuca ovina* was investigated (Chapter 5).

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CHAPTER 2: MUNICIPAL SOLID WASTE COMPOSTING AND POTENTIAL COMPOST MARKETS

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A shortened version of this paper is currently under review at Bioresource Technology

2.1 Abstract

Mechanical Biological Treatment (MBT) of mixed waste streams is becoming increasingly popular as a method for treating Municipal Solid Waste (MSW). Whilst this process can separate many recyclates from mixed waste, the resultant organic residue can contain high levels of heavy metals and physical and biological contaminants. This review assesses the potential end uses and sustainable markets for this organic residue. Critical evaluation reveals that the best option for using this organic resource is in land remediation and restoration schemes. For example, application of MSW-derived composts at acidic heavy metal contaminated sites has ameliorated soil pollution with minimal risk. We conclude that although MSW-derived composts are of low value, they still represent a valuable resource particularly for use in post-industrial environments. A holistic view including life cycle assessment should be taken when regulating the use of such composts, taking into account the specific situation of application and the environmental pitfalls of alternative disposal routes.

2.2 Introduction – The waste problem

The production of large amounts of Municipal Solid Waste (MSW) is an inevitable consequence of today's consumer society. Finding safe, sustainable and cost effective alternatives to the disposal of MSW in landfills represents a major challenge to the waste management industry. Recycling and composting are seen as

attractive waste management options, providing that there are few negative effects on the environment.

In many nations there are now strict mandatory targets to reduce the amount of Biodegradable Municipal Waste (BMW) entering landfill due to the lack of available landfill space and increasing concerns about climate change (EC, 1999). Further some countries also advocate that any waste that does enter landfill must first be treated to reduce its environmental impact. Treatments options include incineration (with landfill of the ash produced), separation of recyclable and compostable materials at source by householders etc, or the raw waste undergoing some form of Mechanical Biological Treatment (MBT), with the residuals being landfilled. Treatment is defined as physical, thermal, chemical or biological processes (including sorting) that change the characteristics of waste in order to reduce its volume or hazardous nature, facilitate its handling or enhance recovery (DEFRA, 2005). Where legislation requires that MSW must be pre-treated before landfill, it is expected that there will be a large increase in the amount of low grade compost produced. The use of lower quality composts such as MBT residuals has been questioned due to quality concerns (LGA, 2004). The purpose of this review is to critically evaluate MSW- and MBT-derived composts, covering their production, potential pollution issues and end uses.

2.3 Composting

Composting is defined as the biological decomposition of organic matter under controlled aerobic conditions to form a stable, humus-like end product (Epstein, 1997). The process is facilitated by a diverse population of microbes, whose population dynamics vary greatly both temporally and spatially, and generally involves the development of thermophilic temperatures as a result of biologically produced heat (Swan *et al.*, 2002). The organic matter used as compost feedstocks can range from garden and food waste to mixed household wastes, the biodegradable proportion varying from 50-90% depending upon country (Déportes *et al.*, 1995). Within the UK, it is currently estimated to be 68% but is predicted to fall to 54% by 2020 due to increased collection of source-segregated waste (SU, 2002).

Thermophilic aerobic composting on a commercial scale uses systems of varying complexity (Kwawe, 2002), of which there are essentially two main types:

turned or forced aeration systems. Turned systems are commonly based upon the windrow system, which entails the feedstocks being piled in elongated heaps up to 2 m high and 50 m in length (Swan *et al.*, 2002). These piles are turned with decreasing frequency throughout the period of active composting to maintain O₂ and moisture levels, and to release spent air. Turned windrows are predominantly used outside in open systems, however the process may also be undertaken indoors to allow waste containment and to prevent access from wild animals which have been implicated in pathogen spread from composts that are partway through the sanitisation process (DEFRA, 2008). Indoor systems also allow some process control in addition to minimising the visual impact, odour emissions and potential for bioaerosol release.

In contrast to turned systems, actively aerated systems are often more complex with computer controlled aeration regimes, and generally offer greater control over the process conditions. Having greater process control is often desirable with highly heterogeneous wastes such as MSW as this aids the operator in adapting the process to suit the chemical and physical makeup of the feedstock. In an optimised forced-aeration composting system, there are three main stages of composting (Stentiford, 1996; Swan *et al.*, 2002). The first stage is the 'sanitisation' stage, where vigorous aeration regimes are used to encourage rapid microbial breakdown of readily biodegradable substrate within the feedstock. The energy released during this rapid microbial respiration produces heat which typically raises the temperature of a compost vessel to >70°C (Kwawe, 2002). This stage is a requirement of most compost standards to ensure destruction of both plant and animal pathogens (WRAP, 2002). Whilst high temperatures are required for pathogen eradication (WRAP, 2002; DEFRA, 2004; Stentiford, 1996) this is not optimal for organic waste breakdown. Consequently, a secondary biodegradation phase of 45-55°C is required to facilitate rapid substrate degradation (de Bertoldi *et al.*, 1983). The tertiary phase for composting maturation is similar for both aerated and turned composts and requires little active management. Typically, this stage facilitates the conversion of potentially toxic NH₄⁺ to NO₃⁻, allows loss of phytotoxic volatile compounds and stabilisation of the microbial community. At this stage mesophilic fungi and actinomycetes colonise the compost which are thought to be responsible for the breakdown and transformation of humic substances and lignin (Swan *et al.*,

2002). This crucial final stage is frequently given insufficient time, or is even missed out altogether, in order to save space and increase the throughput of composting plants. However, it is a vital stage if the composts are to be applied to plants, and to improve the overall physical and chemical quality of the finished compost (Swan *et al.*, 2002).

With the exception of aerated static piles (Swan *et al.*, 2002), aerated systems are typically enclosed systems which permit a high level of process control. Consequently, these systems incur higher operational and capital costs in comparison to open piles (de Bertoldi *et al.*, 1983). Within many countries, enclosed, in-vessel systems are a legal requirement for composting wastes containing food and animal by-products (e.g., MSW-derived waste). Further, some countries (e.g., UK) require that sanitisation temperatures are met twice in a two-stage batch process to ensure complete pathogen kill (DEFRA, 2008).

Enclosed systems can be either static or agitated, and can have their air circulation tailored for optimisation of the different stages of composting. Forced aeration can be operated in three modes, either positive, negative or a mixture of the two (Stentiford, 1996). Using a mixture of the two aeration regimes gives flexibility of operation, allowing a wider range of moisture contents and carbon-to-nitrogen ratio wastes to be accepted. Under the correct conditions, MSW and MBT residues have been shown to compost effectively, behaving in a similar to green waste-derived composts. Further information detailing the process of composting and the numerous variables that affect the process can be found in de Bertoldi *et al.* (1983), Swan *et al.* (2002) and Sharma *et al.* (1997).

2.4 Municipal solid waste compost

2.4.1 Mechanical biological treatment (MBT)

The role of MBT in waste management is predicted to grow for the foreseeable future (WRAP, 2002). The primary aim of MBT plants is to recover a large percentage of recyclables from mixed waste streams (e.g., MSW and curbside collection schemes). Once this has been achieved, the main objective of the subsequent biological section of the treatment is to produce a material with low

environmental impact fit for disposal or land application (WRAP, 2002). Using a range of technologies, MBT plants are designed to separate all recoverable recyclables / energy rich waste with a typical screen cut off of > 40 mm (e.g., glass, plastics, paper, metals; Clemens and Cuhls, 2003). The fraction smaller than this is known as Mechanically Sorted Organic Residuals (MSOR), and is usually composted (Robinson *et al.*, 2004). The production of mixed-waste derived compost will increase as nations move towards meeting statutory targets.

Although mass reduction during composting can be between 20-40%, the expected increase in the volume of MSW composts poses a problem for disposal as most countries are suffering from ever diminishing landfill space. Its placement in landfill or use as landfill cover is not deemed sustainable, environmentally desirable or politically acceptable. Consequently, other disposal options are rapidly required. Indeed, the literature on MBT gives an incomplete picture of whether or not the biological treatment of wastes before landfilling is actually an environmentally sustainable option. Mature MBT residue compost has been shown to produce a “low impact” waste which yields 82% less greenhouse emissions than untreated landfilled waste (Adani *et al.*, 2004). Long maturing times (>6 months) may, however, prove inconvenient for plant operators due to storage costs and lack of space. In contrast to these results, Binner and Zach (1999) conclude that poor aeration at the start of the biostabilisation process can result in poor reductions in emissions. Their study only covered a period of 22 weeks, and postulated that even this length of composting would be prohibitive, given that the waste is only to be landfilled once processed and is therefore of no monetary value. If the MBT composts are landfilled they still produce gaseous and leachate emissions, albeit at a lower rate than for untreated waste (Zach *et al.*, 2000). Laboratory scale reactors have indicated that although leachates from MBT residues have a reduced BOD₅, COD and NH₄⁺ levels, they still posed an environmental risk (Zach *et al.*, 2000). In contrast, Robinson *et al.* (2004) found that levels of non-degradable COD are often higher in MBT-compost derived leachates than in standard methanogenic leachates. Despite the hope that MBT wastes will be suitable for ‘final storage’ style landfill sites, it is apparent that landfills containing MBT residues will require an aftercare period similar to conventional MSW landfill (i.e. 50-100 years after site closure). However, further research is required in

this area to assess the timescales in which management activities may be curtailed after the initial aftercare period.

In conclusion, optimised aerobic treatment of MBT-derived organic residues can effectively reduce the mass of material whilst also mitigating its potential to produce greenhouse gases and reducing leachate volume and toxicity if subsequently landfilled. However, given that landfill void space is a finite resource, alternative sustainable uses for the composts produced from mixed MSW must be sought.

2.4.2 Chemical properties of MSW and MBT derived composts

MSW is an extremely heterogeneous substrate, of which 50-70% is potentially biodegradable (Déportes *et al.*, 1995). There are however, major concerns over the quality of compost derived from MSW. Such wastes are expressly excluded from UK composting standards (BSI, 2005), and are restricted to use as daily cover on landfill sites in many countries, unless the resultant compost meets quality standards (WRAP, 2002), the most difficult of which being solids contamination. Such contamination by glass shards and non-biodegradable plastic fragments is inevitable in such a mixed waste, even with excellent source separation and pre-treatment. It is not only this physical contamination that poses a problem for potential users of MSW composts, however, as the material can also contain chemical and biological contaminants.

2.4.2.1 Heavy metals

High levels of heavy metals (e.g., Cd, Cr, Cu, Pb, Ni and Zn) in composts represent an obvious concern if they are to be applied to food crops (Gillett, 1992; Richard and Woodbury, 1992; Déportes *et al.*, 1995; Bhattacharyya *et al.*, 2001b). Heavy metals do not degrade throughout the composting process, and frequently become more concentrated due to the microbial degradation and loss of carbon and water from the compost (Richard, 1992). The levels at which these elements are found can vary from negligible background levels in 'clean' composts such as source-separated food waste, to potentially toxic levels in some mixed waste based composts. Table 2.1 summarises the total heavy metal contents of several MSW composts in comparison to current compost quality standards. It is clear that MSW

composts exceed the tolerable levels for most metals in comparison to UK standards (WRAP, 2002; BSI, 2005).

Table 2.1 Typical heavy metal concentrations of MSW, MSW-derived composts and legislative standards. All data in mg kg⁻¹

| Substrate / Standard | Cd | Cr | Cu | Hg | Ni | Pb | Zn | Reference |
|-------------------------------------|----|-----|-----|----|-----|-----|------|-------------------------------------|
| UK compost standard | 2 | 100 | 200 | 1 | 50 | 200 | 400 | BSI (2005) |
| Italian compost standard | 3 | | 300 | 3 | 100 | 280 | 1000 | WRAP (2002) |
| Green waste compost (mean, n = 336) | 1 | 46 | 51 | 1 | 22 | 87 | 186 | WRAP (2002) |
| Organic fraction of MSW | | 118 | 130 | | 12 | 113 | 263 | Zorpas <i>et al.</i> (2000) |
| Biowaste compost (mean, n = 28) | 1 | 26 | 96 | 1 | 24 | 86 | 289 | WRAP (2002) |
| Composted MSW (mean, n = 100) | 5 | 122 | 162 | 2 | 60 | 318 | 542 | WRAP (2002) |
| Composted MSW | 2 | 578 | 205 | | 45 | 335 | 1801 | Zorpas <i>et al.</i> (2000) |
| Composted MSW | 2 | | 153 | | | 274 | 520 | Bhattacharyya <i>et al.</i> (2001b) |
| Composted MSW | | | 346 | | 28 | 480 | 732 | Lasaridi <i>et al.</i> (2006) |
| Composted MSW | | | 272 | | 29 | 643 | 497 | Lasaridi <i>et al.</i> (2006) |
| Composted MSW | | | 286 | | 38 | 770 | 565 | Lasaridi <i>et al.</i> (2006) |
| Composted MSW | 4 | 324 | 756 | 1 | 134 | 337 | 743 | Kaschl <i>et al.</i> (2002) |
| Composted MSW | 3 | 21 | 170 | 1 | | 99 | 370 | Hincklenton <i>et al.</i> (2001) |
| Composted MSW | 2 | 11 | 270 | 1 | | 14 | 610 | Hincklenton <i>et al.</i> (2001) |
| Composted MSW | 7 | 83 | 548 | | 81 | 681 | 1325 | Marcote <i>et al.</i> (2001) |
| Composted MSW | 3 | 141 | 443 | | 104 | 545 | 920 | Albiach <i>et al.</i> (2000) |
| Composted MSW | 3 | | 120 | | | 310 | 340 | Breslin (1999) |
| Composted MSW | 1 | 24 | 53 | | 18 | 34 | 96 | Baldwin and Shelton (1999) |
| Composted MSW | 2 | | 362 | | | 385 | 396 | Pérez-de-Mora <i>et al.</i> (2006a) |
| Composted MSW | | | 128 | | 23 | 98 | 261 | Madrid <i>et al.</i> (2007) |
| Composted MSW | | | 312 | | 54 | 172 | 494 | Madrid <i>et al.</i> (2007) |
| Composted MSW | | | 244 | | 39 | 203 | 512 | Madrid <i>et al.</i> (2007) |
| Composted MSW + biosolids | 2 | | 320 | | | 250 | 660 | Breslin (1999) |

There are many sources of heavy metals within household waste many of which can pass through mechanical screens designed to remove non-biodegradable components (e.g., Ni, Zn and Cd containing batteries; Richard and Woodbury, 1992). The potential for contamination of MSW is exacerbated by the poor availability of

recycling facilities for hazardous wastes and poor public attitudes to waste management (Slack *et al.*, 2007). In addition to the obvious 'point sources' of heavy metals (e.g., batteries), other materials such as paints, electronics, ceramics, plastics and inks/dyes can all contribute to the heavy metal burden of MSW (Richard and Woodbury, 1992; Déportes *et al.*, 1995; Sharma *et al.*, 1997). Overall, however, information on the sources, quantities and behaviour of heavy metals and other hazardous substances in MSW is lacking (Slack *et al.*, 2004).

Total metal contents in compost are of concern when repeated applications to land occur (Pinamonti *et al.*, 1997). Field trials involving MSW compost application to soil have all reported an increase in soil and plant metal concentrations (e.g., Ni, Pb, Zn and Cu; Ramos and López-Acevedo, 2004). Generally, whilst increasing the overall heavy metal burden of the soil may be undesirable, application of composts poses little risk in terms of phytotoxicity or metal contents of crop tissue (Pinamonti *et al.*, 1997). This is probably due to the relatively small proportion of the heavy metal contained in the compost that are environmentally available (Greenway and Song, 2002). Metal bioavailability also reduces with length of composting due to several processes which bind metals including complexation and sorption with organic matter, microbial immobilisation and oxidation (Richard, 1992; Greenway and Song, 2002). Of these, humification of organic matter which creates sorption sites, is thought to be the primary mechanism affecting metal availability during the composting process (Wong and Selvam, 2006). Conversely, the amount of water-soluble organic carbon, which complexes metals rendering them non-bioavailable, tends to decline during composting (Castaldi *et al.*, 2006). It is therefore clear that the compost needs to be mature to ensure that heavy metal availability is reduced, particularly as partially oxidised composts are known to reduce crop yields (Lisk *et al.*, 1992). In conclusion, while some concerns have been raised about potential disruption to localised ecosystem functioning (Gillett, 1992), there is also a great deal of evidence to suggest that dilution factors of soil and water reduce this risk to a minimum (Déportes *et al.*, 1995). The risk of metal contamination from MSW-derived composts is of similar magnitude to that posed by biosolids application to land which is now a widely accepted practice.

2.4.2.2 Organic pollutants

Compost feedstocks are known to contain significant levels of various organic contaminants, including polynuclear aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins / polychlorinated dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) (McGowin *et al.*, 2001), however, there is still scant information on their concentrations and behaviour in MSW-derived composts (Houot *et al.*, 2001). These organic contaminants can have a pronounced mutagenic and carcinogenic potential, and can be extremely persistent in the environment. In addition, some compounds such as PAHs are barely affected by abiotic degradation processes such as hydrolysis and photodegradation (Lazzari *et al.*, 2000). Kitchen wastes and organic household wastes are expected to be contaminated with Persistent Organic Pollutants (POPs) due to co-disposal with non-biodegradable wastes (e.g., plastics and electrical equipment; Brändli *et al.*, 2005; Fig. 2.1). In a range of green waste composts, the median PAH concentration was 1.7 mg kg^{-1} , as opposed to 1.9 mg kg^{-1} in composted MSW suggesting little difference. Similar results were also obtained for PCBs and PCDD/Fs (Brändli *et al.*, 2005). As yet no international standards exist for organic pollutants in compost. It also remains difficult to compare studies due to differences in sample preparation and instrumentation used in analysis. Further, our experience is that the multitude and complex nature of organic compounds in compost makes the potential for experimental bias and error extremely large (e.g., incomplete extraction, compound misidentification and inaccurate quantification). Despite these reservations, Houot *et al.* (2001) demonstrated generally low levels of PAHs in 24 industrial composts, with levels below those permitted for biosolids destined for agricultural land. Current evidence suggests that composting is crucial for reducing the pollutant load of MSW and MBT residues. The initial thermophilic phase is suitable for removing volatile pollutants whilst other more labile compounds are broken down by bacteria and actinomycetes (e.g., low MW PAHs; Amir *et al.*, 2005). The final maturation phase, where mesophilic fungi become prevalent, is the most effective for the removal of more recalcitrant POPs (e.g., high MW PAHs; Houot *et al.*, 2001). Many POPs also become bound into hydrophobic organic residues during the composting phase making them less bioavailable at least in the short term (Loick *et al.*, 2008).

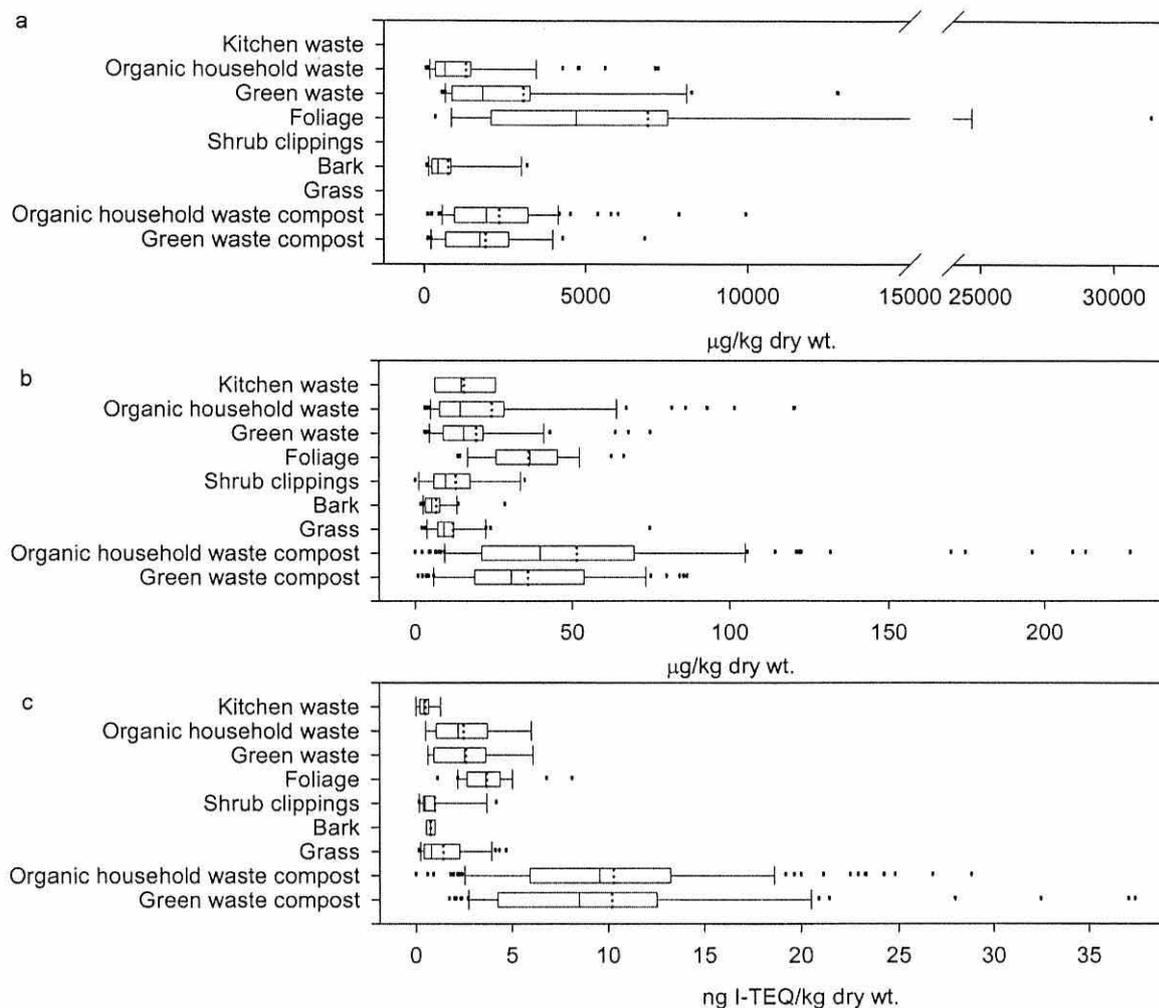


Figure 2.1 PAHs, PCBs and PCDD/Fs - Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values. Figure 2.1(a): Sum of 16 USEPA polycyclic aromatic hydrocarbons (Σ 16 PAHs; $\mu\text{g}/\text{kg}$ dry wt.) in kitchen waste (not available [NA]), organic household waste ($n = 69$, one study only), green waste ($n = 31$), foliage ($n = 13$, one study only), shrub clippings (NA), bark ($n = 18$, one study only), grass (NA), compost containing organic household waste ($n = 78$), and compost originating from green waste ($n = 23$). Figure 2.1(b): Sum of six polychlorinated biphenyls (Σ 6 PCBs; $\mu\text{g}/\text{kg}$ dry wt.) in kitchen waste ($n = 8$, one study only), organic household waste ($n = 82$), green waste ($n = 41$), foliage ($n = 29$), shrub clippings ($n = 12$, one study only), bark ($n = 20$), grass ($n = 39$), compost containing organic household waste ($n = 124$), and compost originating from green waste ($n = 55$). Figure 2.1(c): Sum of 17 polychlorinated dibenzo-*p*-dioxins and -furans (Σ 17 PCDD/Fs; ng international toxicity equivalent [I-TEQ]/kg dry wt.) in kitchen waste ($n = 9$, one study only), organic household waste ($n = 9$), green waste ($n = 9$), foliage ($n = 28$), shrub clippings ($n = 12$, one study only), bark ($n = 4$), grass ($n = 36$), compost containing biowaste ($n = 124$), and compost originating from green waste ($n = 61$). (Brändli *et al.*, 2005)

In conclusion, composting provides a critical step in the treatment of MSW and MBT residues for organic pollutant removal, however, our understanding is lacking in several key areas. Firstly, the amount and concentration of many POPs and their temporal and spatial variability has yet to be established both within the feedstock material and the resulting compost. Secondly, the optimal conditions for organic pollutant removal during composting have yet to be established preventing effective management and the formulation of industrial guidelines. Thirdly, the relative importance of the mechanisms by which organic pollutants are made less available (volatile phase, solid phase immobilisation, microbial breakdown) needs investigation to assess whether further technological advancements can be made to enhance their removal.

2.4.2.3 *Endocrine disruptors*

Endocrine disrupting chemicals (EDCs) are ubiquitous in the environment (van der Kraak, 1998), due mainly to industrial (pharmaceuticals, plastic softeners etc) and agricultural activity. They are responsible for reproductive defects and disruption of the endocrine system in both aquatic and land animals and typically only very low concentrations are required to trigger environmental damage. It is likely that MSW compost will contain a plethora of both natural and synthetic EDCs. There has been little work studying the degradation of EDCs during composting, and this is an area for further research. In the case of compost feedstocks, MSW may contain less EDCs than composts containing biosolids or animal manure. Hakk *et al.* (2005) concluded that the natural EDCs 17 β -estradiol and testosterone were reduced by composting, but that their degradation was incomplete, allowing leaching to take place after land application.

Whilst estrogens and testosterone are of concern in composts, industrial products and pharmaceuticals such as phthalate esters, ibuprofen and 4-nonylphenol may also be present in relatively high quantities in mixed wastes (Buyuksonmez and Sekeroglu, 2005). Zhang *et al.* (2007) report that bacteria capable of degrading bisphenol A (an important chemical intermediate in the manufacture of many plastic-based products) have been isolated from MSW compost leachates, indicating that

composting may be effective in reducing its concentration in MSW. Bagó *et al.* (2005) investigated the effect of composting on the concentration of di-(2-ethylhexyl)phthalate (DEHP) in sewage sludge for agricultural land application, concluding that again, composting significantly reduces levels of this artificial EDC. In contrast, however, a study by Patureau *et al.* (2008) has indicated that EDCs increased following biosolids composting indicating that the behaviour of EDCs in MSW may be difficult to predict. We conclude from the work of Buyuksonmez and Sekeroglu (2005), Bagó *et al.* (2005), and Zhang *et al.* (2007) that composting MSW and MBT residuals may provide an effective mechanism for reducing and removing EDCs from primary wastes. However, the study by Patureau *et al.* (2008) clearly highlights the need for an integrated approach in assessing EDC behaviour in these matrices.

2.4.2.4 Nutrients

Whilst the low quality nature of MSW composts is largely attributed to physical contaminants in the mixed waste stream, it is undeniable that these composts contain a significant amount of both slow and quick release nutrients (Table 2.2, Crecchio *et al.*, 2001). Indeed, in many cases the levels of nutrients can be so high that they inhibit plant growth by inducing osmotic stress or NH_4^+ toxicity. The high level of inorganic salts in the composts is caused by the often protein rich feedstock material and their intrinsically high rates of biodegradation, a process that releases inorganic nutrients. For this reason, pure MSW composts often perform poorly in comparison with 'higher quality' peat-based composts (Murillo *et al.*, 1995; Manios, 2004; Bhattacharyya *et al.*, 2001a). Whilst these factors may inhibit the use of pure MSW composts for containerised horticulture and arboriculture, the nutritive value of MSW composts can be utilised quite effectively, particularly if diluted with a relatively inert mineral material. For example, a study comparing blends of MSW composts with peat and composted pine bark found that a blend of 75% MSW compost and 25% composted pine bark actually increased the growth of *Lepidium sativum* over a control treatment using 100% peat (Moldes *et al.*, 2006). Similarly, Manios (2004) also recorded a positive effect on the yield of tomatoes after three additions of MSW compost compared to an unamended control treatment. They recommend an

optimal compost application limit of 50-70 t ha⁻¹. This is supported by Tambone *et al.* (2007) who noted that soil N and P content, as well as pH were increased by an application rate of 85 t ha⁻¹. Importantly, this was achieved without a significant increase in available heavy metal concentrations in either the plant tissue or soil. Similarly, food crops grown after MSW compost application have shown little accumulation of heavy metals in the soil and crop (Ozores-Hampton *et al.*, 2005). In conclusion, composts derived from MSW and MBT residues are rich in a wide range of plant-available nutrients which can significantly enhance plant growth. In addition, the high level of some nutrients (e.g., Ca²⁺) can also suppress the uptake of heavy metals present in the compost. However, it must also be noted that these heavy metals can similarly constitute a valuable source of micronutrients (e.g., Cu, Zn) particularly in high pH environments (e.g., calcareous soils).

2.4.2.5 Biological contaminants

Hazards to human health associated with the application of MSW composts to land have received relatively little attention. Composts are known to contain a wide diversity of microorganisms of which most are harmless. Some human pathogenic strains of *Escherichia coli* and *Salmonella* have, however, been reported to be present even in green waste compost, due to contamination with faecal matter (Droffner and Brinton, 1995; Williams *et al.*, 2006). Although total coliforms and *Salmonella* spp are often used as indicator organisms to check for complete compost sanitisation (BSI, 2005), it must be recognised that most strains of *E. coli* and *Salmonella* are actually non-toxic to humans.

Table 2.2: Typical nutrient content of MSW and other composts. All data in mg kg⁻¹ dry mass unless otherwise stated

| Compost type | K (mg kg ⁻¹) | P (mg kg ⁻¹) | C:N ratio | Total N (g kg ⁻¹) | NH ₄ ⁺ (mg kg ⁻¹) | NO ₃ ⁻ (mg kg ⁻¹) | OM (%) | EC (dS cm ⁻¹) | pH | Reference |
|-----------------------|-----------------------------|-----------------------------|--------------|----------------------------------|--|--|-----------|------------------------------|----|---------------------------------|
| MSW compost | | | 30 | 21 | | | | | | Crecchio <i>et al.</i> (2004) |
| MSW compost | 3390 | 2817 | 16 | 11 | 71* | | | | | Wolkowski (2003) |
| MSW compost | 5559 | 3281 | 12 | 14 | 122* | | | | | Wolkowski (2003) |
| MSW compost | 4100 | 5000 | 9 | 14 | | | 33 | 7 | 8 | García-Gil <i>et al.</i> (2000) |
| Pruning waste compost | | | 33 | 10 | 8.27 | 16 | | 0 | 8 | Benito <i>et al.</i> (2003) |
| Manure compost | | | 12 | 25 | 510 | 2372 | | | 7 | Han <i>et al.</i> (2004) |

*Total mineral nitrogen i.e. NH₄⁺ + NO₃⁻

The main sources of pathogenic microbes in MSW are nappies, pet litter and food residues (Dimambro *et al.*, 2007). In one study, Déportes *et al.* (1998) found more than 40 pathogenic viruses, bacteria, fungi, protozoa and helminths. They concluded that when carried out correctly, composting can provide an efficient mechanism for MSW disinfection. Similarly, Dimambro *et al.* (2007) also reported low levels of faecal coliforms in several MSW composts with *Salmonella* spp. being absent completely. Droffner and Brinton (1995), however, found that *Salmonella* and *E. coli* survived for more than five days at 55°C in a mixed compost including biosolids, food waste and yard trimmings, and recommended that composting temperatures must exceed 55°C for a period of at least two weeks to ensure pathogen removal. British standards for in-vessel composting of waste containing food waste dictate that temperatures of greater than 60°C must be met for 48 hours in two consecutive vessels before a compost can be declared safe (BSI, 2005). It is important that these temperatures are reached throughout the compost pile, as both *Salmonella* and *E. coli* have been found to develop increased thermal tolerance when exposed to sub-lethal heat shock and can quickly re-infect the compost in the later maturation phase (Droffner and Brinton, 1995). In conclusion, provided that MSW composting is carried out correctly and conforms to temperature standards (e.g. BSI, 2005), we conclude that there is little risk to human health from feedstock-borne pathogenic organisms.

2.5 Uses of MSW derived composts

Several potential end uses exist for MSW derived composts. One rather extreme study has evaluated the potential use of municipal wastes as an animal feedstuff (García *et al.*, 2005). In this investigation, the authors concluded that after heat treatment (65°C for 20 min) all the wastes were effectively sanitised and suitable for animal consumption. However, this is almost certainly unable to eradicate Transmissible Spongiform Encephalopathies (TSE) and other zoonotic diseases present in the material. In addition, the household waste tested in their study also contained higher levels of Pb and Cd than are permitted in animal feedstuffs within the EU. Regardless as to whether or not MSW could theoretically be legally and safely used in the production of animal feedstuffs, this would not be a socially acceptable practice. With the exception of this animal feedstuff study, most research has focused

on land application of MSW-derived composts with very few other novel uses currently documented.

2.5.1 Agriculture

Agronomic and horticultural use represents a large potential market for MSW compost (Shiralipour *et al.*, 1992). The nutritive value of MSW composts and their potential to enhance soil quality makes them ideal for agriculture, provided that correct precautions are taken to mitigate against environmental damage and to gain public acceptance. The addition of compost to agricultural land may unnecessarily increase the heavy metal content of the soil (Ramos and López-Acevedo, 2004). At normal application rates, however, there is little risk to plants or the wider environment (Greenway and Song, 2002). When applied to land, these residues have the potential to significantly increase soil organic matter (SOM) contents, an aspect that is in critical decline in many regions of the world, particularly in more arid environments (Bellamy *et al.*, 2005). Maintaining and increasing soil organic matter stocks, a key soil quality indicator, is now seen politically as a key priority for preserving ecosystem function. Numerous trials have shown that addition of MSW compost to soil can at least transiently increase SOM contents as well promoting soil biological activity. Additional benefits of compost addition also include reduced erosion losses, a decrease in bulk density and improved structural stability (Tejada and Gonzalez, 2007). Ultimately, however, almost all of the compost residues will be mineralised and repeated applications may be necessary to preserve SOM levels. Therefore, from a disposal perspective soils potentially represent an almost infinite sink for organic residues.

Regardless of the risks of heavy metal pollution, if applied in moderation MSW compost can improve nutrient availability and plant uptake in agricultural soils. MSW compost can provide similar amounts of P to mineral fertilisers in some soils (Mkhabela and Warman, 2005). However, inorganic N should be added due to the slow release nature of the predominantly organic N within the compost. It has been estimated that only 5-15% of the total N contained in composts is available to plants in the first year of application, falling to 2-8% in the second year, with N

mineralisation dynamics primarily determined by the relative soil and compost carbon-to-nitrogen ratio, soil texture and water holding capacity (Amlinger *et al.*, 2003). For typical application rates of 10-100 t ha⁻¹, the uncertainty over nutrient availability during a cropping season also makes it difficult to accurately predict crop demands and therefore optimal compost application rates in comparison to conventional inorganic fertilisers. In a study investigating the growth and nutrient content of maize under different additions of MSW compost, Tambone *et al.* (2007) found that although yield did not increase over their control treatment, maize grains from compost-treated plots were enriched in C, N and P as a result of the increased nutrient status of the soil. Similarly, Zheljzkov *et al.* (2006) found that MSW compost produced comparable yields to chemical N addition, and improved forage yields over solid manure addition. Quality of the crop (fibres and energy), and residual nitrates were similar to those from the inorganic treatment.

It is not just the chemical properties of composts that are of interest, however. Soil degradation is a major environmental issue globally, leading to large potential threats to both present and future crop yields (Pagliai *et al.*, 2004). Organic matter is central to erosion resistance, long term fertility (Ros *et al.*, 2006), and also indirectly affects the interactions between the soil and the air and water within the soil through its effects on the soil physical structure (Pagliai *et al.*, 2004). In an experiment on an alluvial calcisol, Pagliai *et al.* (2004) demonstrated that the addition of compost to a sorghum field greatly improved soil structure, compared to the unamended control. In a constructed seed bed experiment, Bresson *et al.* (2001) also showed that MSW compost delayed soil water runoff, reducing the risk of soil erosion and flash floods in susceptible catchments. Their work demonstrated that these outcomes are caused by an interaction effect between the compost and the soil, and not simply an effect of the change in soil bulk density as a result of incorporating the lighter organic substrate. Similarly, Tejida and Gonzalez (2007) found that although cotton and olive waste composts were superior, MSW compost did yield improvements over the unamended control in terms of reduced soil loss and improved structural stability. Using statistical approaches, they found that improvements in soil structure were strongly correlated with compost humic acid content. If MSW composts are left to mature for long periods of time, they may be of greater benefit to soils in terms of

structural stability, given that compost humic acid content and complexity increases with composting time (Huang *et al.*, 2006).

In addition to erosion reduction and increased soil stability, the addition of composts to agricultural soils has been found to increase the water holding capacity of soils (Shiralipour *et al.*, 1992). The application of two paper-based composts increased the amount of water held both at field capacity (-0.05 MPa) and permanent wilting point (-1.5 MPa) in a loamy sand soil (Foley and Cooperband, 2002). Since the increase in water held at field capacity increased to a greater extent than at wilting point, it can be inferred that plant available water increases following compost addition to soil. Another study by Mamo *et al.* (2000) on the growth of maize on a loamy sand soil using MSW composts produced mixed results, increasing the soil water holding capacity without greatly increasing the estimated plant available water within the soil. They concluded that increases in water stress in the corn may also be due to increased salt loading in the soil due to the relatively high electrical conductivity of the compost. However, one year after the application of MSW compost, soil water content increased, along with corn yield, and an associated reduction in plant water stress. There is unfortunately a shortage of data on the effects of different compost amendment regimes on plant available water within soils, and further research is required in this area. With future changes to climate and rainfall patterns, this area of research will become increasingly important. Green waste-derived composts have been shown to reduce plant pathogen infection in a range of plant species, however, no such trials have been done with MSW-derived composts. Similarly, there are few integrated studies that consider changes in soil quality with MSW compost addition alongside potential benefits in crop yield and quality, economic benefits from changes in water and fertiliser use, and environmental effects in terms of primary resource use and greenhouse gas emissions. There is therefore a clear need to undertake a holistic Life Cycle Assessment (LCA) of the use of MSW compost in agricultural systems in comparison to conventional agronomic practices.

2.5.2 Horticulture

Recently, there has been increasing concern over peat extraction and the destruction of peatlands by the horticulture industry and consequently viable alternatives to peat are urgently needed (Cruickshank *et al.*, 1995). MSW compost provides one alternative as it is intrinsically rich in organic matter and nutrients and benefits from dilution with peat to reduce its electrical conductivity (Silva *et al.*, 2007). The major obstacle to its use, however, is the large amount of other higher quality green waste-derived composts which are "flooding" the marketplace. The potential for MSW compost use in containerised horticulture therefore remains extremely limited. In field horticulture, however, there are greater market opportunities although its use on root crops and salads is unlikely due to the potential for physical contamination. The success of MSW compost use in field horticulture has been demonstrated by Obreza and Reeder (1994) who showed that the yield of field-grown tomato increased by 16% and watermelon by 54% when grown on a sandy soil in successional rotation. Although green waste composts have been proved useful in maintaining soil moisture and in plant disease suppression, no parallel studies with MSW compost have yet been performed. An LCA of compost use in horticulture is also urgently required to ascertain its overall environmental benefit in comparison to other fertilisers or organic supplements.

2.5.3 Remediation

2.5.3.1 Re-vegetation of blocky mineral wastes

Mineral waste tips composed of non-toxic blocky hard rock waste (> 95% stones > 10 cm diameter) are often uninhabitable to plants and animals due to their inherent lack of nutrients and exceedingly poor water holding capacity (Rowe *et al.*, 2005). Such waste tips are common worldwide, and their natural attenuation and restoration can ultimately take many hundreds of years (Yuan *et al.*, 2006). One of the major obstacles to restoration of these sites is the lack of finely textured substrate which is capable of retaining water and providing nutrients. Waste-derived composts can potentially provide a cost effective and practical solution to this problem

providing that they can be sourced locally and applied safely without subsequent risk of water and wind erosion (Jones *et al.*, 2009). While green wastes have been employed successfully to restore such sites, no published material exists on the use and success of MSW composts in large scale restoration schemes. This is mainly due to current legislative constraints preventing the spreading of MSW compost. In addition, both Rowe *et al.* (2005, 2006) and Yuan *et al.* (2006) agree that difficulties in site evaluation and investigation, as well as the vast sums of money required for engineering solutions (e.g., slope re-grading) are often prohibitive to scientific investigation and practical outcomes. Recently however, there has been increased interest in the revegetation of inert waste tips, especially how to sensitively and sustainably recreate the natural vegetation of the surrounding area without destroying other habitats to obtain topsoil or peat for restoration. Theoretically, there is no reason to prohibit the use of MSW-derived composts for the restoration of blocky mineral wastes. In addition, they may offer benefits for the restoration of oligotrophic habitats as they can possess a lower nutrient content than conventional green waste or sewage sludge derived composts, particularly if they can be blended with a relatively inert mineral material (e.g., rock dust).

In the case of finer textured mineral waste, the constraint to restoration is rarely substrate water holding capacity but rather lack of nutrient capital required to sustain plant growth. As inorganic fertilisers are prone to rapid loss by leaching, composts offer a better solution in that they provide an instantaneous supply of nutrients (those held in solution and on exchange sites etc) alongside a long-term supply created as the compost breaks down. One potential issue is that there should not be excessive paper based material in the initial MSW feedstock as this may transiently lock up nutrients (e.g., N and P) limiting plant growth in the short term. However, based upon published C-to-N ratios of MSW compost (Table 2) this is unlikely to occur.

The early stage of plant colonisation is crucial for the restoration of mineral waste (Rowe *et al.*, 2006; Yuan *et al.*, 2006). Initial imbalances or excesses in compost nutrient availability or pH compared to the surrounding natural habitats may severely alter the restoration trajectory for above- and below-ground species ultimately leading to low diversity and a negative ecological site value. Whilst increasing plant

cover on such sites may be considered an aesthetic improvement in comparison to 'bare' rock spoil, it must be remembered that these tips may already support a highly diverse and rare floral and faunal community which will be lost when the process of anthropogenic restoration starts. Therefore current advice suggests that blanket coverage is often not environmentally desirable and that restoration with MSW composts should take a more patchwork approach that creates a mosaic of habitats.

In conclusion, MSW-derived composts may provide a low cost solution to the remediation of post-industrial mineral waste sites and for use in the restoration of brownfield sites (e.g., landfill capping after closure) where quality and public perception are not a high priority. They are, however, unsuited for use in restoration schemes where public access is likely (e.g., new housing schemes, public parks etc) due to health and safety concerns (e.g., glass shards). Further, field trials are clearly required to evaluate the benefits and environmental risk posed by using MSW composts in comparison to other substrates used for restoring non-contaminated land (e.g., biosolids).

2.5.3.2 Remediation of heavy metal contaminated sites

Considering the large environmental and economic cost associated with cleaning up land contaminated with heavy metals using conventional strategies (e.g., excavation followed by landfill), it is not surprising that alternative technologies are being sought for metal decontamination. This search has recently accelerated due to the legislative pressures in some countries preventing contaminated soil from entering landfill. There are several references to the use of MSW composts in the remediation of heavy metal contaminated sites (Pérez-de-Mora *et al.*, 2006ab). The main environmental issues associated with heavy cleaning up metal contaminated land are: (1) the prevention of vertical and horizontal movement to protect surface and ground water, (2) minimising metals entering the food chain (e.g., plants, animals), and (3) minimise wind erosion and exposure to dust. Theoretically, MSW compost application to contaminated land should be capable of positively addressing all three of these issues.

Water migration of heavy metals in contaminated soil is largely dependent on the soil's pH, redox status and organic matter content (Strobel *et al.*, 2005). MSW compost application is known to add nutrients, raise soil pH and increase soil organic matter and humic substance levels. Its application should also help aerate the soil increasing the redox status of the soil facilitating the precipitation of metal oxyhydroxides. While composts cannot remove metals from the soil they can stabilise or immobilise them on the solid phase. This is achieved by alkalinising the soil thereby inducing metal precipitation and also by binding metals on the added organic matter (Chang Chien *et al.*, 2007). Heavy metal contamination is typically only a major environmental problem in acid soils and therefore it is unlikely that MSW composts would be used for metal alleviation in calcareous soils unless extremely contaminated. Care must also be taken to ensure that well humified wastes are preferred to immature composts, which contain much higher levels of soluble organic carbon, yet lower levels of humified substances.

Unlike agricultural and horticultural uses, where the relatively high metal content of 'poorer quality' MSW composts may lead to the unwanted accumulation of heavy metals in soil and plant tissues (Hargreaves *et al.*, 2008), contaminated soils frequently contain heavy metals in concentrations greatly in excess of those applied in MSW composts. This therefore diminishes any possible pollution risks caused by their application to soil. This is supported by an investigation using sequential chemical extraction methods which found that only small fractions of compost-derived trace elements were bioavailable in comparison to that present in the contaminated substrate (Pérez-de-Mora *et al.*, 2007b). Current evidence suggests that trace metal inputs from organic amendments are largely immobile and pose little risk to the environment (e.g., via leaching or plant uptake processes). This extraction approach, however, has been criticised as a method to assess metal bioavailability as no single extraction protocol is suitable for all metals and substrates (Tandy *et al.*, 2005). Whilst most extraction methods seem not to accurately reflect bioavailability of heavy metals (Menziez *et al.*, 2007), an exciting prospect for heavy metal pollution risk assessment is the combination of either single or sequential extractions with stable isotope heavy metal analysis (Bacon and Davidson, 2008). A comparison of the isotopic signatures of MSW compost, soil chemical extracts and associated plants

would reveal the whether the MSW compost was directly (i.e. MSW derived metals) or indirectly (i.e. by mobilising soil derived metals) enhancing plant metal accumulation. Given that bioremediation by composts is based mainly on the binding and sorption of toxic elements to the compost, and not their actual removal from soil (Kiikkila *et al.*, 2002), it must also be noted that measurements of substrate total metal content are inappropriate for policy formulation. These studies imply that the only absolute way to quantify risks of metals entering the food chain is to directly analyse plant metal accumulation.

The success of compost use in metal remediation schemes can also vary spatially and temporally. This is typically due to the composts interactions being context specific (i.e. dependent on many factors such as changes to the physical structure of the soil, its water holding capacity, and changes in microbial community function and structure, as well as direct chemical changes such as pH buffering and chemical sorption of metals all of which are time dependent). This is exemplified by the container study of Pérez-de-Mora *et al.* (2006b), who showed initial increases in grass growth and reductions in shoot metal accumulation one year after MSW compost addition (Cd, Cu, Zn and Pb), however, no differences in growth or metal content were observed in the subsequent 2 years in comparison to areas receiving no compost. Despite their potential, there is still a paucity of work describing the use of MSW composts for remediating heavy metal contaminated sites, particularly at a field-relevant scale. The main concerns over the use of these composts are uncertainty of risk of the added burden of heavy metals to the soil. New techniques such as isotope tracing and more rigorous biochemical assays are therefore required to provide definitive evidence that they pose minimal environmental hazard.

2.5.3.3 Remediation of organically polluted sites

When directly incorporated into soil or applied as a surface mulch, green waste-derived composts have been shown to stimulate microbial activity and the biodegradation of a range of organic pollutants in soil. Composts also have the potential to chemically immobilise (POPs) making them less prone to leaching and plant uptake. Despite their potential, however, there have been few published

reports on the use of MSW compost to remediate organic compounds in soil. To date, the main field of study has concentrated on the practice of *ex-situ* co-composting of PCB and PAH contaminated soil using bespoke green waste mixtures (Antizar-Ladislao *et al.*, 2005), bark chips and straw compost (Laine and Jørgensen, 1997), mushroom compost mixture (Šašek *et al.*, 2003) and corn cobs with manure or biosolids (Potter *et al.*, 1999). These trials all suggest that composting is an effective method for the reducing the POP load of contaminated soil, regardless of soil or contamination type. As compost feedstock type also had negligible effect on the degradation of POPs, it would indicate that MSW composts could play an active role in this area. Antizar-Ladislao *et al.* (2005) found that optimal POP biodegradation occurred at 38°C, however, significant losses also occur at lower temperatures. One major problem is that after an initial rapid mineralisation phase the rate of POP greatly slows leading to incomplete removal which still may not comply with statutory decontamination limits. This is probably due to the POPs binding to the surface of the organic materials making them poorly bioavailable (Potter *et al.*, 1999).

Whilst composting may greatly reduce the concentration of POPs in contaminated soil, rarely do they completely remove pollutants. To enhance their effectiveness we suggest that MSW compost applications need to be actively combined with other bioremediation and phytoremediation based technologies.

2.6 Conclusions and recommendations

It is clear that volumes of MSW composts are likely to increase in many countries and that we urgently need sustainable ways for their disposal. From a legal viewpoint, composts derived from MSW remain *wastes* (rather than compost) even after successful processing to remove pathogenic microbes and organic matter stabilisation. This can be due to the risk from heavy metals and organic pollutants alongside the physical risks from sharps, glass shards, and the aesthetical problem of plastic scraps that remain highly visible even after the composting process. This legal barrier prevents the wholesale application of MSW composts to agricultural/horticultural land (potentially the largest market for composts), despite strong evidence of increases in soil and crop quality after application. Although, there is a risk that the application of MSW compost will increase the heavy metal content of

agricultural soils, we conclude that there is limited risk of excessive plant uptake and environmental damage. In contrast, MSW composts have the potential to play an extremely beneficial role in the remediation and regeneration of a variety of contaminated and post-industrial sites. Further, if composting is carried out optimally, the practice should carry very low biological risk from pathogens.

MSW composts can increase plant yield on post-industrial sites and enhance soil quality and structural stability reducing the risk of soil erosion. In the case of contaminated sites, the heavy metal content of MSW composts is typically very low in comparison to that already present on site. In addition, the metals contained in the MSW are poorly bioavailable nullifying the 'risk' of applying contaminated compost. Due to the chemical risks presented by MSW composts, their wholesale use is unadvisable without proper investigation into the contaminant levels and an associated full risk assessment for use on the target land area. Despite the dearth of studies, most investigations report positive benefits of MSW compost use in remediation schemes, however, further field-scale trials are required. This underpinning knowledge is especially needed if changes in the legislative framework are to be made to permit its widespread use. In addition, more work is needed to assess the concentration and behaviour of organic pollutants both present within the MSW composts and on application to contaminated soil. Given the current waste management options of either landfill or incineration of MBT residues, a life cycle assessment of these different strategies is also required to evaluate the benefits of applying MSW compost to land. This should be balanced against a holistic risk assessment for use in different land use sectors.

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CHAPTER 3: HEAVY METAL CONTAMINATION OF A MIXED WASTE COMPOST: SPECIATION AND FATE

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Richard Furniss assisted in the sampling and laboratory analysis of the composting phase of this work. However, all experimental design, data processing and writing was carried out independently.

3.1 Abstract

We successfully composted a high C-to-N ratio mixed biodegradable municipal solid waste (MSW) feedstock on its own and in combination with green waste. Changes in heavy metal speciation throughout the composting process were studied using the modified BCR sequential extraction protocol. We found that total Cu, Pb and Zn concentrations increased over time due to the progressive mineralisation of the compost feedstock. Metals were fractionated differently within the two feedstocks, although only Cu showed significant redistribution (mostly to the oxidisable fraction) over the 5 month composting period. We examined the performance of the MSW-derived composts in a series of plant growth trials, and found that it performed comparably with other commercially available composts. Plant metal accumulation was not influenced by the heavy metals present in the MSW-derived compost implying that they are not plant available. We recommend the use of these relatively low value/quality composts for remediation of acidic heavy metal contaminated sites.

3.2 Introduction

Identifying the most sustainable disposal route for Municipal solid waste (MSW) remains an important issue in almost all industrialised countries due to a range of legislative, environmental and economic and social drivers (Adani *et al.*, 2000). European Union (EU) Council Directive 1999/31/EC (EC, 1999) on the landfill of waste has set down strict mandatory targets for reduction in the amount of Biodegradable Municipal Waste (BMW) reaching landfill. The EU directive also states that no waste may be deposited in landfill without it first being treated in some way. Mechanical Biological Treatment (MBT) is a generic term for the treatment and separation of mixed solid wastes into reusable and recyclable fractions. Thermophilic composting can be used to treat the residual organic fraction from the MBT process, to produce a stabilised compost-like substance (Binner and Zach, 1999). Whilst according to EC (1999), this is suitable for landfill, it is desirable to find alternative uses for this mixed waste 'compost'. As soil organic matter levels have declined to critical levels in many regions of the world (Dregne, 2002), it is advantageous to use this 'waste' organic matter to replenish soil reserves. However, this application must occur without unduly increasing the loading of contaminants onto unpolluted soils (Tandy *et al.*, 2008).

Heavy metals such as Cd, Cu, Pb, Ni and Zn are found in all composts, and there are obvious concerns about such toxic elements entering the food chain through food crops to which composts have been applied as fertiliser (Gillett, 1992). Heavy metals do not degrade throughout the composting process, and can become concentrated due to the loss of carbon and water from the compost through microbial respiration (Richard, 1992). In order to regulate the application to land of potentially contaminating composts, standards such as the PAS100 in the UK (BSI, 2005) have been developed. Whilst these standards provide useful guideline total values for heavy metal levels, these fail to take into consideration the availability of heavy metal contaminants within the composts, and may significantly over-estimate the potential risk. When properly executed, the aerobic composting of organic wastes has the ability to immobilise the exchangeable pool of heavy metals within an organic waste (Paré *et al.*, 1999). Sequential extractions such as those proposed by Tessier *et al.* (1979) and Ure *et al.* (1993) can be used to investigate changes in the speciation of

heavy metals during the composting process (Greenway and Song, 2002), and should provide a more accurate measure of risk to the environment than that of total levels.

It is widely accepted that no single chemical extraction procedure can truly represent the phytoavailability of individual heavy metals in soil (Tandy *et al.*, 2005; Menzies *et al.*, 2007). Consequently, other techniques such as microbial biosensors and plant bioassays can be used to assess the risk of compost-borne heavy metals entering the food chain (Tandy *et al.*, 2005). Whilst 'standard' plant species can be used as bioindicators of metal availability / toxicity and can provide an immediate measure of phytoavailable levels of heavy metals, this approach is somewhat limited by the wide genetic variability in metal accumulation that exists both within and between species (MacNair, 2002). An alternative approach for assessing phytoavailability is to use metal hyperaccumulator species such as *Thlaspi caerulescens* which have a high demand for metals (Brooks, 1998). These plants are capable of tolerating high metal concentrations, and in the case of the *T. caerulescens* Ganges ecotype, high levels of Cd and Zn in particular. The roots of *T. caerulescens* contain a high density of Zn transporters and demonstrate active root foraging, yet they do not enhance metal mobilisation by root exudation (Zhao *et al.*, 2001). In a study of a sewage sludge treated soil and a polluted mine spoil, Hutchinson *et al.* (2000) demonstrated that *T. caerulescens* could not mobilise metals which chemical extracts indicated was potentially bioavailable.

To assess the changes to metal speciation during the composting of mixed BMW, we set up a small industrial scale composting plant to investigate speciation changes of heavy metals within the compost. The resultant compost was then tested in three different growth trials to assess optimum dose, effect on differing soil types, and comparability to other composts. *Lolium perenne*, *Trifolium repens*, and the metal hyperaccumulator *Thlaspi caerulescens* cv. Ganges were grown to investigate soil metal phytoavailability.

3.3 Materials and methods

3.3.1 *In-vessel composting*

Municipal solid waste was collected from the municipal district of Dwyfor Meirionnydd, Gwynedd, UK and transferred to the Ffridd Rasus waste treatment facility located at Harlech, Gwynedd, UK (52°52'59"N, 4°06'43"W). The MSW waste was then processed through a commercial DANO Drum pulverisation plant (Keppel-Seghers UK Ltd., Wolverhampton, UK) and the fine, largely biodegradable fraction collected after passage through a trommel screen with 38 mm mesh size. Green waste (GW) was obtained from the Dwyfor Meirionnydd district and shredded prior to use at a municipal green waste collection and processing facility located at Glanllynau Farm, Pwllheli, Gwynedd, UK (52°54'81"N, 4°17'85"W).

Composts were produced using a commercially-available CT-5[®] and EcoPOD[®] in-vessel composting system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA) located at Ffridd Rasus waste treatment facility. Two different types of composts were produced from, (1) 15 t of shredded green waste (SGW) and 15 t of the fine fraction of MSW mixed together (MSW + SGW), and (2) 30 t of the fine fraction of MSW alone. The in-vessel composter was filled with a CT-5[®] feed hopper (3 m³ feedstock volume) which uses a hydraulic ram to push the material through a filling chamber and into an extended 1.5 m diameter green plastic EcoPOD[®] vessel at a fill rate of approximately fill rate 3 m³ min⁻¹. At the same time as filling the EcoPOD[®], a rigid perforated (7.62 cm diameter pipe with 1.59 mm slits) plastic aeration pipe is inserted into the base of the vessel to provide forced aeration. The 30 m long horizontal arrangement of the composter allowed three replicate blocks to be sampled for each treatment.

The aeration regime can be closely controlled by means of a timed fan (Ag-Bag International Ltd, Warrenton, OR, USA) running at a flow rate of 137 l min⁻¹ (Roberts *et al.*, 2007). The timed aeration regime was managed manually in order to maximise the rate of composting. In the initial 18 d, aeration was managed in order to maintain high temperatures and therefore optimal sanitation conditions (typically air pumped through the vessel for 2 min every 10 min). This was changed to on 4 min, off 6 min to compensate for the relatively wet feedstocks on day 18. This continued until day 83,

when the vessel was opened, and the compost was matured in static piles for a further 62 d before being bagged for storage and use in the growth trials.

3.3.2 Compost sampling and analysis

During the active composting phase, triplicate independent samples were recovered from each treatment block by opening replicate holes in the vessel and removing material from a depth of 10 to 50 cm. After removal, the vessel was resealed using Duck[®] tape (Henkel Consumer Adhesives Inc., Avon, OH). Samples were removed from the vessel at day 0, 5, 7, 11, 18, 28, 39, 54, 75 and 83 when the vessel was opened. A final sample was taken at bagging from the mature static piles at day 145.

Standard chemical analyses were carried out in triplicate at every sampling time point, and at $n = 5$ on the substrates used in the growth trials. Moisture content was determined by drying samples at 80°C for 24 h and organic matter content determined as loss-on-ignition at 450°C overnight. pH (Hanna Instruments pH 209 pH meter) and electrical conductivity (EC; Jenway 4010 EC meter) were determined in a 1:2 v/v slurry, after equilibration for 1 h. Total C and N were determined using a CHN2000 analyser (LECO Corp., St Joseph, MI). Prior to total elemental analysis, substrates were air dried (25°C, 14 d) and plant samples dried at 80°C before being ground in a T1-100 vibrating sample mill (Heiko Co Ltd., Fukushima, Japan) equipped with tungsten grinding vessels. Subsamples of the ground material were then digested using a 1:4 HClO₄:HNO₃ concentrated acid mixture (MAFF, 1986). The revised BCR sequential extraction method of Mossop and Davidson (2003) was carried out on the dried and ground compost from days 0, 18, 83 and 145. Nitrate and ammonium were extracted using a 1:5 (w/v) fresh sample : extractant ratio of 1 M KCl (Zhong and Makeschin, 2003), shaken for 1 h on a reciprocating shaker at 250 rev min⁻¹ and extracts analysed with a San⁺⁺ segmented flow autoanalyser (Skalar Inc., Norcross, GA). Available P and K were extracted using 1:5 (w/v) fresh sample : extractant ratio with 0.5 M acetic acid, shaken for 1 h on a reciprocating shaker at 250 rev min⁻¹ and the extracts filtered (Quevauviller, 1998). K in the extracts was determined with a Sherwood 410 flame photometer (Sherwood Scientific, Cambridge, UK) while P was

determined colourimetrically. For the growth trial substrates, extractable heavy metals were extracted using 0.05 M EDTA using 1:10 (w/v) fresh sample : extractant ratio (Quevauviller, 1998). Heavy metals were determined by F-AAS using a SpectrAA 220 FS AAS in acetylene / air flame mode except for the sequential extraction samples, which were analysed by ICP-MS using a Fissions PlasmaQUAD II Turbo ICP-MS.

3.3.3 Growth trial substrates

Chemical properties of all composts and soils used in the growth trials are presented in Table 3.1. Approximately 200 kg of soil from 5 locations were collected and each mechanically homogenised before use. The Eutric Cambisol (BE), Dystric Gleysol (GL) and Haplic Podzol (PD) soils types were collected from different fields at the Henfaes Research Centre, Abergwyngregyn, Gwynedd, UK (53°14'24"N, 4°01'03"W; 53°13'58"N, 4°01'23"W; and 53°13'48"N, 4°01'01"W respectively). A sandy textured Ranker soil (SS) was obtained from the site of the former Shotton Steel Works, Flintshire, UK (53°14'20"N, 3°02'36"W), whilst the contaminated soil (CS) was obtained from spoil heaps at the former Parys Mountain copper and zinc mine, Anglesey, UK (53°23'22"N, 4°20'52"W).

MSW Compost (MSWC) and Green Waste and MSW Compost (GWMC) were produced in the EcoPOD[®] experiment outlined in section 2.1. The uncomposted MSW fines material (MSWF) was collected the day prior to use from the DANO drum facility at the Ffridd Rasus waste treatment facility, and was produced in an identical manner to the feedstock for the composting experiment. For comparison, commercially-available Peat Free (PF), Peat Based (PB) and Vitalizer[®] (V) composts were all used as delivered from 80 litre sacks. In addition, a Green Waste Compost (GWC) was obtained from Flintshire County Council's open windrow composting facility at Greenfield, Flintshire, UK (53°17'04"N, 3°11'30"W).

Table 3.1: (over page) Chemical properties of compost feedstocks and growth trial substrates.
Feedstocks: MSW = MSW fines material, GWM = shredded green waste and MSW fines material.
Composts: MSWC = MSW Compost, GWMC = shredded green waste and MSW compost, MSWF = uncomposted MSW fines material, GWC = green waste compost, V = PAS100 specification green waste compost, PF = commercially available peat free compost, PB = commercially available peat based compost. Soils: BE = Eutric Cambisol, GL = Dystric Gleysol, PD = Haplic Podzol, SS = Ranker sandy soil, CS = contaminated soil. All values in mg kg^{-1} dry matter unless otherwise stated ^a EC = Electrical Conductivity, ^b BD = Below limit of detection ($< 3.75 \text{ mg kg}^{-1}$ for heavy metals, $< 0.01 \%$ for N), ^c ND = Not determined.

| Variable | Soils | | | | | Growth trial composts | | | | | | | Compost feedstock | |
|--|-----------------|-----------|-----------|-----------|-----------|-----------------------|-----------|-----------|-----------|-----------|-----------------|-----------|-------------------|-----------|
| | CS | SS | PD | GL | BE | PB | PF | V | GWC | MSWF | GWMC | MSWC | GWM | MSW |
| Moisture content (%) | 13.4±0.5 | 3.6±0.3 | 7.3±0.7 | 32.7±0.9 | 23.0±0.7 | 59.7±0.2 | 44.3±7.5 | 41.6±0.4 | 41.9±0.5 | 39.1±6.0 | 51.7±2.5 | 56.7±1.7 | 57.1±1.4 | 53.3±1.8 |
| Organic matter (%) | 2.5±0.2 | 1.3±0.2 | 2.3±0.3 | 10.2±0.7 | 5.6±0.2 | 93.7±0.2 | 83.0±7.3 | 56.5±0.5 | 38.7±0.6 | 49.8±9.4 | 45.6±5.1 | 42.2±3.7 | 63.0±5.3 | 67.0±1.9 |
| pH | 2.27±0.03 | 8.22±0.04 | 4.55±0.01 | 5.27±0.03 | 5.64±0.06 | 5.51±0.11 | 6.95±0.03 | 6.55±0.04 | 7.90±0.11 | 6.39±0.11 | 8.07±0.02 | 7.28±0.03 | 6.80±0.71 | 6.32±0.63 |
| EC ^a (mS cm ⁻¹) | 2.98±0.06 | 0.07±0.01 | 0.05±0.01 | 0.29±0.03 | 0.10±0.01 | 0.73±0.07 | 0.27±0.03 | 1.5±0.1 | 2.3±0.2 | 3.7±0.1 | 1.1±0.1 | 3.6±0.8 | 2.5±1.1 | 5.2±0.5 |
| Total C (%) | BD ^b | ND | ND | ND | ND | 39.9±0.1 | 41.4±0.6 | ND | ND | ND | ND ^c | 24.6±4.3 | 34.7±0.5 | 34.1±1.2 |
| Total N (%) | BD | ND | ND | ND | ND | 1.04±0.01 | 1.23±0.04 | ND | ND | ND | ND | 0.97±0.17 | 0.91±0.08 | 0.76±0.05 |
| Available NO ₃ ⁻ | 1.7±0.1 | 6.8±1.0 | 4.6±0.2 | 78.1±5.7 | 6.2±1.9 | 587±24 | 0.8±0.2 | 366±65 | 259±27 | 6.3±0.7 | 16.0±5.1 | 21.9±11.8 | 0.3±0.2 | 2.9±2.6 |
| Available NH ₄ ⁺ | 13±1 | 3±1 | 14±2 | 46±12 | 6±1 | 662±29 | 888±159 | 68±5 | 1±1 | 958±144 | 8±2 | 29±6 | 177±46 | 264±119 |
| Available P | 0.6±0.1 | 8.4±2.7 | 0.9±0.1 | 2.1±0.1 | 7.8±2.6 | 604±37 | 260±35 | 744±130 | 863±897 | 423±139 | 616±83 | 33±8 | 193±60 | 340±83 |
| Available K | 9±1 | 50±7 | 25±4 | 74±5 | 156±32 | 2743±22 | 1498±201 | 4538±694 | 6722±952 | 3630±68 | 3789±224 | 2926±382 | 2044±263 | 2583±190 |
| Total Cd | 7.51±0.51 | 0.24±0.14 | BD | 0.02±0.01 | 0.27±0.09 | 0.25±0.02 | 0.43±0.01 | 0.60±0.02 | 1.30±0.08 | 1.11±0.46 | 0.49±0.04 | 0.69±0.06 | 0.27±0.07 | 0.56±0.23 |
| Total Cu | 2368±201 | 8±3 | 27±3 | 15±3 | 32±6 | 33±5 | 6±1 | 29±1 | 63±3 | 66±12 | 276±17 | 261±14 | 131±8 | 135±7 |
| Total Ni | 3±1 | 8±1 | 27±1 | 24±1 | 27±1 | 3±1 | 6±1 | 10±1 | 20±1 | 19±2 | 37±1 | 46±2 | 47±1 | 56±3 |
| Total Pb | 5727±643 | 56±34 | 23±1 | 68±21 | 37±1 | 5±1 | 18±2 | 61±1 | 198±11 | 135±20 | 232±11 | 614±53 | 135±6 | 134±7 |
| Total Zn | 2218±49 | 73±2 | 98±2 | 79±6 | 109±3 | 16±1 | 62±1 | 223±16 | 369±20 | 284±37 | 213±7 | 269±9 | 153±4 | 145±6 |

3.3.4 Effect of MSW compost application rate and soil type on plant performance

A fully randomised complete block design was set up in one litre pots in an unheated greenhouse with natural light during summer 2005. Five replicates of *Lolium perenne* L. (perennial ryegrass) and *Trifolium repens* L. (white clover) were grown for a period of 6 weeks in the Eutric Cambisol soil blended with different proportions of MSWC (0, 20, 40, 60, 80 and 100% v/v), giving 60 pots. After this period, the pots were destructively harvested, and aboveground biomass determined after drying at 80°C (24 h) and shoot heavy metal content determined following acid digestion as described previously.

In addition, a fully randomised complete block design was set up as described above except that two applications rates of MSWC were used (0 and 40% v/v) with the five different soils.

To evaluate the relative performance of the MSW-derived compost, plant growth and shoot heavy metal content were evaluated in plants grown in each of the seven composts blended with the Eutric Cambisol soil at two applications rates (0 and 40% v/v). The design of the experiment was as described previously but included a control treatment of Eutric Cambisol with no compost amendment.

3.3.5 Use of *Thlaspi caerulescens* to investigate phytoavailable Cd and Zn

The three plant growth trials detailed above were repeated using *Thlaspi caerulescens* cv. Ganges grown in one litre pots for a period of 10 weeks, after an initial germination period of one month in John Innes seed compost (John Innes, Harrogate, UK). Specimens of average size were transplanted as plugs into the treatments outlined in section 2.4, and on completion of the trial were analysed for Cd and Zn content. For comparison, the EDTA extractable levels of these two heavy metals were also determined in the compost/soils to assess the reliability of EDTA to predict phytoavailable heavy metal levels.

3.3.6 Statistical analysis

All data were inputted into SPSS v14.0 (SPSS Inc., Chicago, IL), and repeated measures GLM procedures were carried out to assess the effects of time, sequential extraction fraction and compost type on heavy metal concentration over the composting period. Where sphericity was not met, the Huynh-Feldt correction was applied to allow univariate results to be used. Univariate GLM procedures were used to analyse the effects of treatment on plant biomass and metal uptake in the growth trials. Where necessary, results were split by species and re-analysed using a 1-way ANOVA with Tukey's honestly significantly difference post-hoc test used to examine differences between individual treatments. Linear regression was also carried out to investigate how well the EDTA-extractable and total heavy metal concentration represented phytoavailable levels by comparison to plant content. All graphical figures were produced in SigmaPlot v10.0 (Systat Software Inc., San Jose, CA). All nutrient and heavy metal content values are expressed on a dry weight basis.

3.4 Results

3.4.1 Composting of MSW fines

During the initial stages of composting both waste types reached 60°C indicating that thermophilic conditions had been achieved (Fig. 3.1). Whilst the temperature of the MSW compost decreased steadily to ambient levels by day 75, that of the mixed feedstock fell sharply to ambient levels by day 18, rising again to 50°C by day 54, before returning back to ambient temperatures at day 75. pH increased rapidly by ca 1.5 units to 8.04 ± 0.12 by day 7 in the mixed MSW and green waste compost, whereas an initial dip to 5.58 ± 0.08 at day 5 was observed before a sharp increase to 7.95 ± 0.17 by day 18 in the MSW compost. C:N ratios for both compost types fell sharply over the first 18 days, then progressively declined until 145 d. Available P concentrations fell sharply in both feedstocks during the active composting phase to reach $7 \pm 5 \text{ mg P kg}^{-1}$; subsequently, however, a sharp increase in available P occurred during the maturation phase ($38 \pm 8 \text{ mg P kg}^{-1}$) but only in the mixed MSW and green waste compost. In the initial composting phase, nitrate concentrations remained low (ca. 2 mg kg^{-1}), however, they progressively rose

throughout the process until an average concentration of $19 \pm 3 \text{ mg kg}^{-1}$ was observed at the end of the maturation phase. Ammonium levels fluctuated throughout the composting period for both feedstocks, but always remained higher in the MSW compost, finishing approximately 5-fold higher than the mixed MSW and green waste compost after the maturation period.

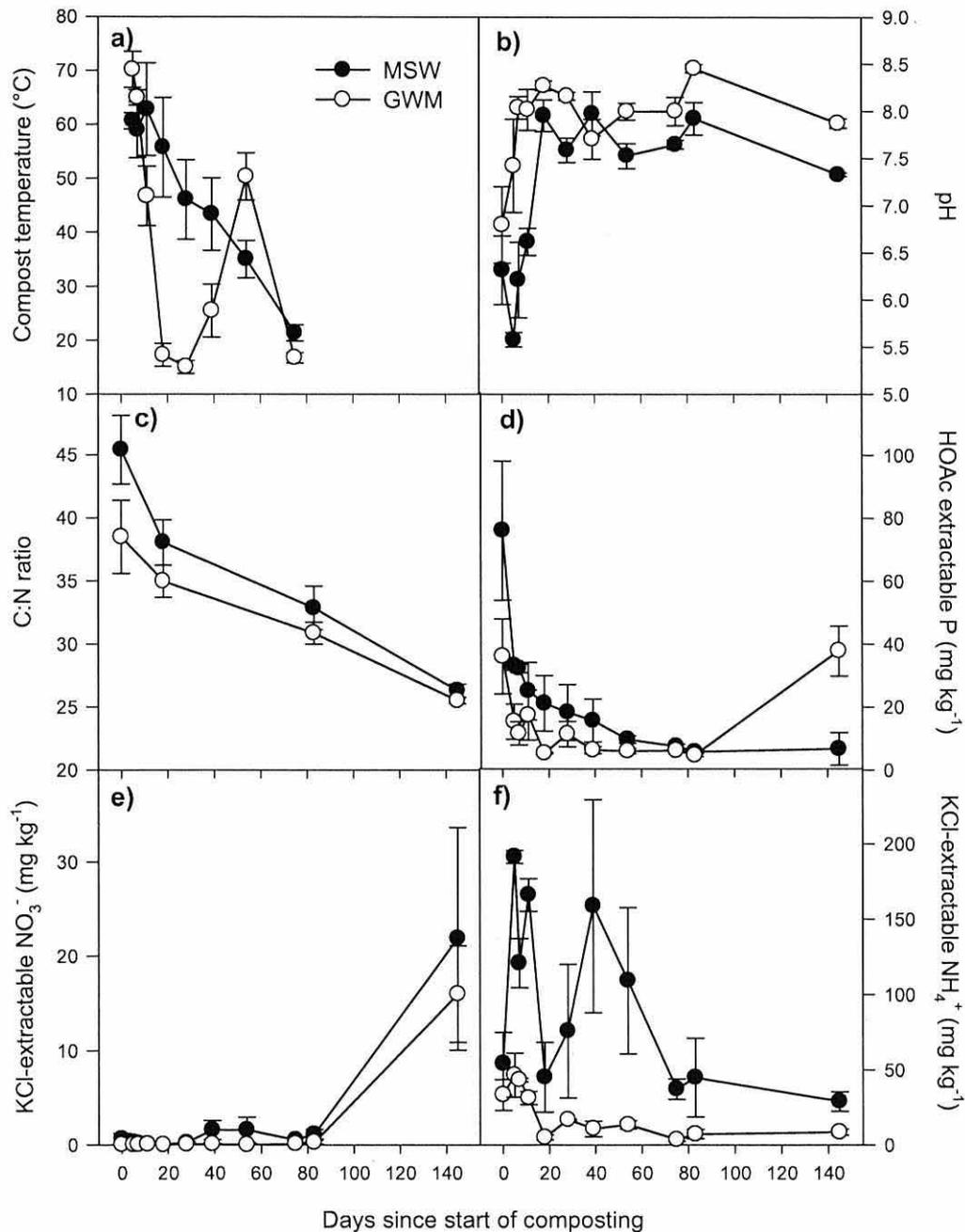


Figure 3.1: Changes in a) temperature at 60 cm depth, b) pH, c) C:N ratio, d) available P, e) KCl-extractable nitrate, and f) KCl-extractable ammonium over the composting period. Closed circles represent data from the MSW compost whilst open circles represent the green waste and MSW compost mixture. Temperature measurements ceased after 75 d when the temperature had fallen

back to ambient levels. The vessel was opened on day 83, and the compost was left to mature in static piles before bagging for use after 145 d. Values represent mean \pm SEM ($n = 3$).

3.4.2 Metal dynamics during composting

Changes in metal partitioning over the period of composting were investigated using a 4-part sequential extraction (Mossop and Davidson, 2003), which classes the pools using the operationally defined variables as: exchangeable, reducible, oxidisable and residual. Results for Cu, Ni, Pb and Zn are presented in Figure 3.2, with the results of the statistical tests presented in Table 3.2. In all samples, Cd levels were very low and too close to the LOD of the instrument to give reliable results. There were significant differences between the amount of metal partitioned to the 4 different fractions for all four elements (Cu, $P < 0.001$; Ni, $P < 0.001$; Pb, $P < 0.001$; Zn, $P = 0.001$). Overall, Cu, Ni and Pb all exhibited small exchangeable fractions (typically less than 5% of the total), whereas 46% of Zn was present in the exchangeable fraction of the MSWC at the start of composting. Ni was mostly present in the residual fraction of both composts, whilst Cu and Pb were predominantly recovered in the oxidisable fraction.

Cu, Pb and Zn increased in their overall concentrations over time ($P = 0.028$, $P = 0.011$, and $P < 0.001$ respectively), whilst Ni exhibited no change ($P = 0.083$). Cu behaved similarly ($P = 0.216$) in both composts, whilst Ni, Pb and Zn were different in their behaviour between composts ($P = 0.012$, $P < 0.001$, $P = 0.002$ respectively). Ni, Pb and Zn were all partitioned differently within each compost type, as indicated by the significant interaction effect of compost \times fraction ($P = 0.031$, $P = 0.014$, and $P = 0.010$ respectively), whilst the proportions of Cu in each fraction remained similar within both composts ($P = 0.080$). Only Cu, however, changed in its fractionation pattern over time ($P = 0.018$), with the amount present in the organic fraction increasing by 33% and 15% in the MSWC and GWMC composts respectively.

Table 3.2: Repeated measures mixed model 3-way ANOVA investigating changes in metal partitioning over time in the two MSW derived composts

| Factor | Cu | | Ni | | Pb | | Zn | |
|----------|------|----------|------|----------|------|----------|------|----------|
| | F | <i>P</i> | F | <i>P</i> | F | <i>P</i> | F | <i>P</i> |
| Time | 3.85 | 0.028 | 2.36 | 0.083 | 5.61 | 0.011 | 16.7 | < 0.001 |
| Compost | 1.65 | 0.216 | 7.94 | 0.012 | 30.0 | < 0.001 | 13.1 | 0.002 |
| Fraction | 211 | < 0.001 | 175 | < 0.001 | 18.5 | < 0.001 | 66.9 | 0.001 |
| C×F | 2.70 | 0.080 | 3.80 | 0.031 | 4.85 | 0.014 | 5.26 | 0.010 |
| T×C | 0.64 | 0.541 | 0.18 | 0.903 | 3.32 | 0.057 | 2.95 | 0.042 |
| T×F | 2.93 | 0.018 | 0.71 | 0.696 | 0.95 | 0.462 | 1.63 | 0.133 |
| T×C×F | 0.08 | 0.998 | 0.81 | 0.603 | 0.86 | 0.519 | 0.46 | 0.873 |

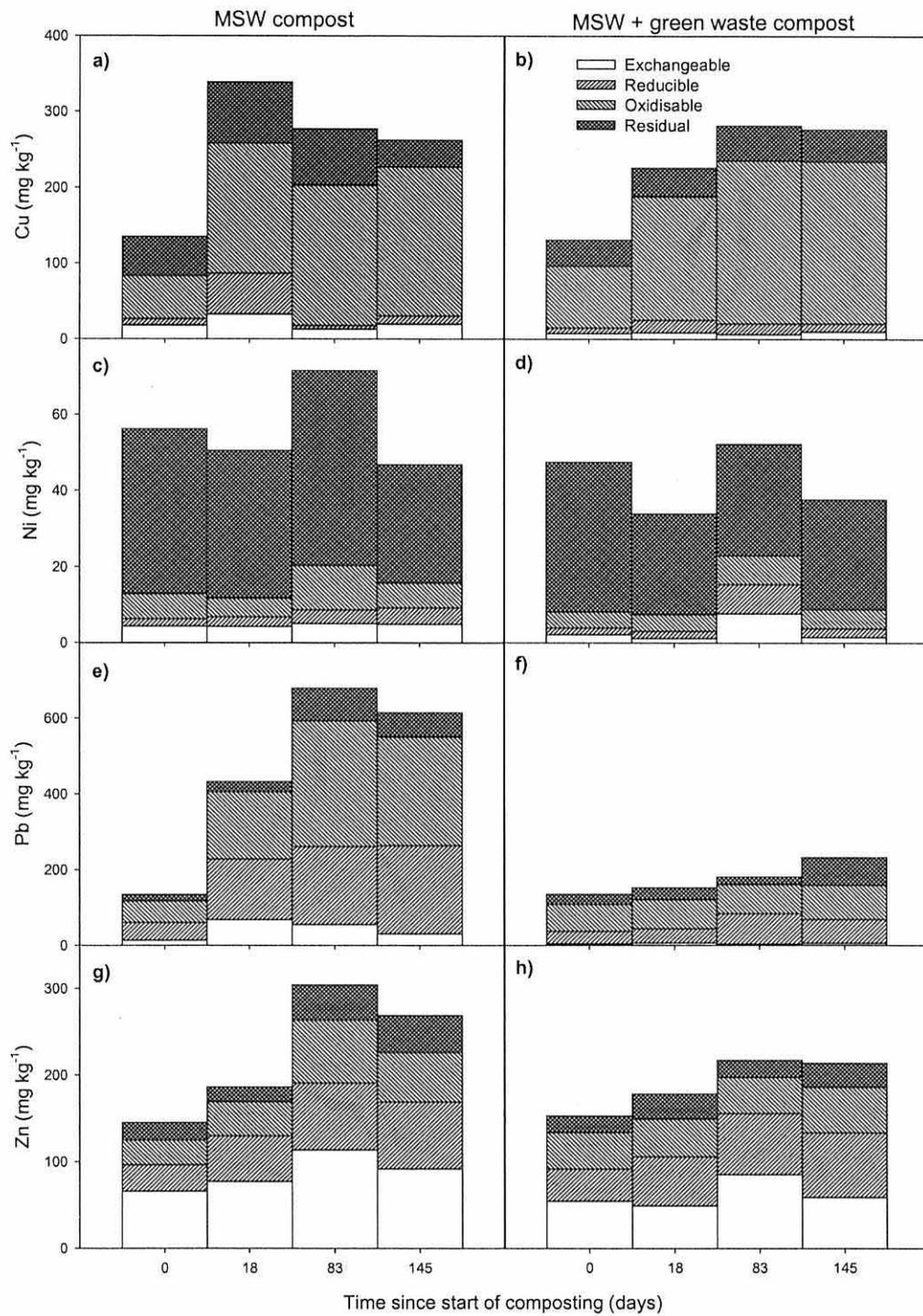


Figure 3.2: Changes in Cu, Ni, Pb and Zn speciation over the period of composting. Left-hand graphs represent the MSW compost, whilst the right-hand graphs represent the mixture of MSW and green waste compost. Exchangeable = 0.11 M Acetic Acid, Reducible = 0.5 M Hydroxylammonium Hydrochloride at pH 1.5, Oxidisable = 1 M Ammonium Acetate extractable at pH 2, after H₂O₂ oxidation, Residual = Aqua Regia digested (method from Mossop and Davidson, 2003). Values represent mean \pm SEM ($n = 5$).

3.4.3 Effect of increasing MSWW compost application on plant growth

The increased dosage of MSW compost to the Eutric Cambisol soil reduced the yield of both *L. perenne* and *T. repens* ($P < 0.001$), however, a slight interaction ($P = 0.062$) indicates that *T. repens* was affected to a greater extent than *L. perenne*, despite there being no statistical significance (Fig. 3.3). With no compost amendment, above ground biomass after 6 weeks growth was $0.35 \pm 0.04 \text{ kg m}^{-2}$ and $0.15 \pm 0.01 \text{ kg m}^{-2}$ for *L. perenne* and *T. repens* respectively, whereas when grown entirely in 100% MSWC, yield was reduced by 75% and 98% respectively (Fig. 3.3). Although *L. perenne* contained higher concentrations of Cd, Ni and Zn than *T. repens* ($P < 0.001$, $P = 0.018$, and $P = 0.010$ respectively), compost addition had no significant effect on metal uptake for any of the five elements tested ($P > 0.05$).

3.4.4 Effect of soil type on the success of MSW compost at promoting plant growth

A compost application rate of 40% to the five different soils had no consistent effect on overall above-ground biomass with plant growth being depressed in some soils (e.g., Eutric Cambisol) whilst being enhanced in others (e.g., contaminated mine soil). However, both soil type and plant species had a highly significant effect on plant growth ($P < 0.001$ for both factors). There was no significant interaction ($P = 0.634$) between soil and species, indicating that the soil types had affected both species equally. However, compost exhibited a strong interaction effect ($P < 0.001$) with species – indicating that *T. repens* was affected to a greater extent than *L. perenne* by the MSW compost – a result mirrored in the previous section. Given that soil and compost also exhibited a strong interaction ($P < 0.001$), it is evident from Figure 3.4 that the compost was particularly beneficial to both the nutrient-poor, acidic soils (PD and CS), whilst having little effect on the more neutral soils.

Soil type had a significant effect on plant uptake of all elements ($P < 0.001$) with the exception of Ni ($P = 0.087$). Levels of Cd, Cu and Ni were significantly higher in *T. repens* ($P < 0.001$, $P = 0.014$, and $P < 0.001$ respectively), whilst Zn was significantly higher ($P < 0.001$) in *L. perenne*. Zn was increased in concentration in *L. perenne* by compost addition, whilst no changes were observed in Zn concentration of *T. repens*, as illustrated by the significant interaction between compost and species

($P = 0.007$). There were no significant differences between the two species for uptake of Pb ($P = 0.512$). Strong three-way interactions between compost, species and soil were exhibited for Cd and Ni uptake, indicating that both species reacted differently in their uptake of these elements in the different treatments.

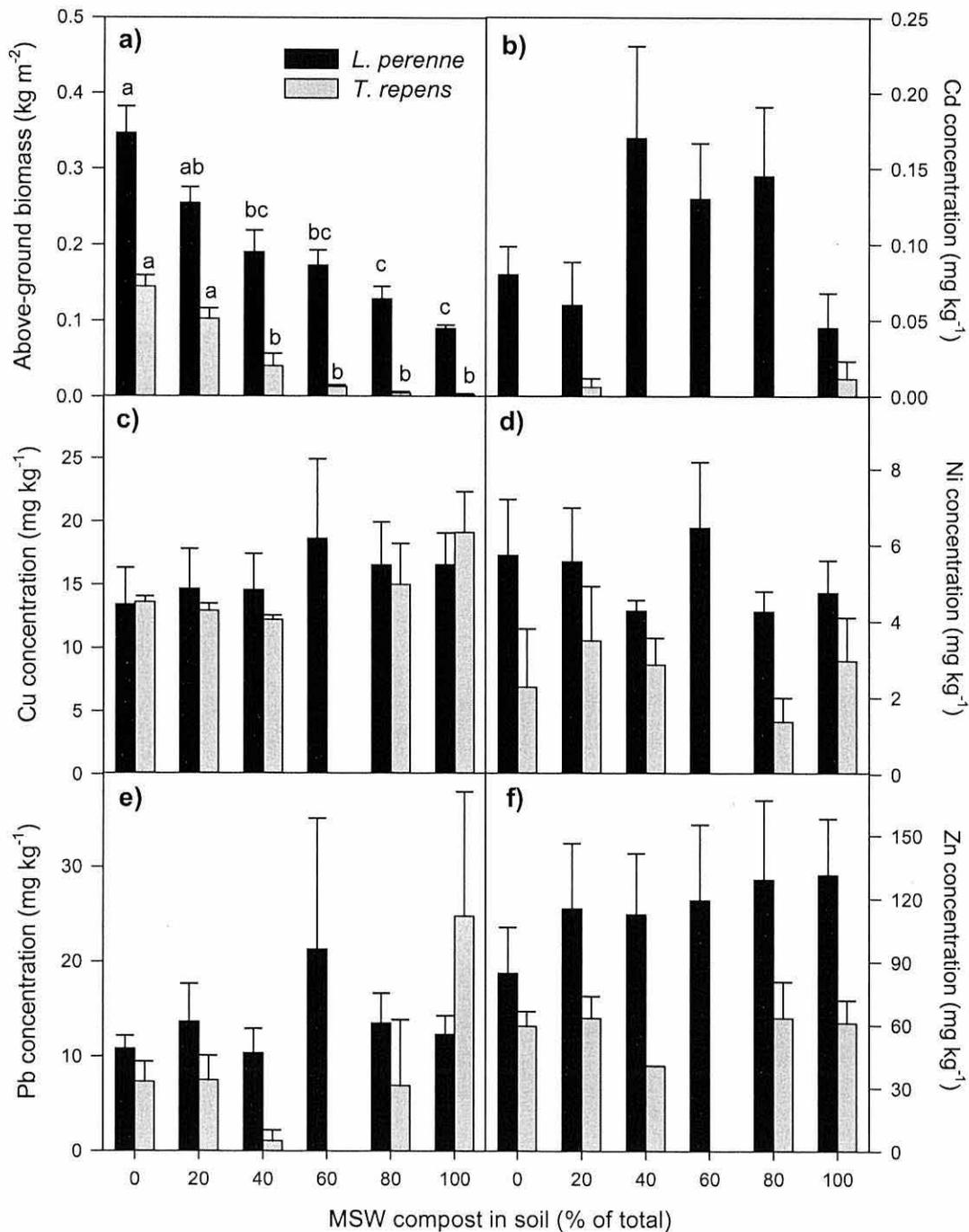


Figure 3.3: Yield and metal uptake by *L. perenne* and *T. repens* when grown in increasing volumes of MSW compost. There was insufficient biomass of *T. repens* at 60% MSW compost to enable heavy metal concentrations to be determined. Values represent mean \pm SEM ($n = 5$).

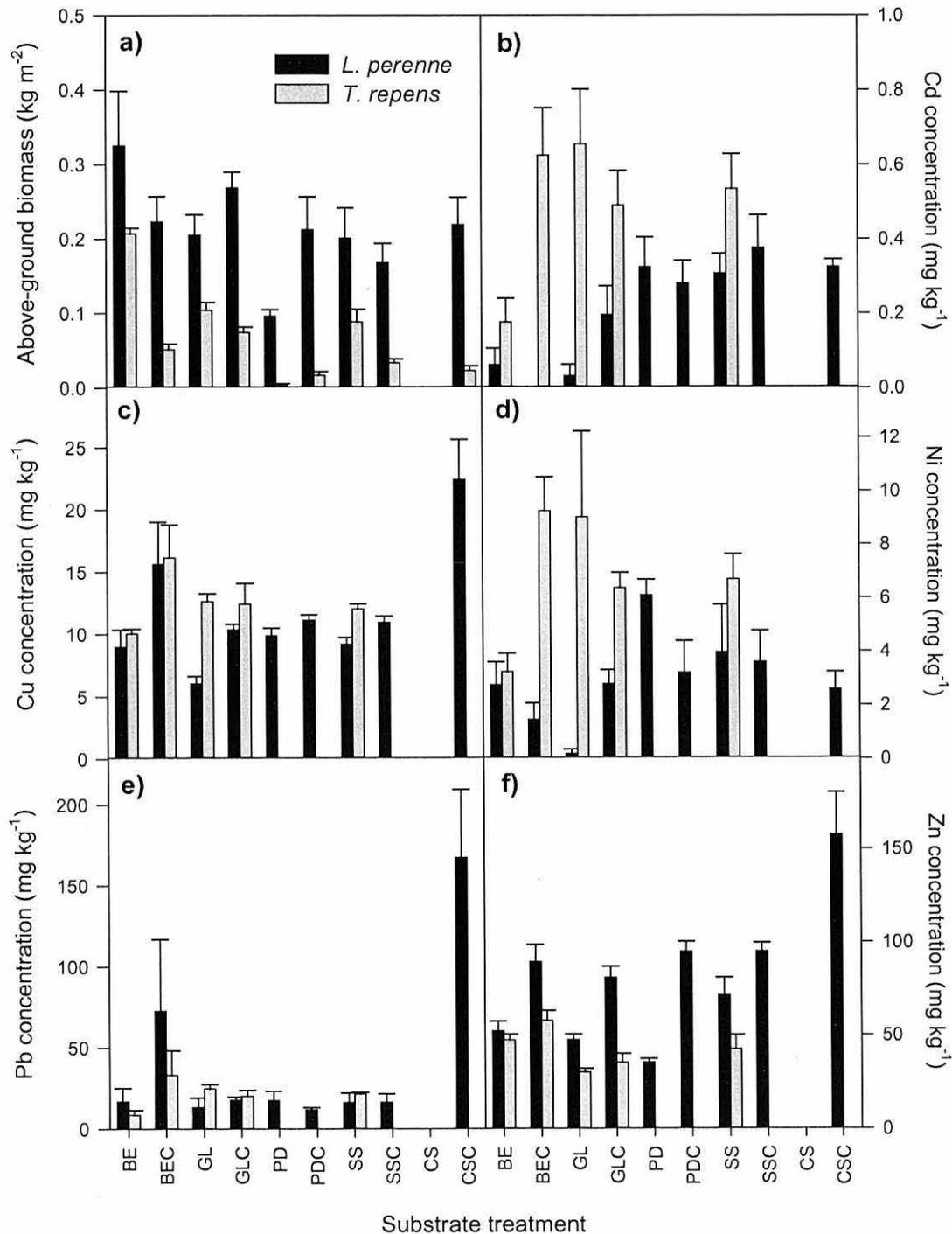


Figure 3.4: Yield and metal uptake by *L. perenne* and *T. repens* when grown in 5 different soils with and without a 40% substitution of MSW compost. The suffix 'C' represents those treatments with compost. BE = Eutric Cambisol, GL = Dystric Gleysol, PD = Haplic Podzol, SS = Sandy Ranker, CS = Contaminated Mine Soil. There was insufficient biomass for both *L. perenne* and *T. repens* in the untreated CS soil, and for *T. repens* for PD, PDC, SS and CSC treatments for heavy metal determination. Values represent mean \pm SEM ($n = 5$).

3.4.5 Performance of MSW compost in comparison to other composts

The seven different compost types produced highly significant effects on the growth of both plant species ($P < 0.001$, Fig. 3.5). Whilst *L. perenne* yield was unaffected or increased by all compost types with the exception of the uncomposted MSW fines material, *T. repens* was reduced in biomass by most composts in comparison to the Eutric Cambisol soil control. Indeed, two commercially sold composts (GWC and V) caused a 52% and 73% decrease in yield respectively for *T. repens*, whilst the same composts increased the yield of *L. perenne* by 64% and 97% relative to the control treatment – as demonstrated by the highly significant interaction effect between species and compost ($P < 0.001$). From the Tukey-HSD test, our MSWC significantly increased the yield of *L. perenne* ($P < 0.05$) in relation to the application of uncomposted MSW fines, advocating the use of composting to make this material more suitable for land application. No significant differences were observed between any of the other treatments, with the exception of the PAS100 specification compost (V), which gave the highest *L. perenne* biomass. *T. repens* produced significantly less biomass than our MSWC treatment in both the uncomposted fines and PAS100 compost treatments, whilst only the peat-based compost gave a significantly higher yield ($P < 0.05$). Therefore, a 40% application of MSWC gave comparable results to all other composts used across both species, and no significant benefits were seen for co-composting the fines material with green waste.

Ni and Pb concentrations were not affected in either species by any compost ($P = 0.334$ and $P = 0.186$ respectively). Compost type did, however, have a significant effect on the concentration of Cd, Cu and Zn in both species (all $P < 0.001$), with MSWF and MSWC giving higher Zn concentrations in both species, MSWF giving a higher Cu concentration in *L. perenne* and MSWC giving a higher Cu concentration in *T. repens*, and all composts apart from MSWF giving higher Cd shoot concentrations for both species.

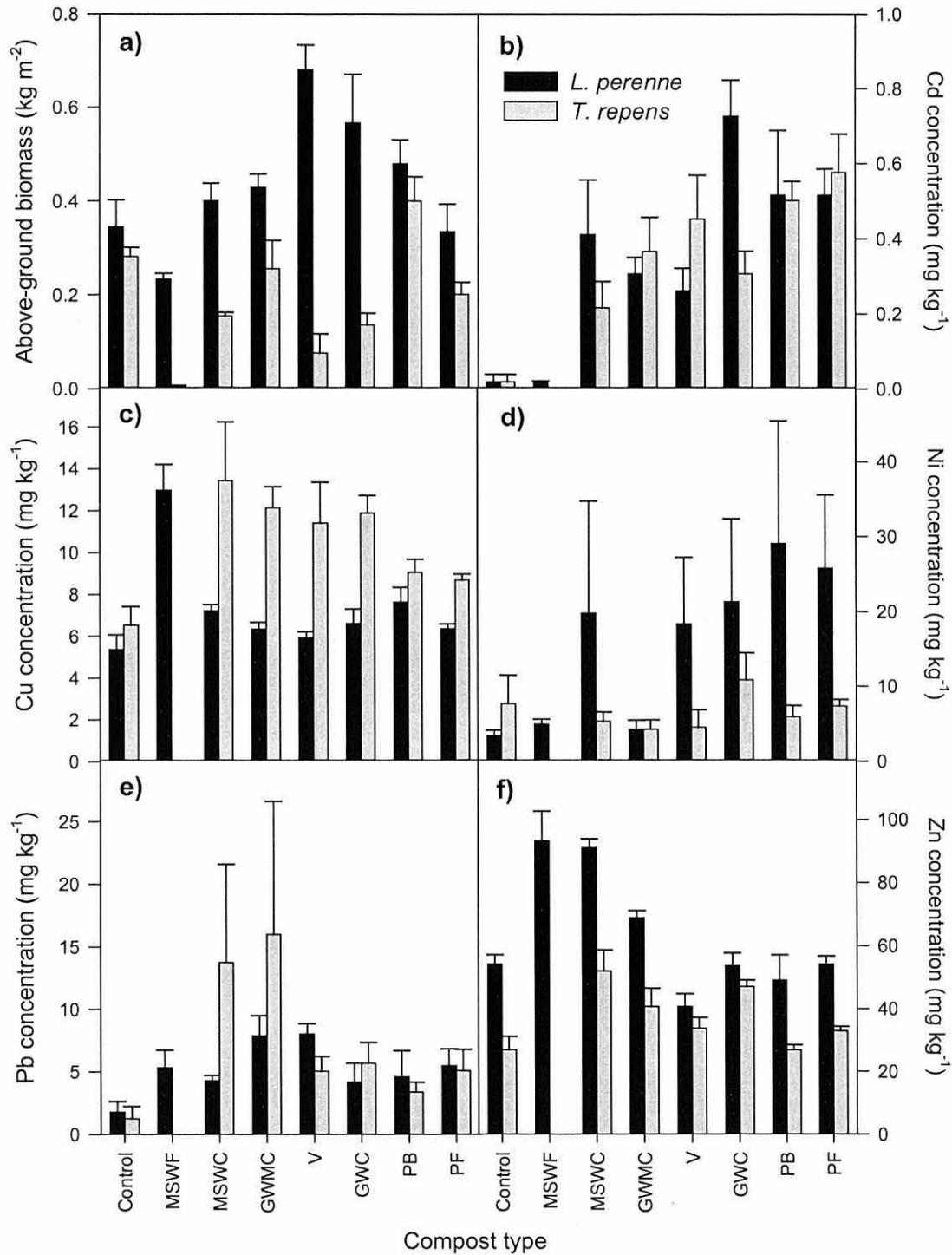


Figure 3.5: Yield and metal uptake by *L. perenne* and *T. repens* as affected by a 40 % application of seven different composts. There was insufficient biomass of *T. repens* with MSWF addition to enable heavy metal concentrations to be determined. MSWF = uncomposted MSW fines material, MSWC = MSW compost, GWMC = MSW + green waste compost, V = commercially available PAS100 specification peat free compost, GWC = green waste compost from a council open windrow facility, PB = commercially available peat based compost, PF = commercially available peat free compost. Values represent mean \pm SEM ($n = 5$).

3.4.6 Comparability of total and EDTA-extractable heavy metals to phytoaccumulated concentrations

Thlaspi caerulescens yield was unaffected by the increased addition of MSW compost (Figs. 3.6a, d, and g), and its Zn concentration was also unaffected ($P = 0.587$ and $P = 0.587$). Cd concentration was reduced as the rate of MSWC addition was increased ($P = 0.006$). MSWC addition had no effect on *T. caerulescens* growth or Cd concentration across the five soil types (Figs. 3.6b, e, and h), however soil type did have a significant effect ($P < 0.001$ for both variables). Both compost addition and soil type affected *T. caerulescens* Zn concentration ($P = 0.012$ and $P < 0.001$ respectively), and a significant interaction effect was observed ($P = 0.014$) between soil and compost, with compost increasing Zn foliar uptake in the Dystric Gleysol and Haplic Podzol, but having no effect on the remaining three soils. In the assessment of effect of different composts (Figs 3.6c, f and i), *T. caerulescens* yield, foliar Cd and Zn were all significantly affected by differing composts ($P < 0.001$ for all three variables). The greatest biomass was recorded in the MSWC treatment, whilst the lowest occurred after the addition of uncomposted MSW fines material. Foliar Cd concentrations were 2-fold higher in the control treatment than in any of the other treatments, whilst the GWC caused a 3-fold increase in foliar Zn concentration compared to the lowest concentration induced by the MSWF treatment.

Figure 3.7 illustrates the relationships between EDTA-extractable and total substrate Cd and Zn and the foliar Cd and Zn concentration in the above-ground biomass of the three plant species, with the regression equations and statistics presented in Table 3.3. The regression analysis showed that EDTA-extractable Cd was only significantly correlated with *T. caerulescens* foliar Cd concentration, and not with *L. perenne* or *T. repens* foliar Cd concentration. Total substrate Cd was also correlated with *T. caerulescens* foliar Cd concentrations, however, no such relationship was seen for either *L. perenne* or *T. repens* Cd foliar concentration. EDTA-extractable Zn correlated well with the foliar Zn concentration in both *L. perenne* and *T. repens*, but contrary to Cd, this did not correlate with the Zn concentration of *T. caerulescens*. Total substrate Zn correlated well with the foliar Zn concentration of all three plant species.

Table 3.3: Linear regression analysis results predicting vegetation Cd and Zn concentration from soil EDTA extractable and total soil Cd and Zn concentrations for three plant species

| Extraction | Species | Equation | R^2 | P value |
|------------|--------------------|--------------------------|-------|-----------|
| EDTA Cd | <i>L. perenne</i> | $y = 2.544 x + 0.1784$ | 0.085 | NS |
| | <i>T. repens</i> | $y = 0.5792 x + 0.2938$ | 0.010 | NS |
| | <i>T. caerulea</i> | $y = 10.75 x + 3.634$ | 0.298 | ** |
| Total Cd | <i>L. perenne</i> | $y = -0.0016 x + 0.3178$ | 0.001 | NS |
| | <i>T. repens</i> | $y = 0.6162 x + 0.3110$ | 0.064 | NS |
| | <i>T. caerulea</i> | $y = 0.3051 x + 5.0794$ | 0.070 | * |
| EDTA Zn | <i>L. perenne</i> | $y = 0.7576 x + 53.90$ | 0.276 | *** |
| | <i>T. repens</i> | $y = 0.2483 x + 35.58$ | 0.198 | *** |
| | <i>T. caerulea</i> | $y = 2.0532 x + 947.3$ | 0.011 | NS |
| Total Zn | <i>L. perenne</i> | $y = 0.0509 x + 70.61$ | 0.187 | *** |
| | <i>T. repens</i> | $y = 0.0734 x + 32.22$ | 0.178 | *** |
| | <i>T. caerulea</i> | $y = 0.3843 x + 911.6$ | 0.096 | *** |

*, ** and *** indicate significant effects at the $P < 0.05$, $P < 0.01$ and $P < 0.001$ level respectively, while NS indicates no significant effect ($P > 0.05$).

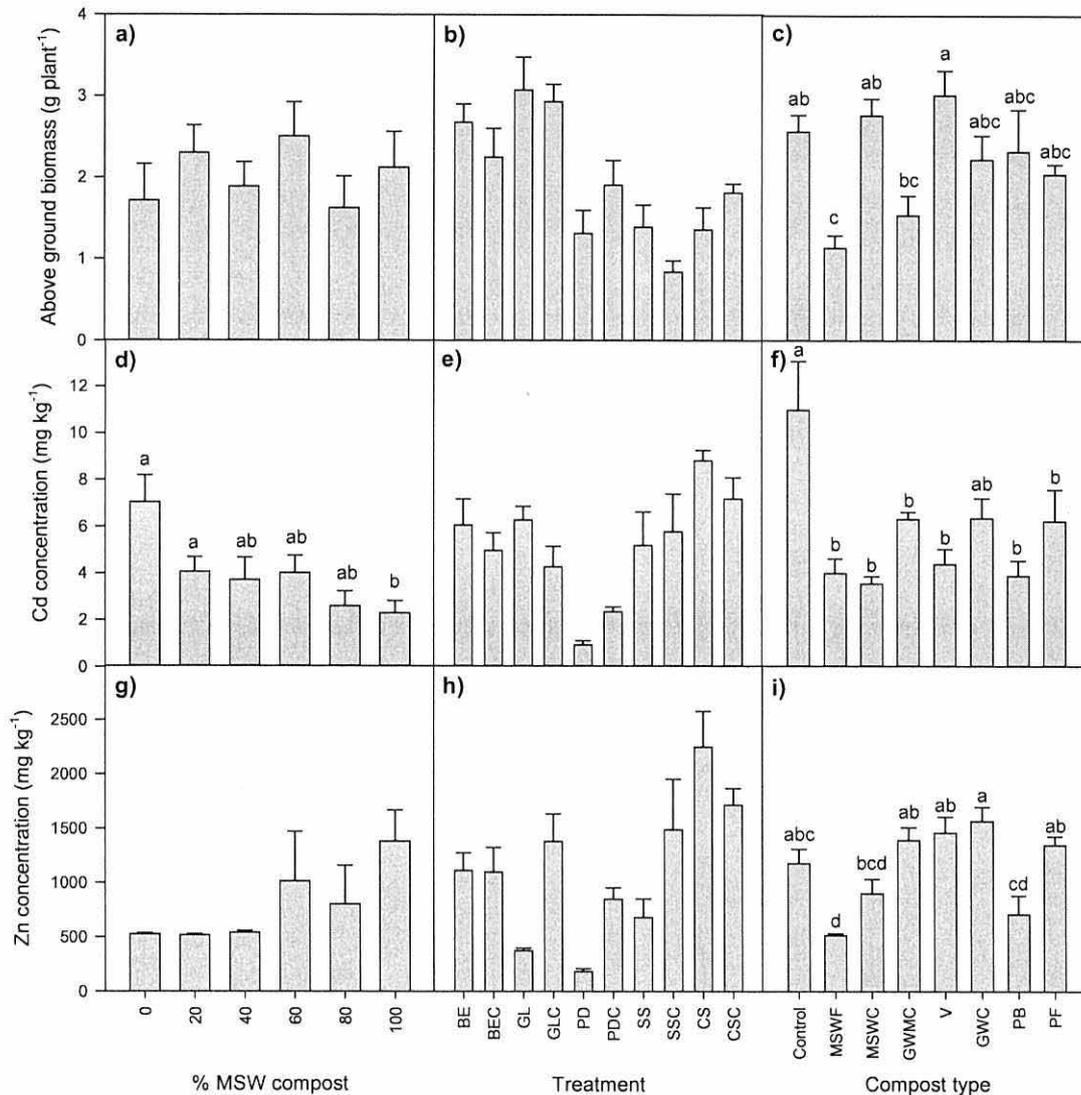


Figure 3.6: Above-ground biomass and Cd and Zn concentration of *T. caeruleus* grown under the conditions outlined in sections 3.3.2-5. Different letters denote significant differences ($P < 0.05$) according to Tukey's HSD post hoc test. Graphs a), d), and g) show the response to increased MSW compost substitution for the brown earth soil (no significant difference in yield or Zn concentration). Graphs b), e), and h) show the response to a 40% compost substitution in 5 different soils: the suffix 'C' represents those treatments with compost (significant differences observed in all treatments except between those with compost addition for Zn – letters omitted for clarity). BE = Eutric Cambisol, GL = Dystric Gleysol, PD = Haplic Podzol, SS = Sandy Ranker, CS = Contaminated Mine Soil. Graphs c), f), and i) show the response to a 40% application of seven different composts. MSWF = uncomposted MSW fines material, MSWC = MSW compost, GWMC = MSW + green waste compost, V = commercially available PAS100 specification peat free compost, GWC = green waste compost from a council open windrow facility, PB = commercially available peat based compost, PF = commercially available peat free compost. Values represent mean \pm SEM ($n = 5$).

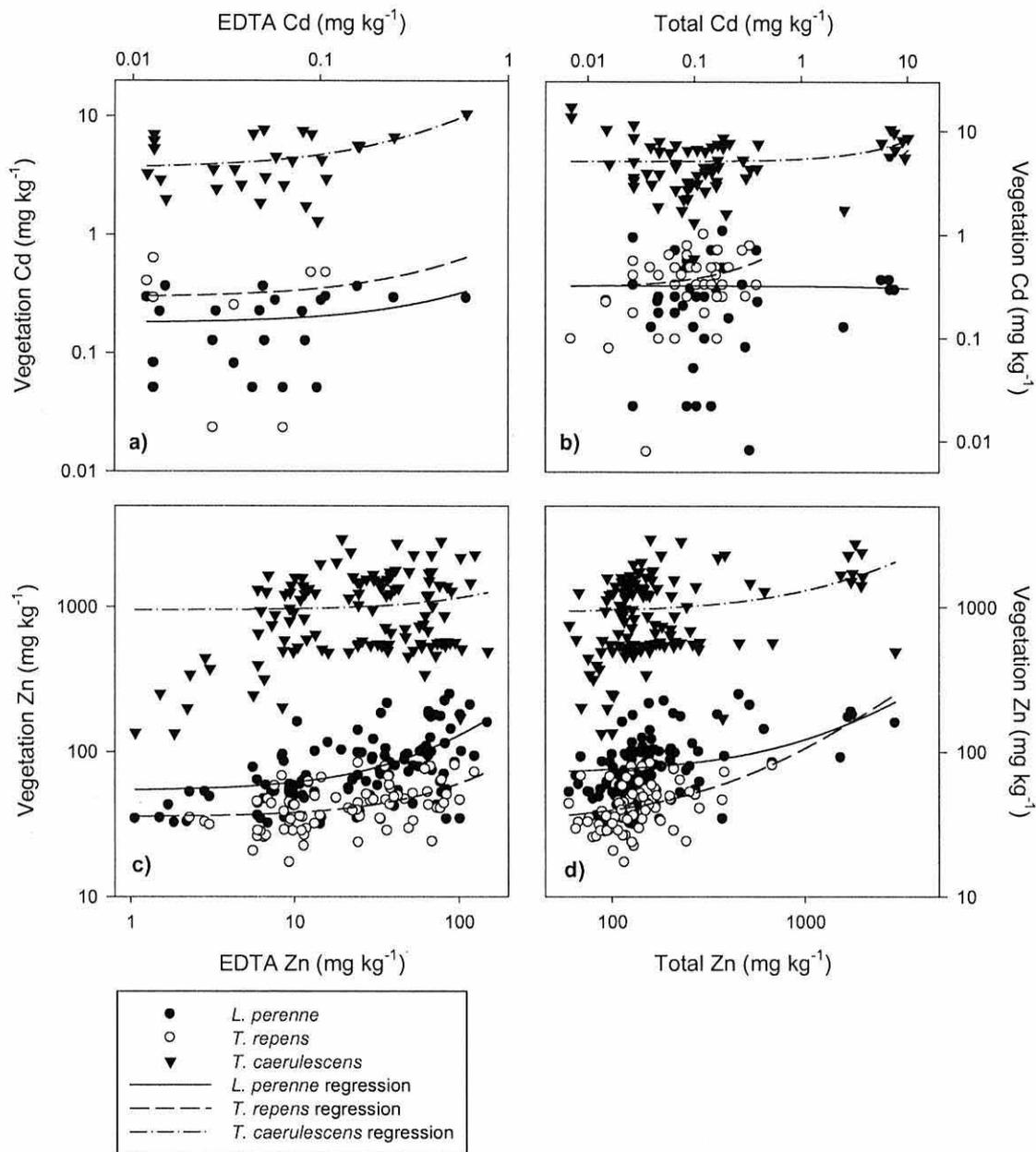


Figure 3.7: Relationships between EDTA extractable and total Cd and Zn against *L. perenne* (closed circles / solid lines), *T. repens* (open circles / dashed lines), and *T. caerulea* (inverted closed triangles / dotted and dashed lines) Cd and Zn concentrations. Note the logarithmic scales on both the x and y axes.

3.5 Discussion

3.5.1 Composting of MSW

We have demonstrated that high C:N ratio MSW fines material can be successfully composted either on its own, or co-composted with shredded green waste. Under UK animal by-products regulations (DEFRA, 2008), feedstocks containing

catering waste must reach 60°C for 48 h, then be re-mixed and reach the same temperature again for a further 48 h. Whilst in this study the re-mixing did not take place due to operational constraints, the rise to a stable pH and steady decrease in C:N ratio to acceptable levels (Sharma *et al.*, 1997) have illustrated that the thermophilic stage of the process was completed satisfactorily for both feedstocks, with a rise in nitrates over the maturation period indicating maturity (Benito *et al.*, 2003).

3.5.2 Metal dynamics during composting

The increase in concentration of heavy metals over the duration of the composting period was expected due to progressive mineralization of organic matter within the compost, and mass loss via respiration over time (Amir *et al.*, 2005). We observed a lower concentration of heavy metals in the co-composted MSW and green waste, reflecting the dilution effect of co-composting mixed wastes with cleaner substrates. Differential partitioning between the compost types was observed, most probably as a response to the change in organic matter type, and a possible increase in humic substances, as well as many other variables. Amir *et al.* (2005) concluded in their study of heavy metal speciation during composting that definitive prediction of metal speciation during composting is confounded by many factors. Our composts exhibited small exchangeable fractions of Cu, Ni and Pb. However, a similar study on green waste composting by Greenway and Song (2002) found that whilst Cu, Ni and Pb in two of the four composts studied were low in their exchangeable fractions, in the other two composts between 20-40% of the total Ni was present in the exchangeable fraction at the start of composting, indicating wide variability across broadly similar feedstock types. Whilst their exchangeable value dropped to 6% by the end of composting, in our study, Ni, along with Zn and Pb, did not change in fractionation over time in either compost, with exchangeable Ni constituting ca. 5% of the total pool throughout the process. In our study, Ni was mainly present in the residual fraction, in agreement with Alloway (1990) who stated that at least 50% of Ni in soils is found in the residual fraction of sequential extractions.

Of the four elements examined in our study, only Cu was found to show significant temporal shifts between fractions during composting, with the amount present in the oxidisable fraction increasing. Cu is strongly sorbed by humic substances (Alloway, 1990), and the composting process is widely recognised to increase the humification of organic carbon within the compost (Epstein, 1997; Hsu and Lo, 2001; Amir *et al.*, 2005). We therefore propose that the Cu that was previously loosely bound to simple organic matter within the compost feedstocks was transformed to tightly bound copper within the humic matrix of the composted organic matter.

In the study by Greenway and Song (2002) Pb was found to be mainly associated with the organic / oxidisable fraction of the compost, whilst in our study, Pb was found to be well associated with both the oxidisable and reducible fractions. Alloway (1990) stated that Pb is highly associated with both organic matter and Fe / Mn oxides (reducible fraction), whilst Amir *et al.* (2005) found that HNO₃ extractable Pb formed the largest fraction in their study of sewage sludge composting.

Finally, a high percentage of Zn in our composts was present in the exchangeable fraction, reflecting higher availability indices compared to the other elements within this study (Alloway, 1990; Hsu and Lo, 2001). In fact, Zn was relatively evenly distributed across the four operationally defined fractions in our study, agreeing with the findings of Greenway and Song (2002). Nonetheless, total levels of Zn remained below statutory PAS100 levels for 'clean composts' so despite the higher proportion of available Zn compared to other elements within the compost, we feel that this is of little concern for potential end users.

3.5.3 Effect of MSW compost on plant growth and metal uptake

The addition of composts has been shown to improve plant yield on degraded and acidic soils (Pérez-de-Mora *et al.*, 2006), whilst on more fertile soils, they have been shown to have a negative effect on growth of some species (Zheljazkov and Warman, 2004a). Our study demonstrated that *T. repens* exhibited a stronger negative response to the presence of MSW-derived compost than *L. perenne*, which generally appeared to exhibit few negative responses to compost addition throughout

the three growth trials. *Rhizobium leguminosarum* bacteria responsible for N fixation in the root nodules of nitrogen-fixing species such as *T. repens* have been shown to be highly sensitive to heavy metals (Tandy *et al.*, 2005) which may partially explain the observed negative response to MSW compost addition. It is also suggested that secondary metabolites from the breakdown of organic matter may have had an allelopathic effect on *T. repens* (Inderjit, 1996). In terms of performance of MSW compost compared to other composts at a 40% application rate, only the PAS100 specification compost (V) produced a significantly higher *L. perenne* biomass, however, this compost also had an unexplained negative effect on *T. repens*. Only the peat-based commercially-available compost out-performed the MSWC in terms of *T. repens* biomass, implying that the MSWC is suitable for use on degraded soils where organic matter is lacking and liming is required.

Addition of MSW compost to the fertile brown earth soil had no effect on the heavy metal content of either species (Fig. 3.3). Some authors (Pinamonti *et al.*, 1997; Zheljazkov and Warman, 2004a) have found that compost-borne heavy metals can increase foliar metal concentrations, and that composts therefore present a risk of bioaccumulation up the food chain. In contrast, other studies (Murillo *et al.*, 1995; Breslin, 1999) argue that the use of total metal values to prevent contaminated composts from being used in agriculture are a blunt instrument, and that such composts can be applied safely provided that metal accumulation is monitored. The use of MSW-derived compost to improve fertility of acidic, heavy metal contaminated soils (e.g. soil CS) shows promise, with above-ground biomass of both species comparable to that of the non-contaminated Eutric Cambisol when amended with the same compost. Pérez-de-Mora *et al.* (2006) demonstrated success with this theory in their study, and the burden of compost-borne heavy metals is negligible compared to the levels already present (Table 3.1). Pichtel and Anderson (1997) concluded that whilst the inevitable build up of heavy metals arising from repeated compost application is unacceptable for agricultural land, the use of lower-grade composts should be encouraged for the remediation of large contaminated sites.

3.5.4 Efficacy of EDTA and total extracts as predictors of phytoaccumulation of heavy metals

T. caerulescens has been shown to accumulate high levels of Cd and Zn, whilst not mobilising non-labile fractions by active use of root exudates (Hutchinson *et al.*, 2000; Zhao *et al.*, 2001). Neither *L. perenne* or *T. repens* are considered metal accumulators, and as discussed above, *T. repens* is known to be sensitive to heavy metals. Whilst the theory of using 'standard' plant species as bioindicators of metal phytoavailability and phytotoxicity can express the immediate phytoavailable levels of heavy metals, hyperaccumulator species such as *T. caerulescens* could be used to assess future toxicity. Our regression analysis found that EDTA-extractable Zn was significantly related to the metal concentration of *L. perenne* and *T. repens*, whilst total Zn was related to the concentration of Zn in all three species. Only *T. caerulescens* demonstrated any significant relationship between EDTA and total metal levels extracted from the soil (Table 3.3 and Fig. 3.7). These findings are somewhat contradictory in nature, and question the usefulness of simple chemical extractions to assess available fractions of heavy metals from soils, especially given that two supposedly different fractions correlate across species in predominantly similar ways, whilst not correlating across two chemically similar elements. Menzies *et al.* (2007) suggest that whilst complexing agents such as EDTA are widely used within the scientific literature, overall they correlate poorly with phytoavailable levels of heavy metals, indicating that cross-comparison of results between differing soil types can be misleading. Consequently, further work is required to assess more reliable predictors of heavy metal phytoavailability in composts arising from different sources, especially given the complexities of shoot-root transfer and metal partitioning within plants.

3.5.5 Conclusions

We have demonstrated that high C:N MSW fines can be composted successfully without the need to dilute with clean feedstocks to facilitate better composting. The co-composting of green waste and MSW fines did however reduce the total heavy metal content of the final compost, and some differences occurred in the fractionation of Ni, Pb and Zn between the two feedstocks. The addition of MSW

compost negatively affected plant biomass at high application rates, but had no significant effect on plant heavy metal concentration. The MSW compost performed better on poorer soils, giving increases in above ground biomass when compared to the unamended control, and was comparable to most commercially available composts in terms of both yield and heavy metal uptake. We therefore conclude from our study that whilst the MSW-derived compost contained total heavy metals levels in excess of regulation limits, they may be suitable to apply to agricultural land provided care is taken to ensure that repeated applications do not lead to an accumulation of heavy metals within the soil. MSW composts would be ideally suited to the restoration of already contaminated sites, where additional loading of heavy metals would be negligible by comparison to the levels already present. However, we agree with Zheljzkov and Warman (2004b) that as the organic material to which compost-borne heavy metals are bound degrades within the soil, redistribution of heavy metals may occur, and this may tend towards more labile pools, as well as more permanent residual fractions. We therefore recommend long-term monitoring and research into the fate of compost-bound heavy metals after application to soil.

3.6 References

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CHAPTER 4: USE OF COMPOSTS IN REMEDIATION OF A HEAVY METAL CONTAMINATED SOIL

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4.1 Abstract

High levels of heavy metals in soil can ultimately lead to pollution of drinking water and contamination of food. Consequently, sustainable remediation strategies for treating soil are required. The potential ameliorative effect of several composts derived from source-separated and mixed municipal wastes were evaluated in a highly acidic heavily contaminated soil (As, Cu, Pb, Zn) in the presence and absence of lime. Overall, metal amelioration was enhanced by compost whilst lime had little effect and even exacerbated metal mobilisation (e.g. As). The most effective were the peat-based and mixed waste composts, with green waste giving a poor response. All composts reduced soil solution heavy metal levels and raised soil pH and nutrient levels and are well suited to revegetation of contaminated sites. However, care must be taken to ensure correct pH management (pH 5-6) to optimise plant growth whilst minimising metal solubilisation, particularly at high pH. In addition, 'metal excluder' species should be sown to minimise metal entry into the food chain.

4.2 Introduction

Effective treatment of municipal solid waste (MSW) represents an important environmental, social and economic issue in most industrialised countries, and is associated with major long term problems when not adequately processed (Adani *et al.*, 2000). Council Directive 1999/31/EC (EC, 1999) on the landfilling of waste has set down strict mandatory targets for reduction in the amount of Biodegradable Municipal Waste (BMW) reaching landfill. The directive (EC, 1999) also states that no waste may be deposited in landfill without it first being treated to reduce its environmental footprint. Mechanical Biological Treatment (MBT) can be used to treat residual mixed wastes after recyclables have been removed to produce a stabilised, compost-like substance (Binner and Zach, 1999). Whilst according to EC (1999), this is suitable for landfill, it is desirable to find alternative uses for this mixed waste 'compost'. As soil organic matter levels have declined greatly in recent years (Bellamy *et al.*, 2005), it is advantageous to recycle as much of this 'waste' organic matter as possible, without unduly increasing the loading of contaminants onto uncontaminated soils. Due to the negative perception associated with the addition of waste products to agricultural land, one proposed use for mixed waste composts is in the restoration of post-industrial sites and in the remediation of land contaminated with heavy metals and organic pollutants (Hickman and Reid, 2008).

For successful long-term remediation, heavy metals in soil must be either removed or stabilised into a less environmentally available form (Kiikkilä *et al.*, 2001). Removal strategies for heavy metals are generally carried out "ex situ", however, this causes a significant deterioration of soil structure and often comes at a high economic cost, limiting its use on large contamination areas. In contrast, biostabilisation techniques are typically carried out "in situ" and are less expensive. Soils can naturally reduce mobility and bioavailability of heavy metals as they are retained in soil by sorption, precipitation and complexation reactions (Pérez-de-Mora *et al.*, 2005). This natural attenuation process (natural remediation) can be accelerated by the addition of organic amendments (Bolan and Duraisamy, 2003). Brown *et al.* (2003) concluded in their study that the use of a high application of biosolids was highly successful in increasing plant growth on a former mine site in Idaho, whilst Kiikkilä *et al.* (2001) found that an application of an organic mulch to a heavy metal contaminated forest

soil decreased the toxicity of soil solution to bacteria. Liming is the most common method of treatment, and can lead to the precipitation of heavy metals as metal-carbonates, and significantly reduces the exchangeable fraction of heavy metals within soils (Lee *et al.*, 2004). An investigation by Krebs *et al.* (1998), into the effect of organic and inorganic fertilisers +/- lime, found that lime reduced the uptake of Cd, Cu and Zn compared to fertilised but un-limed soils.

We propose that due to their similar properties to sewage sludge and mulch, composts can be used for the successful biostabilisation of heavy metal contaminated soil. The aim of this study was to evaluate the success of contrasting compost types to raise the pH and nutrient status of the soil, promote plant growth, decrease the environmentally-available metal pool in soil and reduce plant metal uptake.

4.3 Materials and methods

4.3.1 Substrate characteristics

Chemical characteristics of the soil and composts used in the experiment are listed in Table 4.1. A heavy metal contaminated soil (ca. 200 kg) was collected one day before the onset of experimentation from Parys Mountain, Anglesey, North Wales (53°23'22"N, 4°20'54"W). Parys Mountain was extensively mined for copper ore from the 18th century until the 20th century. The site covers an area of 200 ha and is covered with heavy metal contaminated mine spoil, dominated by sulphide minerals including pyrite, chalcopyrite, sphalerite and galena, with lesser amounts of other minerals (Walton and Johnson, 1992).

Table 4.1: Chemical properties of the substrates used in the plant growth trials. All values in mg kg⁻¹ dry matter unless otherwise stated.

| | Soil | | Composts | | | |
|--|-----------------|-------------|-------------|-------------|-------------|-------------|
| | C | G | GF | GFP | MSW | PB |
| Moisture content (%) | 13.4 ± 0.1 | 41.2 ± 2.5 | 52.7 ± 3.8 | 55.9 ± 1.1 | 56.7 ± 1.7 | 59.7 ± 0.2 |
| Organic matter (%) | 2.5 ± 0.2 | 25.2 ± 2.9 | 44.2 ± 1.9 | 39.8 ± 2.2 | 42.2 ± 3.7 | 93.7 ± 0.2 |
| pH | 2.27 ± 0.03 | 8.11 ± 0.18 | 7.80 ± 0.16 | 8.12 ± 0.09 | 7.28 ± 0.03 | 5.51 ± 0.04 |
| EC ^a (mS cm ⁻¹) | 2.9 ± 0.1 | 0.7 ± 0.2 | 1.5 ± 0.4 | 1.4 ± 0.4 | 3.6 ± 0.8 | 0.7 ± 0.1 |
| Total C (%) | 0.7 ± 0.3 | 13.2 ± 0.9 | 22.7 ± 3.8 | 21.9 ± 0.3 | 24.6 ± 4.3 | 39.9 ± 0.1 |
| Total N (%) | BD ^b | 0.62 ± 0.06 | 1.20 ± 0.21 | 1.37 ± 0.88 | 0.97 ± 0.17 | 1.05 ± 0.01 |
| Total P (mg g ⁻¹) | ND ^c | 2.8 ± 0.6 | 5.0 ± 1.3 | 5.9 ± 0.7 | 0.9 ± 0.2 | 0.5 ± 0.1 |
| Total K (mg g ⁻¹) | 15.4 ± 1.3 | 7.4 ± 1.1 | 9.9 ± 2.3 | 10.8 ± 0.6 | 10.1 ± 0.6 | 5.0 ± 0.1 |
| Total Ca (mg g ⁻¹) | 6.5 ± 0.6 | 2.2 ± 0.4 | 4.1 ± 1.2 | 7.8 ± 0.6 | 51.8 ± 5.3 | 11.1 ± 1.1 |
| Total Na (mg g ⁻¹) | 1.5 ± 0.1 | 1.1 ± 0.2 | 2.0 ± 0.7 | 2.5 ± 0.1 | 8.3 ± 1.1 | 0.9 ± 0.1 |
| KCl-extractable NO ₃ ⁻ | 1.7 ± 0.1 | 1.2 ± 0.5 | 176 ± 72 | 170 ± 16 | 21.9 ± 11.8 | 587 ± 24 |
| KCl-extractable NH ₄ ⁺ | 13 ± 1 | 33 ± 2 | 71 ± 8 | 51 ± 12 | 29 ± 6 | 663 ± 29 |
| Olsen P | 3 ± 1 | 119 ± 5 | 248 ± 27 | 267 ± 43 | 132 ± 32 | ND |
| NH ₄ OAc-extractable K | 9 ± 1 | 1113 ± 230 | 1283 ± 211 | 1070 ± 226 | 2925 ± 382 | 2743 ± 23 |
| Total As | 259 ± 59 | BD | BD | BD | 17 ± 7 | BD |
| Total Co | 3.1 ± 1.8 | 25.2 ± 6.7 | 14.4 ± 1.6 | 13.8 ± 2.2 | 14.5 ± 13.3 | 4.3 ± 0.8 |
| Total Cr | 0.6 ± 0.1 | 37.4 ± 2.8 | 18.9 ± 2.2 | 20.1 ± 1.8 | 48.1 ± 13.3 | 4.5 ± 0.3 |
| Total Cu | 4735 ± 1023 | 66.4 ± 39.5 | 36.5 ± 10.3 | 37.4 ± 3.4 | 329 ± 83 | 14.9 ± 0.8 |
| Total Mo | BD | BD | BD | BD | 9.4 ± 0.6 | 12.1 ± 0.6 |
| Total Ni | BD | 31.3 ± 2.3 | 32.5 ± 12.0 | 18.2 ± 2.2 | 87.2 ± 19.2 | 8.6 ± 4.4 |
| Total Pb | 16883 ± 1753 | 40.0 ± 2.2 | 59.6 ± 4.5 | 45.7 ± 6.7 | 906 ± 324 | 14.5 ± 1.3 |
| Total Zn | 846 ± 68 | 56.5 ± 3.3 | 57.0 ± 11.7 | 54.8 ± 9.9 | 505 ± 216 | 5.4 ± 1.5 |

^a Electrical conductivity, ^b BD = Below limit of detection (< 3.75 mg kg⁻¹ for heavy metals, < 0.01 % for N), ^c ND = Not determined

Green waste-derived compost (G), Green waste and catering waste-derived compost (GF), green waste, catering waste and paper waste-derived compost (GFP), and municipal solid waste-derived compost (MSW) were produced using a commercially available CT-5[®] and EcoPOD[®] in-vessel composting system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA) located at the Ffridd Rasmus Waste Treatment Facility, Harlech, North Wales (52°52'59"N, 4°06'43"W). The in-vessel composter was filled with a CT-5[®] feed hopper (3 m³ feedstock volume) which uses a hydraulic ram to push the material through a filling chamber and into an extended 1.5 m diameter green plastic EcoPOD[®] vessel at a fill rate of approximately fill rate 3 m³ min⁻¹. At the same time as filling the EcoPOD[®], a

rigid perforated (7.62 cm diameter pipe with 1.59 mm slits) plastic aeration pipe is inserted into the base of the vessel to provide forced aeration. The aeration regime can be closely controlled by means of a timed fan (Ag-Bag International Ltd, Warrenton, OR, USA) running at a flow rate of 137 l min^{-1} (Roberts *et al.*, 2007). The timed aeration regime was managed manually in order to maximise the rate of composting. In the initial 18 d, aeration was managed in order to maintain high temperatures and therefore optimal sanitation conditions (typically air pumped through the vessel for 2 min every 10 min). This was changed to 3 min on, 7 min off to compensate for the relatively wet feedstocks on day 19. On day 80, the duration of aeration was increased to 2 min on, 4 min off and the direction was reversed to extract moisture from the pile. This continued until day 112, when the vessel was opened, and the compost bagged manually for storage for use in the growth trials. The green waste compost (G) was made from 4.0 t of source-separated shredded municipal green waste obtained from the Penhesgyn Gors Landfill Site, Anglesey, North Wales ($53^{\circ}14'45''\text{N}$, $4^{\circ}11'45''\text{W}$). The GF compost was made from a mixture of 1.2 t of source-separated catering waste collected from commercial hotels and restaurants and 2.8 t source-separated shredded green waste. The GFP compost was made from 2.0 t source-separated shredded green waste, 1.6 t source-separated catering waste, and 0.4 t source-separated shredded waste paper. The MSW compost was made 8.0 t mixed municipal waste which had been pre-processed through a commercial DANO Drum pulverisation plant (Keppel-Seghers UK Ltd., Wolverhampton, UK) and the fine, largely biodegradable fraction collected by passage through a trommel screen with 38 mm mesh size. Only the fine fraction (<5 cm) was used, and this contained $64 \pm 3 \%$ organic matter ($n = 18$).

4.3.2 Plant growth trials

A fully factorial, randomised complete block design experiment was set up with two litre plastic plant pots in a heated greenhouse with a day/night rhythm of 20/18°C photoperiod of 16 h and augmented with 400 W Sun SON-T horticultural lamps. Six substrates were used in the trials including: Contaminated soil (Control; C), the four composts described above (G, GF, GFP and MSW) and a commercially-

available peat-based compost (PB; Humax[®], L & P Peat Ltd, Carlisle, UK). Each of the composts were mixed 40:60 (v/v) with the contaminated soil. All treatments were carried out with and without lime addition to the growing media (Gem[®] Garden Lime, 53% CaO, Gem Gardening, Accrington, UK), applied at rates determined by the SMP lime requirement method ($n = 6$) (Sims, 1996), giving a dose of 109 g lime per pot. This gave a total of 12 individual treatments, replicated 6 times to give a total 72 pots in the experiment. The soil and compost were mechanically homogenised before lime addition. *Agrostis capillaris* L. (Common bent grass) was sown in all pots at a density of 4 g seed m⁻², and the plants grown for 64 d before being harvested.

4.3.3 Sampling and analysis

Standard chemical analyses were carried out in triplicate on each growth substrate. Moisture content was determined by drying samples at 80°C for 24 h and organic matter content was determined as loss-on-ignition at 450°C overnight. pH (Hanna Instruments pH 209 pH meter) and electrical conductivity (EC) (Jenway 4010 EC meter) were determined in a 1:2 (v/v) slurry, after mixing for 1 h. Total C and N were determined using a CHN2000 analyser (LECO Corp., St Joseph, MI). Prior to total elemental analysis, substrates were air dried (25°C, 14 d) and plant samples dried at 80°C before being ground in a T1-100 vibrating sample mill (Heiko Co Ltd., Fukushima, Japan) equipped with tungsten grinding vessels. Subsamples of the ground material were then digested using HNO₃ (Havlin and Soltanpour, 1980). Nitrate and ammonium were extracted with 1 M KCl at a 1:5 (w/v) fresh sample:extractant ratio for 1 h on a reciprocating shaker at 250 rev min⁻¹ (Zhong and Makeschin, 2003). Nitrate and ammonium were determined using a San⁺⁺ segmented flow analyser (Skalar Inc., Norcross, GA). Plant-available nutrients were extracted with 1 M NH₄OAc (pH 7.0) using a 1:5 (w/v) fresh sample:extractant ratio for 1 h on a reciprocating shaker at 250 rev min⁻¹. K, Na and Ca were analysed using a Sherwood 410 flame photometer (Sherwood Scientific, Cambridge, UK). Extractable heavy metals and P were extracted using 0.5 M acetic acid using 1:5 (w/v) fresh sample:extractant ratio (Quevauviller, 1998). Heavy metals were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Fissions PlasmaQUAD II Turbo ICP-MS.

Phosphate was determined colourimetrically using the method of Murphy and Riley (1962).

Plant-available metals were determined in soil solution. Soil solution was collected from each pot overnight at each sampling interval using 10 cm Rhizon-MOM® *in situ* soil solution samplers (Rhizosphere Research Products, Wageningen, The Netherlands), and was analysed using the same methods as detailed for the extracts from the substrate samples. In addition, total phenolics in soil solution were determined according to Swain and Hillis (1959). Humic substance-C in soil solution was estimated by measuring the absorbance at 400 nm on a VERSAmax tunable microplate reader (Molecular Devices Corp., Sunnyvale, CA) and calibration with a commercial humic acid standard solution of known dissolved organic C content (H16752 Humic acid Na salt; Sigma Chem. Co., St Louis, MO).

4.3.4 Statistical analysis

All data were inputted into SPSS v14.0 (SPSS Inc., Chicago, IL), and a 2-way fully factorial ANOVA was performed, using lime as the primary factor, and compost treatment as the secondary factor. Tukey's Honestly Significant Difference (HSD) post hoc test was used to differentiate between the compost treatments. Pearson's correlations were also carried out to assess the effect of each variable on plant biomass. Means and standard errors were computed using Microsoft Excel 2003 (Microsoft Corp., Redmond, WA), and all graphical figures were produced in SigmaPlot v10.0 (Systat Software Inc., San Jose, CA). With the exception of soil solution data, all nutrient and heavy metal content values are expressed on a dry weight basis.

4.4 Results

4.4.1 Substrates and plant growth

The initial chemical analysis of the substrates illustrated that the contaminated soil was extremely acidic, nutrient poor and contained extremely high levels of heavy metals, especially Cu, Pb and Zn (Table 4.1). In comparison to the

source-separated and commercial composts, the MSW-derived compost was very similar in most of its chemical and physical properties, with the exception of its higher EC and heavy metal content. Whilst these metal values were significantly greater than the other composts, and may cause concern if repeatedly applied to agricultural land, the concentrations of Cu, Pb and Zn remained very low (< 10 % for Cu and Pb, < 50 % for Zn) in comparison to those already present in the contaminated soil.

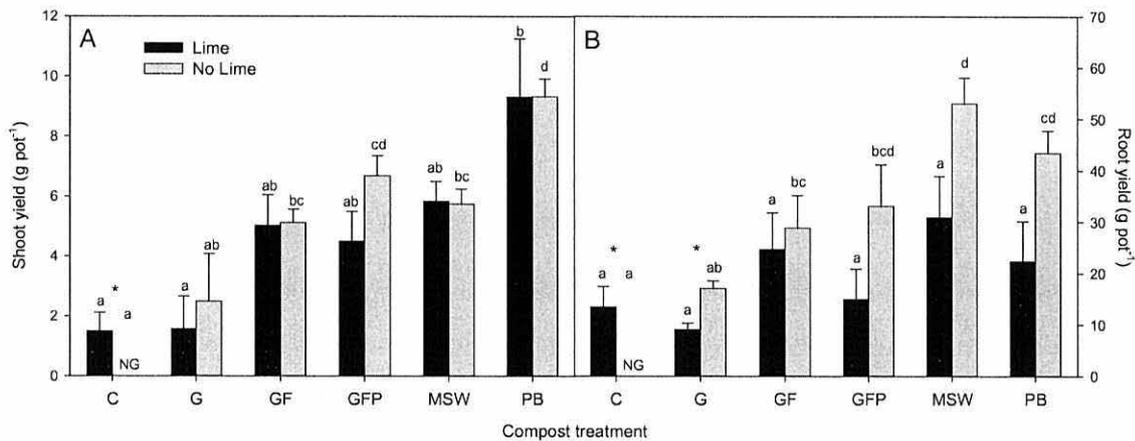


Figure 4.1: Influence of compost type and lime application on root and shoot biomass after being grown in a heavy metal contaminated soil for 2 months. * denotes significant difference ($P < 0.05$) between lime treatments for each compost treatment, while different letters for each lime treatment denote significant differences ($P < 0.05$) between compost treatments. NG = no growth.

Table 4.2: (Over page) Chemical properties of the soils and soil solutions from each treatment after 64 days of growth. Soil solution values in mg l^{-1} , all other values in mg kg^{-1} , apart from where stated separately. BD = Below LOD ($< 3.75 \text{ mg kg}^{-1}$ for total metals, and $< 0.05 \text{ mg kg}^{-1}$ for extractable metals)

| | Soil (Control) | | Treatment PB | | Treatment MSW | | Treatment GFP | | Treatment GF | | Treatment G | |
|---------------------------|----------------|-----------|--------------|-----------|---------------|-----------|---------------|-----------|--------------|-----------|-------------|-----------|
| | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime |
| Moisture content (%) | 13.3±1.7 | 10.1±1.7 | 26.7±4.8 | 29.6±2.8 | 24.4±2.5 | 20.6±1.5 | 23.3±1.7 | 21.1±2.9 | 21.0±1.4 | 20.4±1.6 | 22.4±1.6 | 20.5±1.4 |
| Organic matter (%) | 2.6±0.2 | 5.4±3.2 | 9.0±2.1 | 12.4±1.4 | 9.8±2.8 | 7.2±1.2 | 8.7±0.3 | 8.0±1.8 | 9.9±1.5 | 6.3±1.6 | 7.8±1.7 | 6.7±0.8 |
| Soil solution pH | 2.91±0.04 | 7.08±0.07 | 4.28±0.09 | 7.27±0.04 | 7.29±0.02 | 7.27±0.03 | 6.94±0.06 | 7.34±0.04 | 6.92±0.07 | 7.19±0.06 | 6.83±0.19 | 7.24±0.03 |
| Soil solution EC(mS cm-1) | 1.0±0.1 | 1.5±0.3 | 1.0±0.1 | 1.6±0.4 | 2.4±0.2 | 1.6±0.3 | 2.5±0.6 | 2.1±0.4 | 1.7±0.3 | 2.1±0.3 | 0.8±0.1 | 1.0±0.1 |
| Soil solution NO3- | 2.69±0.54 | 0.50±0.20 | 1.61±0.13 | 1.38±0.19 | 1.26±0.09 | 1.16±0.20 | 1.40±0.10 | 2.33±1.12 | 1.35±0.14 | 0.92±0.18 | 1.02±0.18 | 0.76±0.07 |
| Soil solution NH4+ | 5.10±0.61 | 0.12±0.07 | 0.03±0.01 | 0.11±0.08 | 0.07±0.01 | 0.02±0.01 | 0.15±0.07 | 0.06±0.02 | 0.07±0.01 | 0.05±0.02 | 0.04±0.02 | 0.03±0.01 |
| Soil solution P | 0.20±0.00 | 0.25±0.02 | 0.19±0.01 | 0.24±0.01 | 0.23±0.01 | 0.26±0.02 | 0.29±0.02 | 0.27±0.02 | 0.61±0.30 | 0.27±0.02 | 0.31±0.02 | 0.32±0.03 |
| Soil solution K | 6.56±1.21 | 1.68±0.94 | 0.71±0.11 | BD | 13.6±3.0 | 11.5±4.9 | 85.6±33.8 | 109±22 | 164±28 | 122±44 | 79.9±22.5 | 89.3±16.8 |
| Soil solution Na | 30.8±5.3 | 25.8±4.8 | 53.8±7.9 | 86.9±24.5 | 205±30 | 136±27 | 188±41 | 182±42 | 145±22 | 156±33 | 40.6±5.6 | 63.4±14.7 |
| Soil solution Ca | 16.7±4.8 | 158±22 | 78.0±10.1 | 151±39 | 195±15 | 162±22 | 179±32 | 156±27 | 124±19 | 160±13 | 66.1±11.0 | 88.2±11.5 |
| Soil solution humic C | 0.64±0.46 | 1.86±1.05 | 0.56±0.04 | 5.19±0.44 | 3.44±0.34 | 2.96±0.37 | 5.50±0.97 | 5.67±0.69 | 7.99±0.80 | 5.51±1.38 | 4.35±0.79 | 4.96±0.43 |

| | Soil (Control) | | Treatment PB | | Treatment MSW | | Treatment GFP | | Treatment GF | | Treatment G | |
|-----------------------------------|----------------|-----------|--------------|-----------|---------------|-----------|---------------|-----------|--------------|-----------|-------------|-----------|
| | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime |
| Total As | 259±60 | 352±38 | 406±32 | 332±83 | 525±101 | 445±26 | 423±23 | 454±43 | 412±68 | 421±103 | 335±42 | 472±67 |
| Total Co | BD | 9.14±0.70 | BD | 4.32±1.67 | BD | BD | BD | 8.29±6.20 | BD | 5.61±1.09 | BD | 6.35±0.49 |
| Total Cr | BD | BD | BD | BD | 6.81±0.25 | 21.0±14.4 | BD | BD | BD | BD | 6.22±1.66 | BD |
| Total Cu | 4736±1023 | 5420±430 | 3564±171 | 4386±586 | 3597±267 | 3112±62 | 3367±100 | 3676±616 | 3279±568 | 3635±160 | 4296±967 | 2610±285 |
| Total Mo | BD | 23.3±1.6 | BD | BD | 5.62±0.46 | BD | 4.64±0.51 | BD | BD | 10.1±8.8 | BD | 26.9±2.4 |
| Total Ni | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD |
| Total Pb (mg g ⁻¹) | 16.9±1.8 | 28.7±2.5 | 21.1±4.5 | 18.6±0.4 | 15.6±1.0 | 15.7±2.6 | 19.4±2.1 | 18.1±1.6 | 14.3±0.9 | 21.0±4.1 | 20.0±0.3 | 32.6±17.7 |
| Total Zn | 846±68 | 1139±160 | 789±82 | 751±79 | 966±159 | 690±41 | 1130±203 | 1525±810 | 781±172 | 934±87 | 894±87 | 742±142 |

| | Soil (Control) | | Treatment PB | | Treatment MSW | | Treatment GFP | | Treatment GF | | Treatment G | |
|---------------------|----------------|-----------|--------------|-----------|---------------|-----------|---------------|-----------|--------------|-----------|-------------|-----------|
| | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime | No lime | Lime |
| HOAc extractable As | BD | BD | BD | BD | BD | BD | 0.37±0.19 | BD | BD | BD | BD | BD |
| HOAc extractable Co | BD | 0.16±0.09 | BD | 0.25±0.06 | 0.15±0.02 | 0.55±0.06 | BD | 0.39±0.06 | BD | 0.28±0.07 | 0.11±0.01 | 0.40±0.02 |
| HOAc extractable Cr | 0.15±0.03 | 0.26±0.03 | 0.23±0.05 | 0.32±0.01 | 0.33±0.02 | 0.35±0.01 | 0.26±0.01 | 0.33±0.00 | 0.26±0.01 | 0.30±0.02 | 0.26±0.01 | 0.37±0.04 |
| HOAc extractable Cu | 1.68±1.04 | 1.23±0.08 | BD | 0.12±0.06 | 6.01±0.69 | 3.12±0.38 | BD | 0.41±0.15 | BD | 0.47±0.30 | BD | 0.70±0.26 |
| HOAc extractable Mo | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD | BD |
| HOAc extractable Ni | BD | 1.23±0.86 | BD | 1.93±0.97 | 1.17±0.23 | 5.30±0.86 | BD | 3.41±0.62 | BD | 2.42±0.70 | BD | 3.15±0.16 |
| HOAc extractable Pb | 138±37 | 917±351 | 137±42 | 246±66 | 201±26 | 219±44 | 104±32 | 345±132 | 75.9±18.5 | 430±113 | 136±46 | 559±82 |
| HOAc extractable Zn | BD | BD | BD | BD | 14.7±1.7 | 11.2±1.9 | 2.08±0.25 | 0.59±0.14 | 1.73±0.12 | 0.30±0.15 | 1.62±0.47 | 0.65±0.04 |

Without any soil amendment, the seeds failed to germinate in the contaminated soil, and even after lime amendment, both the above- and below-ground biomass remained very low (Fig. 4.1). Overall, lime application had no significant effect on the above-ground biomass in any of the compost treatments ($P > 0.05$, $n = 72$), and actually resulted in a negative growth response in the green waste-derived compost treatment ($P < 0.05$, $n = 6$). Apart from this, lime had no significant effect ($P > 0.05$, $n = 30$) on below-ground biomass from any of the other compost treatments. Of all the chemical variables, only pH was significantly affected by lime application across the whole dataset ($P < 0.001$, $n = 72$), although surprisingly there was no significant increase in soil solution Ca in any of the compost treated soils after the addition of lime ($P > 0.05$, $n = 72$).

With the exception of the green waste-derived compost, all the composts enhanced both above- and below-ground biomass production in the contaminated soil in the absence of lime (Fig. 4.1). The peat-based compost produced the highest above-ground biomass ($P < 0.05$, $n = 72$), although there was no significant difference between the GFP, MSW and PB composts in below-ground biomass measurements ($P > 0.05$, $n = 36$). Surprisingly, neither compost nor lime addition induced a significant change in soil solution nitrate, ammonium or phosphate concentration (Table 4.2).

4.4.2 Metal uptake and availability

Figure 4.2 illustrates the heavy metal content of above-ground biomass of *A. capillaris* L. grown in the 12 different treatments (5 composts and control, all with or without lime addition). With the exception of the green waste-derived compost, all the lime-amended composts produced plants with reduced foliar heavy metal content in comparison to the limed control treatment without compost. As there was no plant growth in the non-lime amended control treatment, no similar comparisons could be drawn. Generally, however, foliar metal accumulation was lower in compost treated soils when lime was not added in comparison to soil that had received both lime and compost. From EU and UK regulations (EC, 2003; TSO, 2006), it can be seen that foliar Zn concentrations remained well below the European guidelines for safe animal feedstuffs (limit 150 mg kg^{-1}) for all treatments, whilst only the PB compost complied

with Cu threshold limit of 10 mg kg^{-1} . Similarly, the foliar threshold limit for Pb of 40 mg kg^{-1} was exceeded by all treatments, whereas without lime addition, As was reduced to below detection limits (foodstuff limit 4 mg kg^{-1}) for the GF, GFP, MSW and PB treatments. Foliar Cd concentrations were below the limit of detection for all treatments (data not presented). Although no Ni could be detected in the contaminated soil, significant amounts were accumulated in the above-ground biomass from all compost treatments (range $15\text{-}109 \text{ mg kg}^{-1}$; data not presented) relative to published standards (BSI, 2005).

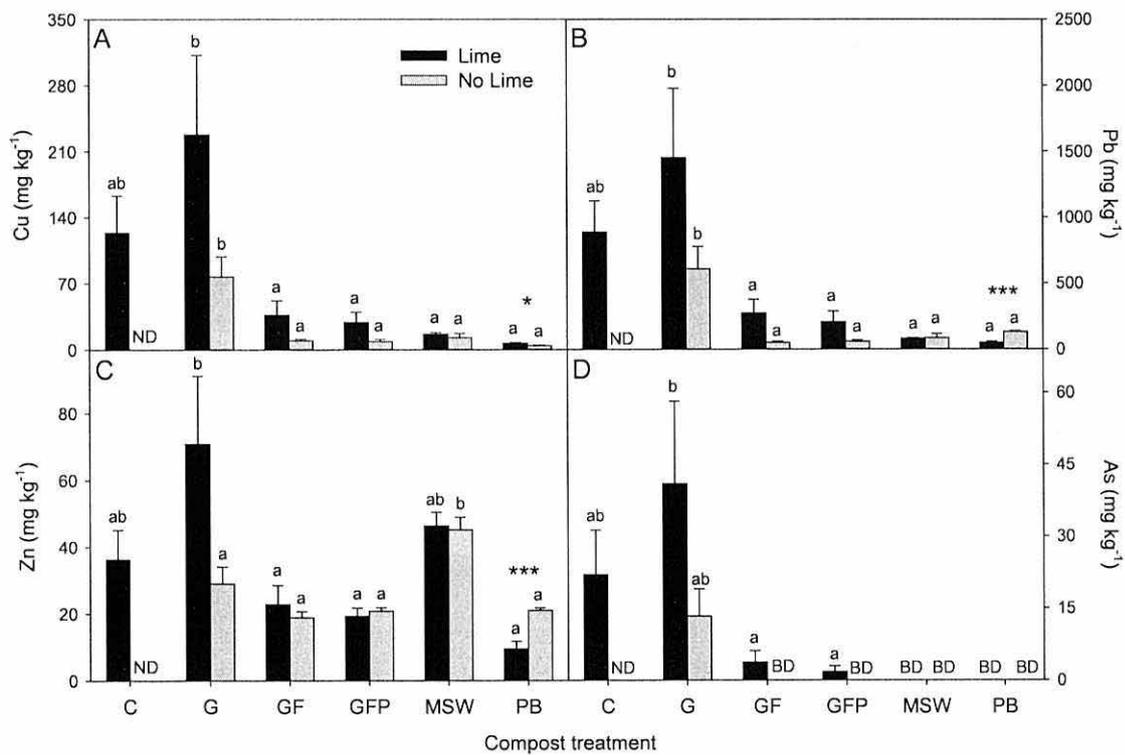


Figure 4.2: Influence of compost type and lime on the foliar metal content of plants grown in a metal contaminated soil for 2 months. * and *** denote significant difference ($P < 0.05$ and $P < 0.001$) between lime treatments for each compost treatment, while different letters denote significant differences between compost treatments for each lime treatment ($P < 0.05$). ND = no growth, BD = below limit of detection ($< 3.75 \text{ mg kg}^{-1}$).

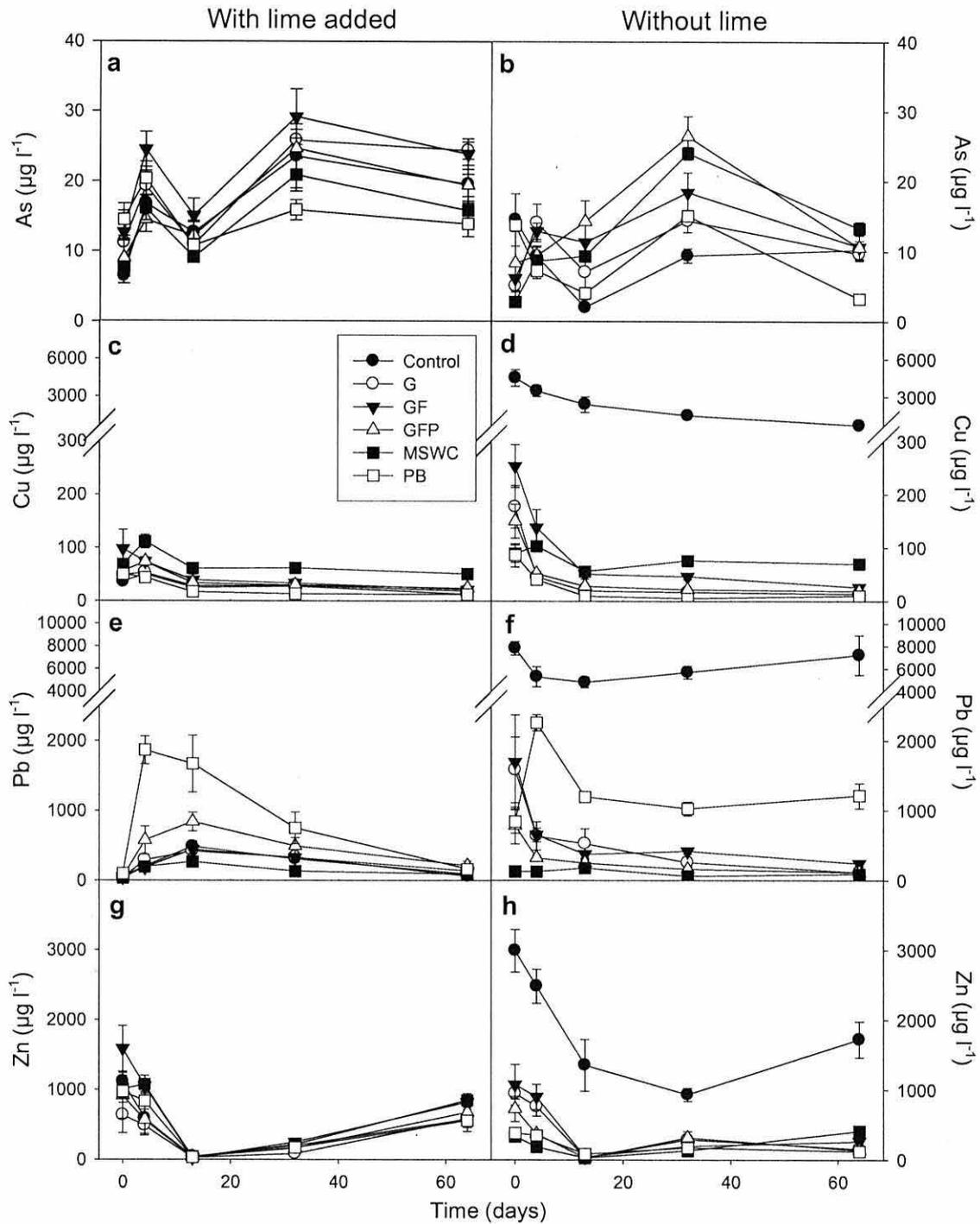


Figure 4.3: Influence of compost type and lime on the temporal dynamics of heavy metals in soil solution over a 2 months growth period. a) Arsenic with lime, b) Arsenic without lime, c) Copper with lime, d) Copper without lime, e) Lead with lime, f) Lead without lime, g) Zinc with lime, h) Zinc without lime. G = green waste compost, GF = green waste and food waste compost, GFP = green waste, food waste and shredded paper compost, MSWC = MSW compost, PB = peat-based compost

4.4.3 Soil solution metal concentration change over time

From Figure 4.3, it can be seen that with the exception of As, the general trend was for all metals to be lowered in concentration in the soil solution over the 64 day experimental period. Lime amendment had a highly significant effect on metal concentrations in the contaminated soil control treatment, inducing a 20-fold reduction in soil solution Cu and Pb concentrations, and a 2-fold reduction in Zn. In contrast, lime addition resulted in a significant rise in soil solution As concentration ($P < 0.01$, $n = 12$). This finding for As is mirrored for all other compost treatments, with the exception of the MSWC treatment, where no significant difference was recorded ($P > 0.05$, $n = 12$). With the exception of the control treatment, lime also caused a significant increase in the amount of Zn in soil solution by day 64. However, no consistent response pattern was observed for Cu and Pb across all the compost amendment treatments.

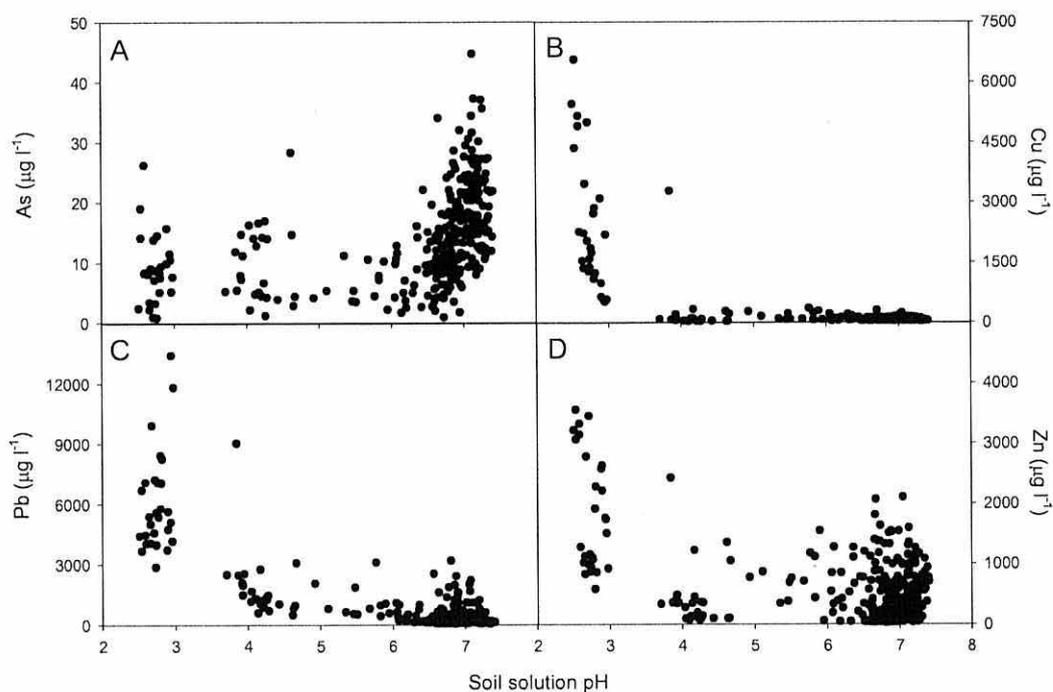


Figure 4.4: Relationship between soil solution pH and heavy metal concentration ($n = 334$); a) As concentration, $r^2 = 0.393$, $P < 0.01$; b) Cu concentration, $r^2 = -0.667$, $P < 0.01$; c) Pb concentration, $r^2 = -0.791$, $P < 0.01$; d) Zn concentration, $r^2 = -0.491$, $P < 0.01$.

The relationship of metal concentrations with soil solution pH is shown in Figure 4.4. Overall, across all time-points and treatments, pH was significantly negatively correlated with soil solution Cu, Pb and Zn ($P < 0.01$, $n = 334$) with the threshold for significant metal solubilisation occurring at around pH 3.5. In contrast, As mobilisation was significantly positively correlated with soil solution pH ($P < 0.01$, $n = 334$) with the threshold value for mobilisation being around pH 6.0.

4.5 Discussion

4.5.1 Metal dynamics in soil

With the exception of As, metal concentrations in the soil solution progressively declined over the 64 days of the trial. This response pattern can be attributed to several factors which were most likely to have occurred simultaneously. Firstly, some leaching of metals from the soil matrix may have occurred in response to the regular watering regime (as evidenced by the lack of a significant increase in soil solution Ca in the limed plots after 64 d). However, based on the vast reserves of metal in the soil and the fact that the contaminated soil has been exposed to decades of leaching (annual rainfall 840 mm) we do not think this can explain all of our findings. This hypothesis is supported to some extent by the decrease in soil solution electrical conductivity in all treatments and particularly for Zn in the unamended control soil where no plant growth occurred. Secondly, a small reduction in soil solution metal concentration could have occurred in response to plant foliar uptake. In this case, however, it would be expected that the soil solution would be rapidly replenished due to desorption of metals from the solid phase. Metals may also have become sorbed onto root surfaces. Although not quantified here due to the impossibility of separating soil particles from roots, a study by Ginn *et al.* (2008) suggests that this could induce significant changes in metal mobility in plant-soil systems. Thirdly, metal reduction could have occurred due to progressive binding of metals to the added compost which is known to be rich in metal binding sites (Kiikkilä *et al.*, 2001; Sebastia *et al.*, 2008). Concurrent with this metal binding, the composts induced a gradual alkalisation of the soil which would induce precipitation of metal hydroxides and carbonates making them less bioavailable (Kumpiene *et al.*, 2007). Although CaCO_3

addition may also have induced metal precipitation in the soil (Bolan and Duraisamy, 2003), the observation that a significant reduction in metal concentration occurred in the non-limed treatments indicates that compost may have a greater liming potential due to its stronger ability to buffer soil pH.

In the case of Pb, the temporal pattern in soil solution appeared to be highly compost specific with the response largely related to the differential compost-induced shifts in pH (Kiikkilä *et al.*, 2001). In some cases, compost addition appeared to transiently stimulate Pb mobilisation. Schwab *et al.* (2007) also reported an increase of 20 mg Pb l⁻¹ in leachate collected from a contaminated soil amended with aged cattle manure. They attributed this increase to high levels of dissolved organic C (DOC) in the manure which would theoretically lead to increased metal complexation, reduced sorption and greater rates of vertical mass transfer in soil. Our results, however, show a significant negative correlation between dissolved humic substances and Pb in soil solution ($r^2 = -0.315$, $P < 0.01$). This relationship can partially be explained by the fact that the treatments with the highest humic substance content also had the highest pH ($r^2 = 0.456$, $P < 0.01$).

Although As binds strongly to both Fe and Al hydroxides, and to a lesser extent organic matter, this binding is inversely correlated with pH as occurred in this study (O'Neill, 1990). From a risk assessment perspective it is unfortunate that both lime and compost stimulated As release into the soil solution. This finding suggests that there is a fine balance between immobilising some heavy metals whilst preventing the release of others. From Figure 4.4 it can be seen that the safest range to bring about soil remediation without risking metal release lies in the range pH 5 to 6. From this perspective, our results suggest that co-addition of lime and compost should not be undertaken. Fortunately, this pH is likely to be suitable for most plant species used in land restoration. As the pH and metal buffering capacity varies significantly between different compost types, the rate of compost application required to achieve the optimal pH for metal immobilisation requires careful consideration. Currently, compost application rates for restoration are normally chosen based on either their availability, economic cost, metal loading or nutrient content but not on their de-acidifying potential. It would therefore be useful to undertake further scientific trials to try and characterise different compost types in terms of 'lime equivalents'. In

particular, a correlation of these buffer potential results with other measures which can be simply implemented by industry would be desirable (e.g. near infrared reflectance spectroscopy; Huang *et al.*, 2007).

4.5.2 Plant growth and metal accumulation

The compost-induced increase in both above- and below-ground biomass in the metal contaminated soil contrasts with findings from some previous studies (Rosario *et al.*, 2007) while remaining in line with others (van Herwijen *et al.*, 2007). This suggests that the impact of compost is highly context specific. In addition, our results show that it is also highly compost specific. This compost induced alleviation of phytotoxicity has been ascribed to an enhanced nutrient availability and physical structure of the substrate. However, it is also possible that the composts introduced keystone microbial species that were previously absent in the highly acidic and contaminated substrate. These new organisms may have provided additional functionality to the soil ecosystem (e.g. mesofauna such as collembola to stimulate organic matter turnover, nitrifying bacteria to facilitate enhanced N cycling, mycorrhizal spores to enable better stress tolerance etc). Although compost application can induce changes in soil microbial diversity (Lejon *et al.*, 2007), in many studies composts have not resulted in a significant shift in microbial community structure (Calabrix *et al.*, 2007; Carrera *et al.*, 2007). This suggests again that compost response is highly context specific and probably relates to the wide diversity in microbial community structure between different compost types as well as that of the substrate it is introduced into (Klammer *et al.*, 2008). Further work is therefore required to determine how changes in diversity may impact upon their subsequent environmental response.

Although routinely used for remediating metal contaminated sites, plants in the lime-treated soil responded poorly in comparison to the composts presumably due its lack of balanced nutrients and an increase in some metals. As discussed previously, the addition of lime is therefore not warranted in remediation schemes where organic matter is being added.

Despite much higher levels of As, Cu, Pb and Zn present in the MSW compost, we found that this had little effect on plant uptake, with the exception of Zn. This suggests that total metal concentrations in composts may not provide a reliable indicator of metal phytoavailability. Further work is therefore required to determine the chemical form and long-term stability of metals in composts added to soil.

4.5.3 Use of composts in land restoration

This study clearly demonstrated that a range of waste-derived composts of varying quality can all be used to alleviate metal toxicity in a heavily contaminated soil. Further, the success of plant establishment was not correlated with legislative compost standards used to conventionally assess compost quality (BSI, 2005). Typically, these standards are formulated specifically for the use of composts destined for agriculture, horticulture and amenity sites (e.g. public parks and gardens). While this approach is justified where public or environmental health may be compromised, we feel that these rigid standards will provide legislative and social barriers for use of composts in post-industrial, contaminated sites. Considering the large amounts of low grade composts (e.g. MBT- and MSW-derived composts) that are now being produced in efforts to divert waste from landfill, there is an urgent need to find good uses for these products. Alongside others, our research suggests that remediation and stabilisation of metal contaminated sites may provide a viable option but that appropriate standards need to be developed to promote industry adoption of this approach. Similarly, research also suggests that these composts can also accelerate the removal and stabilisation of organic pollutants present in soil (Kastner and Mahro, 1996; Tejada *et al.*, 2008).

We conclude that with compost application to metal contaminated sites, careful consideration of soil pH is required to ensure optimal metal immobilisation and that further work be carried out to develop new tools for predicting the neutralising potential of different compost types. Whilst yield was greatly increased, the heavy metal content of the above-ground biomass is of concern, with potentially toxic levels of Cu and Pb present in leaves from most treatments. We therefore suggest that care be taken when selecting species to grow on sites stabilised with

composts to ensure that 'metal excluding' species or varieties (e.g. *Festuca rubra* cv. Merlin) are chosen to reduce the risk of animal toxicity due to grazing and ingestion of high levels of heavy metals. With regard to MSW-derived composts, further work is required to ensure that their higher heavy metals remain in an unavailable form in the long term.

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CHAPTER 5: CHEMICAL MODIFICATION OF COMPOSTS TO ENABLE SUCCESSFUL HABITAT RESTORATION

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5.1 Abstract

1. Use of composts for habitat restoration offers advantages in terms of efficient use of resources, and on blocky mineral substrates composts' high organic matter content and good water holding capacity are advantageous. However, for restoration of heathland acidic grassland, the high pH and nutrient content of composts are disadvantageous.
2. We investigate the ability of chemical amendment of compost to reduce its pH and P-availability in order to improve suitability for use in reclamation of blocky quarry waste spoil and restoration of acidic grassland. As an ecological bioassay, the effect of these amendments was observed on competition between two grass species, *Agrostis capillaris* and *Festuca ovina* which co-exist on acidic to moderately acidic soils in UK.

3. A factorial randomised complete block experiment was set up in 4-litre pots in a temperate greenhouse, using two composts and two control soils collected from upland acidic grassland. Treatments applied to the two composts were with and without addition of S^0 to reduce pH, and addition of three different doses (and without) of $Fe(OH)_3$ from a coal waste treatment plant to reduce soil P availability. Soil solution chemistry was assessed over the trial, and above ground biomass and P concentration of the two species at harvest after 93 days.
4. S^0 significantly reduced soil solution pH and $Fe(OH)_3$ significantly reduced soil solution P concentration. In one compost S^0 reduced the biomass of *F. ovina* whilst increasing that of *A. capillaris*, while $Fe(OH)_3$ had no significant effect on the biomass of either species.
5. Whilst S^0 and $Fe(OH)_3$ did adjust the chemical properties of the soil solution, $Fe(OH)_3$ was incapable of binding P strongly enough to make it unavailable to plants. Further work is required to investigate alternative methods of reducing P availability in composts for restoration of nutrient poor habitats.

Synthesis and Applications: Composts provide a promising media for establishment of acid-grassland species on quarry waste spoil, but further work is required to make them chemically suitable for restoration of nutrient-poor grassland habitats.

5.2 Introduction

The sensitive ecological restoration of post-industrial degraded land is a major challenge for the twenty first century. Quarrying activities have left a legacy of degradation of the previous vegetation and soil composition and structure, as well as in some cases the topography of the site in question (Dobson *et al.* 1997). Blocky hard rock spoil tips (defined by Rowe *et al.* (2005) as containing more than 95% by weight stones larger than 10 cm diameter) are largely inhospitable to plant growth due to their extremely poor water holding capacity and inability to supply plant nutrients. Successful restoration of specific plant communities associated with low productivity sites is as much a matter of preventing the dominance of more competitive plant species as creating substrate conditions that the characteristic species of the

community can tolerate (Verhagen *et al.* 2001); i.e. the site needs to conform to their realised niche, not just their fundamental one (Begon *et al.* 1990). This ensures that the species planted at a restored site can remain if other, more competitive species become naturally introduced, and is particularly true of acidic grasslands that are characterised by the absence or rarity of the fast-growing grass species characteristic of mesotrophic grasslands (Rodwell, 1991).

An early more economic method for restoration, particularly of trees, was planting into pockets of peat-based compost inserted into the surface of the tip (Sheldon 1975). However, its success has been limited by failure to apply sufficient fine material that is retained to meet the water and nutrient demands of growing plants in their post-establishment phase (Rowe *et al.* 2005). As a consequence, these techniques have had to be modified at significant expense of labour required to increase the volume of the compost pocket (Rowe *et al.* 2005). More recent approaches have sought to marry the needs of effective reutilisation of waste organic materials with the needs of restoration of such post-industrial sites. These include large-scale application of biosolids (Monero-Peñaranda *et al.* 2004), de-inking paper fibre (Brown *et al.* 2003), mineral materials such as fine grain slate waste (Rowe *et al.* 2005), and artificial topsoils constructed from both mineral and organic materials (Dudeney *et al.* 2004; Nason *et al.* 2006). Composted wastes represent a promising resource for land restoration since, in addition to providing soil forming material for plant growth, the return of organic matter to land has the potential to increase sequestration of C in soil and thus reduce the rate of atmospheric CO₂ enrichment (Lal 2004; Bellamy *et al.* 2005).

Arnesen *et al.* (2007) found that pH and P were most correlated with floristic gradients in their study of northern vegetation, and these are the two main problems with using composted wastes for restoring biodiverse habitats. Composts are generally either neutral or slightly alkaline (Shiralipour, 1992), which makes them unsuitable for the restoration of mesotrophic and oligotrophic grass and heath land. Elemental sulphur (S⁰) has been used in several studies (Jaggi *et al.* 2005; Green *et al.* 2007) to reduce the pH of soils, and is also widely available as a by-product of the oil refining sector. The resulting reduction in pH can, however, cause an increase in the availability of soil P and trace metals (Jaggi *et al.* 2005; Nason *et al.* 2006; Green *et al.*

2007). This exacerbates the fact that composts often already contain high levels of phosphorus (Wei and Liu 2005).

High soil fertility can lead to a reduction in biodiversity (Grime 1973; Al-Mufti *et al.* 1977; Tilman 1982; Wassen *et al.* 2005; Rowe *et al.* 2006; Stevens *et al.* 2006). A study by Critchley *et al.* (2002) reported an average Olsen P concentration of 14 ± 11 mg kg⁻¹ for 394 mesotrophic grassland soils in the UK, and concluded that low P levels can be used as an indicator of suitable soil conditions for nutrient-poor communities. The high available P levels in composts (ca. 100 mg kg⁻¹ water soluble P (Felton *et al.* 2004), would therefore result in a lower conservation value of restored vegetation. The plant-available N content of composts is generally considered to be low as a percentage of total nitrogen (Petersen 2003; Wolkowski 2003), with limited risk of leaching within the short to medium term (Tarrasón *et al.* 2008), and we therefore focus on P within the scope of this study, as P-limitation has been purported to be the main limiting nutrient in diverse habitats (Wassen *et al.* 2005).

Development of methods to reduce P-availability in composts will improve their suitability for restoration of naturally low-P habitats. Iron-based flocculation chemicals are widely used in the drinking water industry for purification purposes, and once spent are a waste product that is widely available. Iron hydroxides are widely recognised as being effective P binding molecules (Arai and Sparks 2001), and have been used in the reduction of P-availability in manures to reduce the risk of leaching (Dao *et al.* 2001) and in soils to return improved pasture to heathland (Green *et al.* 2007).

The objectives of the present study are to assess the potential to chemically modify compost derived from organic waste materials to make it suitable for the restoration of acidic grassland. It will test a combination of two amendments: S⁰ to reduce pH and iron hydroxide sludge to decrease availability of P.

5.3 Materials and methods

5.3.1 Preliminary studies

A total content of 1% by dry mass S⁰ per volume of compost was used in this work, as determined by Nason *et al.* (2006) to reduce the pH by 2-3 units. The

quantities of iron hydroxide sludge required to achieve the four treatments (0, 0.5, 1 and 2 times the estimated dose required to sorb all of the Olsen P present in three litres of each compost) were determined from estimates of sorption maxima obtained from a Langmuir isotherm fitted to data from a P sorption isotherm (Fig. 5.1, $r^2 = 0.9899$, $n = 36$).

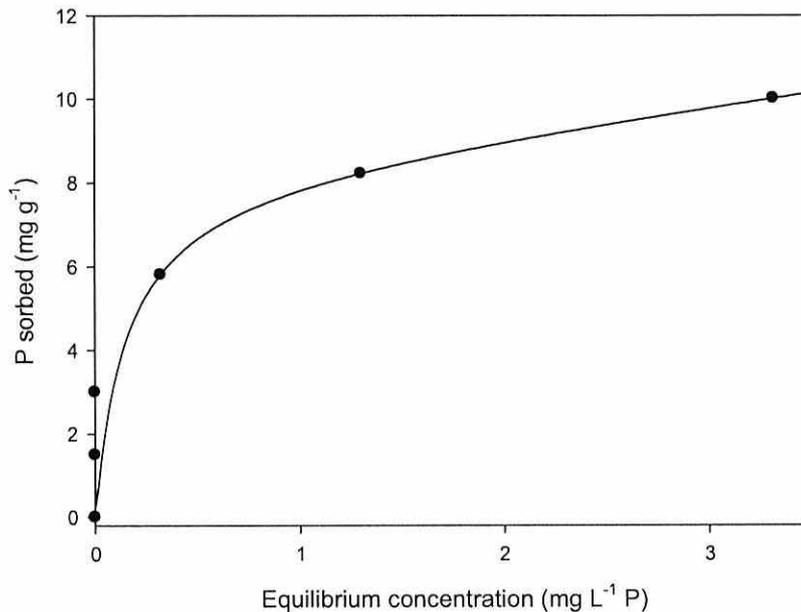


Figure 5.1: Langmuir isotherm of P sorption to iron hydroxide sludge used in this study. $Q_{max} = 9.99$ mg P sorbed per g $Fe(OH)_3$

5.3.2 Autoecology of *Agrostis capillaris* and *Festuca ovina*

Both *A. capillaris* and *F. ovina* are found across the United Kingdom, and are frequently found within nutrient-poor acidic upland grasslands such as UG4 (Rodwell, 1991). *F. ovina* has been found to be outcompeted by *A. capillaris* in high fertility conditions by Mahmoud and Grime (1976), as *A. capillaris* reacts more positively to higher nutrient availability (Grime *et al.* 1988). Ellenberg scores (Ellenberg, 1988) as adapted by Hill *et al.* (1999) for the UK, whilst based on the realised niche of species and not actual soil fertility values, indicate that reducing substrate nutrient content will favour *F. ovina* over *A. capillaris*; whereas an increase in nutrient content (as a by-product of acidification increasing P availability) will favour *A. capillaris*. These species were therefore grown in direct competition with each other to bioassay the chemical changes brought about by the amendments.

5.3.3 Experimental design

A factorial, randomised complete block design experiment was set up in 108 four-litre plastic plant pots in a temperate greenhouse with a photoperiod of 16 h, heated to maintain 20 °C during daytime and 18 °C at night, augmented when necessary by 400 W Sun SON-T horticultural lamps. One litre of slate chips (< 3 cm diameter) (Alfred McAlpine Slate PLC, Penrhyn Quarry, Gwynedd, UK) was placed in the bottom of each pot to enhance drainage and to emulate realistic conditions on a slate spoil tip, and the pots were placed on mesh benches to prevent re-uptake of any leachate. Two composts and two soils were tested (details are in section 5.3.4 below). Three litres of each substrate, amended as described below, was then added on top of the slate chips. Seed mixtures with composition determined from a preliminary germination trial were sown after the amended substrates had equilibrated for one month. Pots were watered lightly daily throughout the trial (before and after sowing). For each of the two composts there was a fully factorial combination of each of the two S^0 and four iron hydroxide doses, while the two soils served as controls with no S^0 or iron hydroxide additions (Table 5.1). This gives a total of 18 individual treatment combinations, each of which were replicated 6 times.

5.3.4 Substrate characteristics

Feedstocks comprising of 2.8 tonnes source-segregated, shredded green waste (Cwmni Gwastraff Mon Arfon, Penhesgyn Gors, Anglesey, UK) and 1.2 tonnes of commercial source-separated catering waste were co-composted (compost GF). Starting materials totalling 55 tonnes of green waste and tertiary treated sewage sludge were composted to produce compost GS, comprising 32 tonnes of source-separated shredded green waste (Flintshire County Council, Greenfields, Flintshire, UK), 17 tonnes of tertiary-treated dewatered biosolids (United Utilities, Bromborough, Wirral, UK), and 6 tonnes chipped wood for aeration purposes. Both composts were produced using a commercially-available CT-5[®] and EcoPOD[®] in-vessel composting system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA), located at Ffridd Rasus Landfill Site, Harlech, Gwynedd, North Wales (52°52'59"N, 4°06'43"W) and Shotton Paper Works, Shotton, Flintshire, North

Wales (53°14'24"N, 3°02'20"W) respectively. One hundred kilogrammes of a Haplic Podzol (HF) and a highly organic upland soil (OV) were collected prior to the experiment from hillsides in North Wales (53°13'40"N, 4°0'48"W and 53°08'34"N, 3°57'10"W respectively).

For the chemical amendment treatments, general purpose reagent-grade elemental sulphur (VWR, Lutterworth, Leicestershire, UK) was used as supplied and iron hydroxide was sourced from a coal spoil runoff treatment plant (UK Coal Mining Ltd, Doncaster, South Yorkshire, UK) and air-dried before use. All treatment combinations were mixed by hand in batches, then divided between the individual pots to give six replicates.

Table 5.1: Details of each treatment

| Substrate | Sulphur | Iron Hydroxide | Code |
|-----------|---------|----------------|--------|
| GF | 1 | 0 | GFS0 |
| GF | 1 | 0.5 | GFS0.5 |
| GF | 1 | 1 | GFS1 |
| GF | 1 | 2 | GFS2 |
| GF | 0 | 0 | GF0 |
| GF | 0 | 0.5 | GF0.5 |
| GF | 0 | 1 | GF1 |
| GF | 0 | 2 | GF2 |
| GS | 1 | 0 | GSS0 |
| GS | 1 | 0.5 | GSS0.5 |
| GS | 1 | 1 | GSS1 |
| GS | 1 | 2 | GSS2 |
| GS | 0 | 0 | GS0 |
| GS | 0 | 0.5 | GS0.5 |
| GS | 0 | 1 | GS1 |
| GS | 0 | 2 | GS2 |
| HF | - | - | HF |
| OV | - | - | OV |

5.3.5 Sampling and analysis

To characterise the four unamended substrates used in the experiment chemical analyses were carried out in triplicate. Moisture content was determined by drying at 80 °C for 24 h and organic matter content was determined as loss-on-ignition at 450 °C overnight. pH (Hanna Instruments pH 209 pH meter) and electrical

conductivity (EC) (Jenway 4010 EC meter) were determined in a 1:2 v/v soil : water slurry, after mixing for 1 h. Prior to total elemental analysis, substrates were air dried (25°C, 14 d) before being ground in a T1-100 vibrating sample mill (Heiko Co Ltd., Fukushima, Japan) equipped with tungsten grinding vessels. Subsamples of the ground material were then digested using HNO₃ (Havlin and Soltanpour 1980), and analysed by Inductively Coupled Plasma – Mass Spectrometry (Fissions PlasmaQUAD II Turbo ICP-MS; Thermo Scientific, Waltham, MA). Total C and N were determined using a CHN2000 analyser (LECO Corp., St Joseph, MI). Nitrate and ammonium were extracted using a 1:5 (w/v) ratio of fresh sample:extractant (1 M KCl), shaken for 1 hour on a reciprocating shaker at 250 rev min⁻¹ (Zhong and Makeshin 2003), and available K was extracted using 1:5 (w/v) ratio of fresh sample:extractant (1 M NH₄OAc, buffered to pH 7.0), shaken for 1 h on a reciprocating shaker at 250 rev min⁻¹ (Helmke and Sparks 1996). Nitrate and ammonium were determined using a San⁺⁺ segmented flow analyser (Skalar Inc., Norcross, GA). K, Na and Ca were analysed using a Sherwood 410 flame photometer (Sherwood Scientific, Cambridge, UK). Phosphate was determined colourimetrically using the method of Murphy and Riley (1962). Chemical characteristics of the two composts and two soils used in the experiment are listed in Table 5.2.

Table 5.2: Chemical characteristics of composts and soils. All values in mg kg⁻¹ dry matter unless otherwise stated. GF = green waste and food waste compost, GS = green waste and tertiary treated sewage sludge compost, HF = Haplic Podzol, OV = Organic mountain soil

| Variable | GF | GS | HF | OV | Slate | Iron hydroxide sludge |
|--|-----------|-----------|-----------------|-----------|-----------------|-----------------------|
| Moisture content (%) | 52.7±3.8 | 45.2±1.5 | 28.1±2.8 | 70.9±0.5 | 0.1±0.0 | 7.24±0.52 |
| Organic matter (%) | 44.2±1.9 | 39.3±4.1 | 16.9±0.7 | 85.9±3.2 | 0.1±0.0 | 27.5±2.5 |
| pH | 7.80±0.16 | 7.56±0.10 | 4.67±0.10 | 4.48±0.05 | 8.58±0.12 | 8.55±0.06 |
| EC ^a | 1510±408 | 1809±554 | 65±9 | 68±2 | 40±1 | 2547±323 |
| Total C (%) | 22.7±3.8 | 19.3±0.3 | ND ^c | ND | 0.04±0.01 | 5.45±0.07 |
| Total N (%) | 1.20±0.21 | 1.08±0.05 | ND | ND | BD ^b | 0.10±0.00 |
| KCl-extractable NO ₃ ⁻ | 176±72 | 21±1 | 13±1 | 36±1 | BD | 2±1 |
| KCl-extractable NH ₄ ⁺ | 71±8 | 21±4 | 102±4 | 44±1 | 14±3 | 7±1 |
| Olsen P | 248±27 | 122±15 | 16±1 | 53±3 | BD | BD |
| NH ₄ OAc extractable K | 1283±211 | 3440±300 | 293±18 | 294±15 | 7±1 | 5±1 |

^a Electrical Conductivity (μS cm⁻¹), ^b BD = Below limit of detection, ^c ND = Not determined

Soil solution was collected from each pot overnight at four sampling times during the first 20 d and four further times during the next 110 d using 10 cm Rhizon-MOM® in situ soil solution samplers (Rhizosphere Research Products, Wageningen, The Netherlands), and was analysed using the same methods as described above. After 128 days, the above ground biomass of the two grass species was harvested, separated between species and dried for 72 h at 80°C before measuring biomass. Samples of the plant material were ashed for 24 h at 400 °C before digestion in 6 M HCl (MAFF 1986) and analysed for P by colourimetry (Murphy and Riley 1962) and Cd and Zn by AAS (Varian FS220 AAS, Varian Inc., Palo Alto, CA).

Table 5.3: Fully factorial ANOVA results for total biomass, biomass by species, and P content by species.

| | Factor | GF | | GS | |
|---|--|-------|---------|-------|---------|
| | | F | P | F | P |
| Total Biomass | S ⁰ | 42.2 | < 0.001 | 0.98 | 0.328 |
| | Fe(OH) ₃ | 0.64 | 0.593 | 1.25 | 0.305 |
| | S ⁰ * Fe(OH) ₃ | 2.13 | 0.112 | 1.00 | 0.402 |
| | S ⁰ | 31.2 | < 0.001 | 1.46 | 0.331 |
| Biomass split by species | Fe(OH) ₃ | 0.48 | 0.701 | 1.86 | 0.308 |
| | Species | 360.8 | < 0.001 | 639.2 | < 0.001 |
| | S ⁰ * Fe(OH) ₃ | 3.49 | 0.202 | 1.49 | 0.408 |
| | S ⁰ * Species | 329.7 | < 0.001 | 0.24 | 0.691 |
| | Fe(OH) ₃ * Species | 2.33 | 0.375 | 0.68 | 0.720 |
| | S ⁰ * Fe(OH) ₃ * Species | 4.14 | 0.142 | 0.44 | 0.833 |
| | S ⁰ | 2.73 | 0.103 | 0.76 | 0.385 |
| P concentration split by species | Fe(OH) ₃ | 2.33 | 0.081 | 5.15 | 0.003 |
| | Species | 105.0 | < 0.001 | 278.5 | < 0.001 |
| | S ⁰ * Fe(OH) ₃ | 9.14 | < 0.001 | 0.26 | 0.855 |
| | S ⁰ * Species | 69.1 | < 0.001 | 7.58 | 0.007 |
| | Fe(OH) ₃ * Species | 3.24 | 0.027 | 2.80 | 0.046 |
| | S ⁰ * Fe(OH) ₃ * Species | 7.28 | < 0.001 | 1.43 | 0.241 |

5.3.6 Statistical analysis

A fully factorial ANOVA was carried out using SPSS v14.0 (SPSS Inc., Chicago, IL) on total yield, yield by species, and P content by species. In order to simplify interpretation of the results the analyses were split by compost type, and these results are presented in Table 5.3. A fully factorial ANOVA was also carried out to assess treatment effects at the peak soil solution P concentrations (T = 35 d for

compost GF and T = 16 d for compost GS). Spearman's r correlation co-efficients were also calculated to assess the relationships between changes over time in pH and soil solution P on other factors. All graphs were produced in SigmaPlot v10.0 (Systat Software Inc., San Jose, CA). All values are expressed on a dry weight basis, except for soil solution data.

5.4 Results

5.4.1 *Substrate properties*

The pH of both composts were similar and three units higher than both soils (Table 5.2); therefore the pH of the composts would need to be drastically reduced to emulate the acidity of such upland soils. In addition, Olsen extractable P concentrations were more than twice as high in both composts than in both of the soils, confirming the basis for the experiment, that availability of P in composts may need to be reduced for them to be used successful in the restoration of acidic grassland vegetation.

The EC of both composts was at least 50 times greater than that of the two soils, whilst inorganic nitrogen levels were eight times higher for nitrate and four times higher for ammonium in the GF than the GS compost (Table 5.2). GS compost contained more than double the concentration of available K of the GF compost, and this was over ten times the level of that present in either of the control soils. Both Cd and Zn concentrations were below the compost quality limits set out in the UK PAS100 (BSI 2005) composting standards. The slate fines base material placed at the base of the pots contained negligible amounts of nutrients, with the exception of ammonium. The $\text{Fe}(\text{OH})_3$ sludge had a high electrical conductivity and Zn content.

5.4.2 *Vegetation growth, P, Cd and Zn concentration*

Sulphur significantly increased total biomass in compost GF ($P < 0.001$), but had no significant effect on the total biomass in compost GS ($P = 0.328$) (Fig. 5.2a). Iron hydroxide had no significant effect on the total biomass from either compost ($P = 0.593$ and $P = 0.305$). The fact that there was no significant interaction effect between

S^0 and $Fe(OH)_3$ on total biomass proves that this treatment is not restricting overall growth of the sward; even with increased acidity due to S^0 addition, which is when the P-binding sites are most active. The total sward biomass in the control soils varied greatly, with HF producing twice the biomass of OV.

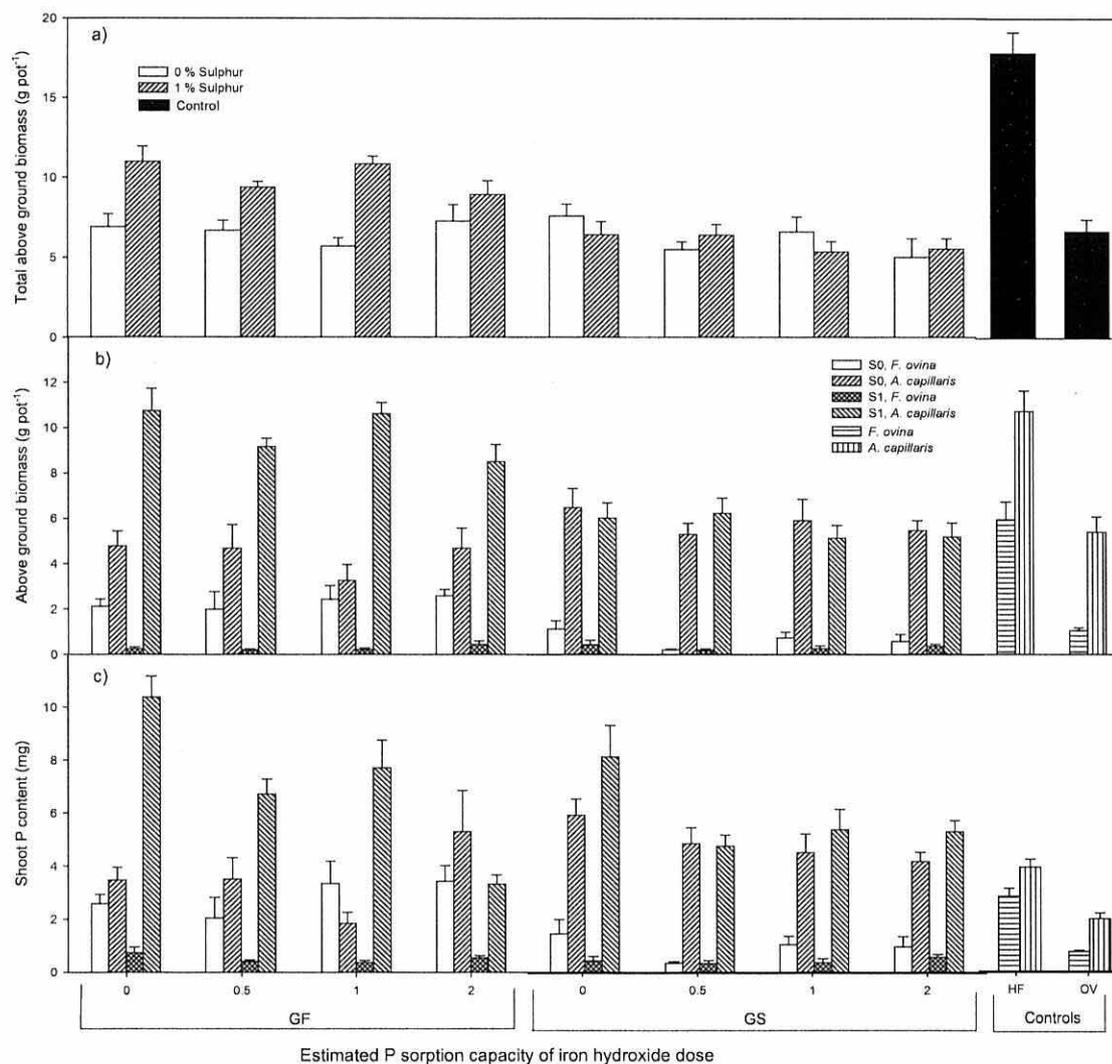


Figure 5.2: Total above ground biomass $g\ pot^{-1}$ (a), above ground biomass per species $g\ pot^{-1}$ (b), and above ground biomass phosphorus content mg (c) after 93 days of growth. GF = green waste and food waste compost, GS = green waste and tertiary treated sewage sludge compost, HF = Haplic Podzol soil, OV = Organic upland soil. Solid bars refer to total biomass in the control soils and horizontal and vertical hatchings refer to *F. ovina* and *A. capillaris* grown on the control soils. Values represent means \pm SEM ($n = 6$).

A. capillaris grew faster than *F. ovina* in all combinations of S^0 and $Fe(OH)_3$ treatments in both composts, and in both control soils (Fig. 5.2b). In the case of

compost GF, S^0 had a negative effect on the competitive ability of *F. ovina*, causing poor growth relative to *A. capillaris* ($P < 0.001$). In contrast, S^0 had no significant effect ($P = 0.280$) on the ratio between the two species in GS compost. Both with and without S^0 addition, $Fe(OH)_3$ addition had no significant effects ($P = 0.375$ and $P = 0.720$ respectively) on the growth of either grass species in either compost types.

The content of P in the plant shoots was greater in *A. capillaris* than in *F. ovina* for all but one treatment combination (Fig. 5.2c). S^0 addition had no significant effect on P content of shoots grown in either compost (GF: $P = 0.103$, GS: $P = 0.385$). $Fe(OH)_3$ addition had no significant effect on P content of shoots grown in compost GF ($P = 0.081$), but did reduce shoot P content in compost GS ($P = 0.003$). There were strong significant differences between the P contents of the biomass of both species for both compost types ($P < 0.001$). There was a significant interaction effect between S^0 and $Fe(OH)_3$ on P content for compost GF ($P = 0.001$) but not compost GS ($P = 0.855$). There was a significant interaction effect between S^0 and species for P content of shoots grown in both composts ($P < 0.001$ and $P = 0.007$ respectively). Shoot Cd and Zn concentration were below limit of detection in all treatments.

5.4.3 Changes in soil solution pH over time

Addition of S^0 caused a large and significant reduction in pH of the soil solution of both composts (Fig. 5.3). In compost GF it reduced pH by 3 units to 4.81 ± 0.20 by 35 d, after which it rose slightly but appeared to have reached a stable level ($pH 5.63 \pm 0.22$) by 128 d. The pattern was comparable for compost GS, though the lowest pH (5.55 ± 0.14 , a drop of 1.8 units) occurred after just 16 d, however, the pH then rose steadily such that by 128 d it was 7.43, a similar value to the pH of 7.22 in the pots without S^0 addition. The reduction in pH achieved by addition of S^0 to GF compost by day 128 gave a pH value 5.45 that was similar to that of control soil HF (pH 5.31), although this was one unit higher than control soil OV (pH of 4.25). The fact that compost GS returned to its original pH indicates a stronger buffering capacity than that of GF, and explains differences in growth and plant P uptake outlined in section 5.4.2.

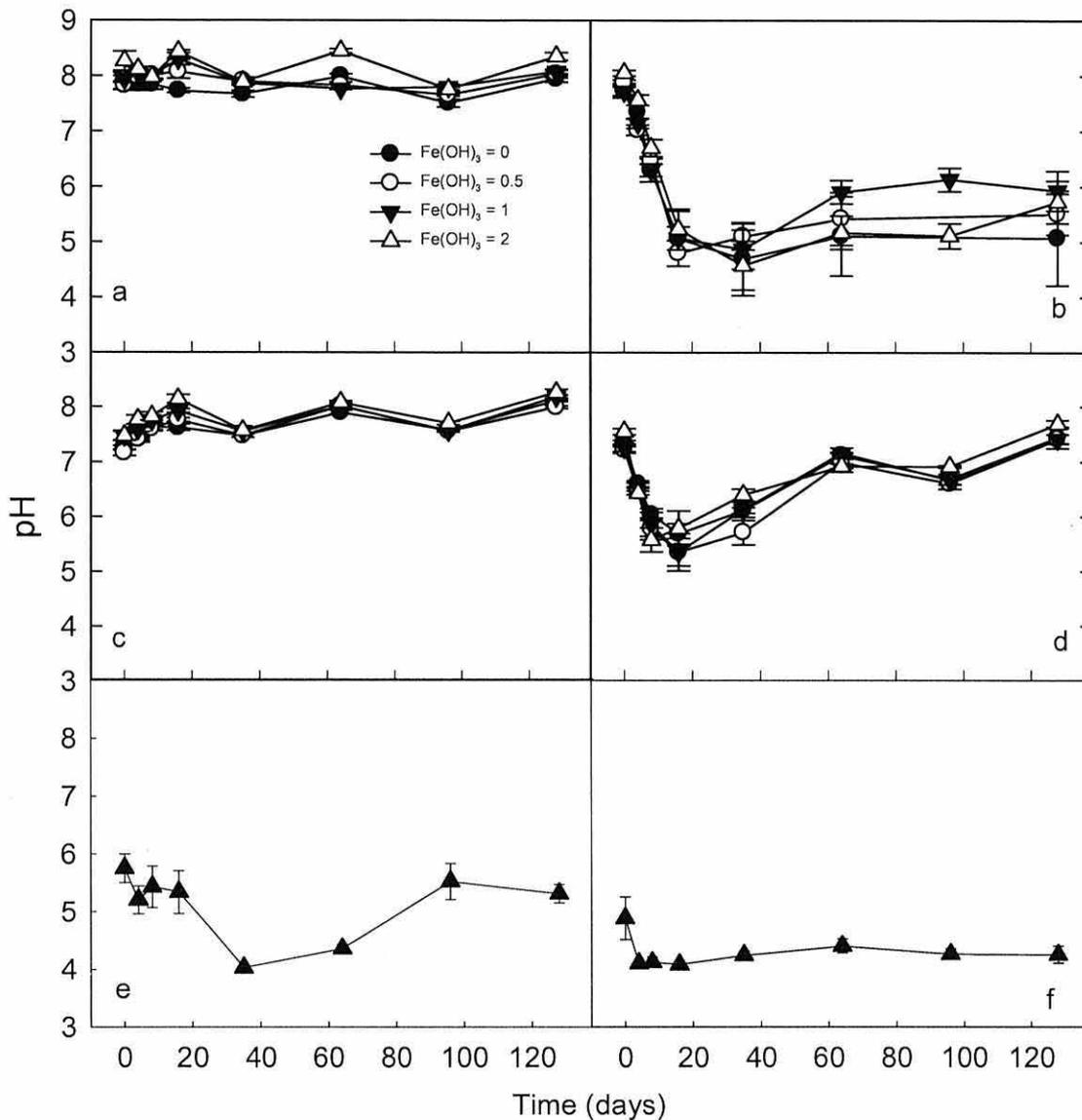


Figure 5.3: Change in soil solution pH over time. Graphs (a) and (b) are compost GF without and with sulphur respectively, graphs (c) and (d) are compost GS without and with sulphur respectively, whilst graph (e) is the HF control treatment, and (f) is the OV control treatment. Values represent means \pm SEM ($n = 6$).

5.4.4 Changes in soil solution phosphorus over time

Addition of S^0 caused a pulsed increase in soil solution P from 16 to 64 d in both composts, being 6 times and 15 times higher than the control at the peak of 35 d in the GF compost and 16 days in the GS compost respectively (Fig. 5.4). At the final two measurements (96 and 128 d after S^0 addition) soil solution P concentrations had returned to the initial levels and there was no difference between the S^0 addition and

control plots. There was little variation over time in soil solution P concentrations in the control pots of either compost unamended with S^0 , although they were higher than both control soils (most time points below limit of detection) at all times.

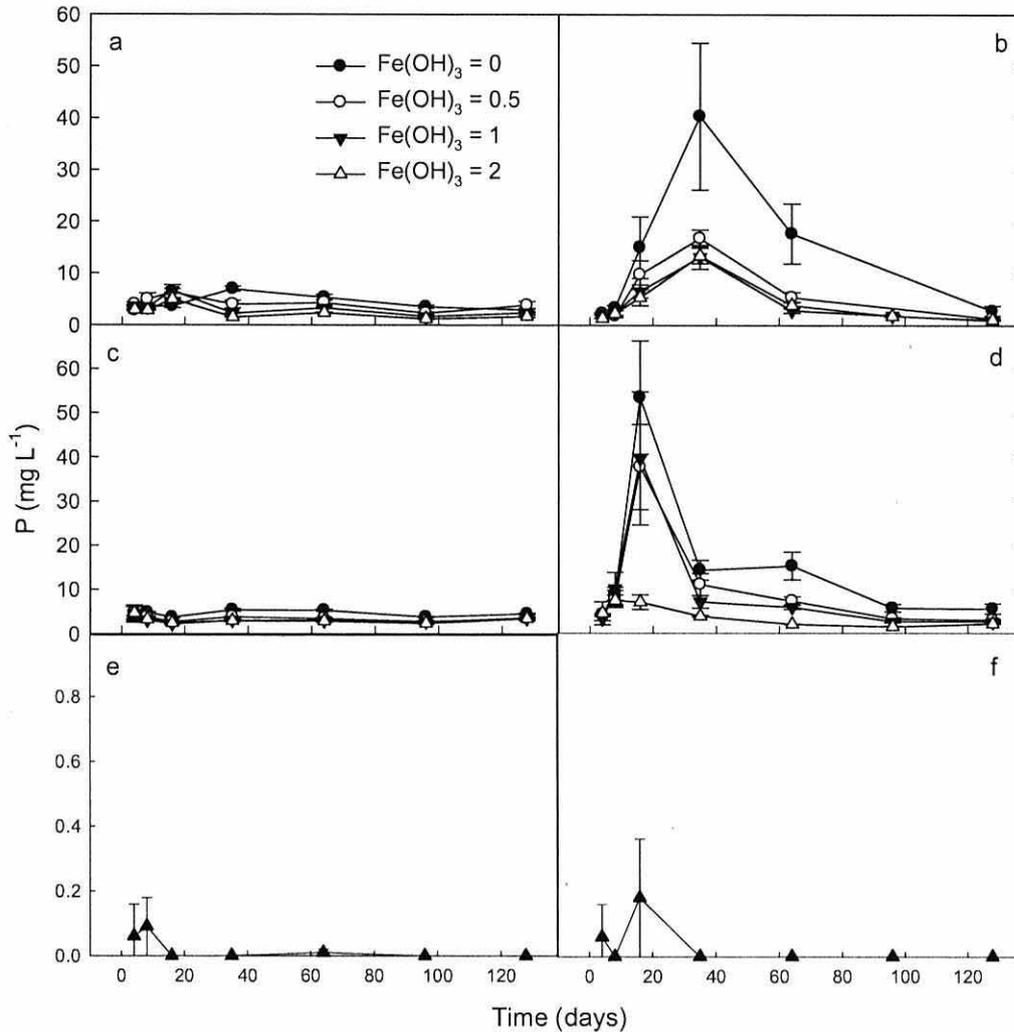


Figure 5.4: Change in soil solution phosphorus (mg L^{-1}) over time. Graphs (a) and (b) are compost GF without and with sulphur respectively, graphs (c) and (d) are compost GS without and with sulphur respectively, whilst graph (e) is the HF control treatment, and (f) is the OV control treatment. Values represent means \pm SEM ($n = 6$).

Soil solution P levels peaked after 16 d for compost GS with S^0 but no $\text{Fe}(\text{OH})_3$ ($53.6 \pm 12.8 \text{ mg L}^{-1}$), and after 35 days for compost GF with S^0 but no $\text{Fe}(\text{OH})_3$ ($40.4 \pm 14.2 \text{ mg L}^{-1}$). At these time points, the effects of $\text{Fe}(\text{OH})_3$ addition were greatest, with the unamended treatments having far greater levels of P present in the soil solution than the $\text{Fe}(\text{OH})_3$ amended treatments. From this time point onwards, treatments with no $\text{Fe}(\text{OH})_3$ always had higher P concentrations in soil solution than those

amended with double the predicted does ($\text{Fe}(\text{OH})_3 = 2$), although some overlap occurred with the lower applications. Whilst $\text{Fe}(\text{OH})_3$ significantly affected soil solution P at these time points for both S^0 treatments, an interaction effect with S^0 was observed, with a five-fold increase in P sorption from the $\text{Fe}(\text{OH})_3 = 2$ treatment with S^0 addition over that with no sulphur added.

5.5 Discussion

5.5.1 Soil solution chemistry

Soil solution represents the natural source of mineral nutrients for plant growth, and therefore its composition should provide good predictions of the effects of chemical changes in the soil environment on plant responses (Wolt, 1994). The addition of both S^0 and $\text{Fe}(\text{OH})_3$ had a significant impact on the chemistry of the soil solution in both compost types. With S^0 addition, soil solution P concentrations dropped after their peaks and this can be attributed to either leaching from the pots or plant uptake. Leaching was expected due to the layer of free-draining slate placed in the base of each.

The doses of $\text{Fe}(\text{OH})_3$ applied were based on those required to absorb the measured concentrations of Olsen P in the composts, yet they failed to prevent the increase in soil solution P caused by S^0 addition. Therefore, on the assumption that the soil solution P was phytoavailable, we share the conclusions of Tibbett and Diaz (2005) that Olsen P may not be effective as an accurate predictor of P phytoavailability for the substrates used in our study. Our results also call into question whether the soil solution P concentration was a reliable indicator of P phytoavailability as, although *A. capillaris* shoot P concentration was strongly positively correlated with soil solution P at the time of final harvest ($T = 128$) ($r^2 = 0.495$, $P < 0.001$), there was no significant correlation between soil solution P and *F. ovina* P content ($r^2 = -0.012$, $P > 0.05$). *A. capillaris* yield was also strongly negatively correlated with pH at the time of the final harvest ($r^2 = -0.466$, $P < 0.001$) and soil solution P ($r^2 = -0.338$, $P = 0.001$). This provides conflicting information; with high soil solution P inhibiting *A. capillaris* plant growth, yet giving a higher shoot P concentration. From Fig. 5.2c, it can be seen that shoot P content greatly reflects

plant growth, indicating that the highly stunted growth of *F. ovina* in the S^0 -treated composts may have caused a bio-concentration effect to be observed, whilst in fact P uptake was lower in *F. ovina* due to the lower yield of this species in our experiments.

One concern of forcing an increase in the acidity of a soil is the increased mobility of heavy metal cations, however, in our study, plant Cd and Zn concentration remained very low in all treatments. Green *et al.* (2007) highlighted the potential risks of increased metal cation uptake in plants at low pHs as a result of S^0 addition. In their study, the effects of S^0 and $FeSO_4$ addition on the chemistry of an improved podzolic grassland were studied and, although the results demonstrated that both amendments reduced the pH of the soil, they did not increase the availability of Cd in the soil, nor the Cd concentration of *A. capillaris* grown in their experimental plots.

5.5.2 Effect of amendments on *Agrostis capillaris* and *Festuca ovina*

Critchley *et al.* (2002) concluded in their study that low P availability can be used as an indicator of substrate suitability for restoration of unimproved mesotrophic grasslands, and this is in agreement with Arnesen *et al.* (2007) that acidity and P are the best correlated variables with alpine vegetation gradients. The evidence from the soil solution chemistry indicated that our hypotheses on the effect of S^0 and $Fe(OH)_3$ on pH and P concentration were correct, this was poorly reflected in the relative growth of either grass species.

The average P concentration of above-ground biomass from the control soils was a quarter ($510 \pm 42 \text{ mg kg}^{-1}$) of the average plant P concentration value (Marschner, 2002); although no adverse effects were observed in terms of yield when compared with the plants grown in compost. It is well known that species differ greatly in their response to soil P concentration and supply, and Bradshaw *et al.* (1960) demonstrated that *F. ovina* exhibited little yield increase in response to increased P availability, as opposed to the doubling of above-ground biomass that *A. capillaris* exhibited over the same range of P concentrations. An extensive study by McCain and Davies (1983) investigated the importance of P availability at the start of shoot growth. Their studies used several phenotypes of *A. capillaris*, and after 6 months growth in sand, irrigated with nutrient solution containing 1 and 40 mg L^{-1} P

as treatments, shoots grown in the low concentration contained an average of 606 mg kg⁻¹ P, compared with 4890 mg kg⁻¹ P in the high concentration treatment. Excluding controls, the average concentration of P in *A. capillaris* across all treatments in our study was 860 mg kg⁻¹ (far below Marschner's (2002) mean figure of 2000 mg kg⁻¹) indicating that the composts actually provide a low level of available P. Although McCain and Davies (1983) verified their initial hypothesis that early P concentration determines future P uptake by a plant with grasses from more fertile sites, phenotypes from poorer soils exhibited high yields despite low shoot P concentrations – a finding that corroborates well with our results. This is further evidenced by comparison of the average P content of *F. ovina* (1720 mg kg⁻¹) in our study with those found by Elias (1982). His work on *Festuca tenuifolia* (closely related to *F. ovina*) with different P concentrations in irrigation water gave a range of 683 mg kg⁻¹ shoot P in 0.003 mg L⁻¹ P water to 5220 mg kg⁻¹ shoot P in 25 mg L⁻¹ P water. Although 25 mg L⁻¹ is an excessively high P treatment, a solution concentration of 1.25 mg L⁻¹ P produced *F. tenuifolia* leaf P concentrations of 5289 mg kg⁻¹ – three times the average concentration of P in *F. ovina* in our study. On this evidence, it can be concluded that even though our composts contained high levels of nutrients, P uptake by *F. ovina* was very low, as evidenced by Fig. 5.2(c).

Tibbett and Diaz (2005) demonstrated that an addition of 2000 kg ha⁻¹ S⁰ in a field trial on improved grassland increased the Olsen P content of the soil by 50 % from 20 to 30 mg kg⁻¹. However, this had no effect on the P uptake by the sward, and they postulated that plant growth in their study site may have been co-limited by sulphur and therefore overall increases in yield were a direct result of sulphur fertilisation. Whilst there may have also been other effects caused by the addition of S⁰ in their (and our) studies, nitrification has been found to be reduced by artificial reductions in soil pH (Kemmitt *et al.* 2005), and overall microbial biomass reduced by iron hydroxides (Jones and Edwards, 1998), implying that if any effects of plant-available N are caused by the additions of S⁰ or Fe(OH)₃, they are negative in their nature, and would not increase plant-available N.

When their growth is limited by shortage of a nutrients, plants may exhibit a variety of responses including increased exudation of organic acids, increased phosphatase activity, extensive root structure modifications and increased efficiency

of transport mechanisms in the root cell membranes (Johnson and Loeppert 2006). The exudation of organic acids such as citrate and malate may desorb phosphate from highly crystalline iron oxides, and may dissolve poorly crystalline oxides (Johnson and Loeppert 2006), with goethitic Fe more resilient to P desorption than haematitic Fe (Guzman *et al.* 1994). This is a probable explanation for the limited effect of our industrial Fe(OH)₃ on plant response and we propose that due to P shortage in the bioassay plants, any phosphate sorbed to the Fe(OH)₃ was made available by modification of the rhizosphere.

There are several confounding factors that prevent simplistic manipulation of soil chemistry from predictably influencing the relative growth of plant species. Firstly the Ellenberg indicator values on which the hypotheses of this study were based are formed from the realised niche that species are commonly found in, as opposed to the fundamental niche where the plant can actually survive (Begon *et al.* 1990). Whilst the realised niche of *A. capillaris* is predominantly acidic mesotrophic grassland, it can survive in a much wider range of soil conditions (Grime *et al.* 1988), especially when grown in a greenhouse environment removing most other environmental limitations to its growth. A limitation of the short-term nature of our trial is that plant communities can take several generations to exhibit their true species balance (Grubb 1977), therefore *F. ovina* may have competed better for the regeneration niche over several growth cycles. As the shoot P concentration of both species grown in this trial was shown to be low in all cases, it is probable that they have responded through root mechanisms such as those highlighted by Johnson and Loeppert (2006), which have enabled an increased rate of P uptake. These may have negated the phosphate sorption in the compost by the applied Fe(OH)₃. This also explains the inconsistency between the observed soil solution chemistry changes and the growth of the grasses.

We conclude that whilst industrial wastes such as S⁰ and Fe(OH)₃ can be used safely to adjust compost chemical properties, difficulties in assessing true phytoavailability of nutrients may make it hard to successfully predict dosage requirements. Further work therefore needs to be carried out into accurate estimation of availability, and then dosages may be reassessed.

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CHAPTER 6: FOOD WASTE COMPOSTING: ITS USE AS PEAT REPLACEMENT

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6.1 Abstract

We successfully co-composted catering waste with green waste and shredded paper to yield two high-nitrogen composts for use in horticulture. Sunflowers (*Helianthus annuus* L.) were grown in various mixtures of the compost and a commercially available peat-based compost to assess the efficacy of catering waste-based composts for peat replacement. Height, head diameter, seed mass and above ground biomass were measured, with all mixtures giving a significant increase in yield or size over the commercially available peat-free control compost. We conclude that differences in physical structure governed sunflower growth over substrate chemistry, and none of the compost mixtures were nutrient deficient. We recommend that catering waste co-compost can be substituted to at least 75 % within *Sphagnum*-based traditional growing media.

6.2 Introduction

Sphagnum peat has long been used as a growing media in horticulture and market gardening due to its high physical and chemical stability, and low degradation rate (Garcia-Gomez *et al.*, 2002). However, peat is a finite resource, and as demand has increased in recent years prices have also risen (Herrera *et al.*, 2008). These economic factors combined with the negative environmental impact of peat extraction have favoured the utilisation of alternative materials as plant growth

substrates in recent years (Benito *et al.*, 2005). Composted organic wastes are increasingly being used as a substitute for, or in combination with traditional peat, and developing such inexpensive alternatives to peat-based substrates is a priority for the horticultural industry.

Several studies have demonstrated that composts derived from municipal wastes such as shredded green waste from gardens, as well as sewage sludge, mixed municipal waste (MSW) and spent mushroom compost have all been used in horticulture (Garcia-Gomez *et al.*, 2002; Benito *et al.*, 2005; Herrera *et al.*, 2008). Composts are high in organic matter and nutrients, and it is commercially advantageous to recycle these commodities. There is also evidence that composts, unlike peat, contain plant growth regulators and pathogenic inhibitors (Atiyeh *et al.*, 2002; Tilston *et al.*, 2002), and these factors give added value to high quality composts.

Safe treatment of municipal solid waste (MSW) is becoming an increasingly important issue in most industrialised countries due to the desire to move towards a more sustainable society (Adani *et al.*, 2000). European Council Directive 1999/31/EC (EC, 1999) on the landfill of waste has set down strict mandatory targets for member states to reduce the amount of Biodegradable Municipal Waste (BMW) reaching landfill. Standards and targets for compost processing and end-product quality exist in many countries. In the UK, the PAS100 (BSI, 2005) sets out voluntary standards for the quality of composts including heavy metal content and germination inhibition limits, with the aim that PAS100 certified composts will provide consumer confidence and enable successful marketing of municipal waste-derived composts. In the light of recent outbreaks of diseases such as foot and mouth disease virus, legislation has been introduced to prevent access to meat-containing wastes by wildlife and agricultural livestock (DEFRA, 2008). As a result of this, wastes that contain or may have come into contact with meat or poultry products must be composted in-vessel, and are required to reach 60°C twice for 48 h, before qualifying as treated waste under UK legislation. Food waste on its own can have a C:N ratio as low as 2:1, and a moisture content in excess of 90% (Adhikari *et al.*, 2008). These properties preclude successful composting due to problems of maintaining sufficient aeration and an optimal C:N ratio for microbial activity. As a result, low C:N wastes such as food waste

and sewage sludge are often co-composed with a variety of wastes including paper or cardboard and green waste (Manios, 2004; Adhikari *et al.*, 2008). Due to poor publicity, composts derived from household wastes have historically had a poor reception from gardeners and horticulturalists, who have viewed them as 'unclean', and poor quality in comparison to peat-based rivals (Borden *et al.*, 2004). Indeed, few studies have considered mixed waste streams for composting (Jones *et al.*, 2009) and therefore scientific studies are required to demonstrate their cleanliness and effectiveness in supplying nutrients.

The present study focuses on two aspects of food waste composting: the composting process and chemical changes that occur within, and the use of the resultant compost as a peat replacement to assess its suitability for use in horticulture. We set up an industrial scale trial in-vessel composting plant to assess the effects of co-composting food waste with two bulk waste streams namely, green waste and shredded paper waste.

6.3 Materials and methods

6.3.1 *In-vessel composting*

Green waste (G), green waste and food waste (GF) and green waste, food waste and paper waste (GFP) composts were produced using a commercially available CT-5[®] and EcoPOD[®] in-vessel composting system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA) at the Ffridd Rasus Waste Treatment Facility located at Harlech, Gwynedd, UK (52°52'59"N, 4°06'43"W). The in-vessel composter was filled with a CT-5[®] feed hopper (3 m³ feedstock volume) which uses a hydraulic ram to push the material through a filling chamber and into an extended 1.5 m diameter green plastic EcoPOD[®] vessel at a fill rate of approximately 3 m³ min⁻¹. At the same time as filling the EcoPOD[®], a rigid perforated (7.62 cm diameter pipe with 1.59 mm slits) plastic aeration pipe was inserted into the base of the vessel to provide forced aeration. The aeration regime can be closely controlled by means of a timed fan (Ag-Bag International Ltd) running at a flow rate of 137 l min⁻¹ (Roberts *et al.*, 2007). The timed aeration regime was managed manually in order to maximise the rate of composting. In the initial 18 days, aeration was managed in order to maintain

high temperatures and therefore optimal sanitation conditions (typically air pumped through the vessel for 2 min every 10 min). This was changed to on 3 min on, 7 min off to compensate for the relatively wet feedstocks on day 19. On day 80, the duration of aeration was increased to 2 min on, 4 min off and the direction reversed to extract moisture from the pile. This continued until day 112, when the vessel was opened, and the compost bagged for use in the growth trials.

6.3.2 Compost analysis

The chemical characteristics of the feedstocks are presented in Table 6.1. The green waste-derived compost (G) was made from 4 t source-separated municipal shredded green waste (mainly grass cuttings and hedge and tree prunings) obtained from the Penhesgyn Gors Landfill Site, Anglesey, UK (53°14'45"N, 4°11'45"W). The food and green waste-derived compost (GF) was made from a mixture of 1.2 t source-separated catering waste collected from commercial catering establishments on Anglesey and 2.8 t source-separated shredded municipal green waste as described above. The paper, food and green waste-derived compost (GFP) was made from 2 t source-separated shredded green waste, 1.6 t source-separated catering waste, and 0.4 t source-separated shredded waste paper. The 40 m horizontal vessel allowed replicate blocks of each compost type to be delineated for sampling purposes.

During the active composting phase, independent samples were recovered in triplicate from each composting treatment by opening the outside of the vessel and removing material from 10-50 cm into the interior of the vessel. After removal, the vessel was resealed using Duck® tape (Henkel Consumer Adhesives Inc., Avon, OH). Compost samples were recovered from the vessel at day 0, 4, 8, 18, 32, 49, 64, 80, 98 and 112 after the onset of composting. Standard chemical analyses were carried out in triplicate at every sampling time point, and at $n = 6$ on the substrates used in the subsequent growth trials.

Moisture content was determined by drying samples at 80°C for 24 h and organic matter content was determined by heating at 450°C overnight. pH (Hanna Instruments pH 209 pH meter) and electrical conductivity (EC) (Jenway 4010 EC meter) were determined in a 1:2 (v/v) compost : distilled water slurry, after mixing for 1 h. Total C and N were determined using a CHN2000 analyzer (LECO Corp., St Joseph,

MI). Prior to total elemental analysis, substrates were air-dried (25°C, 14 d) and plant samples dried at 80°C before being ground in a T1-100 vibrating sample mill (Heiko Co Ltd., Fukushima, Japan) equipped with tungsten grinding vessels. Subsamples of the ground material were then digested using a 1:4 HClO₄:HNO₃ concentrated acid mixture (MAFF, 1986). Heavy metals in the digests were determined by F-AAS using a SpectrAA 220 FS AAS in acetylene/air flame mode. Nitrate and ammonium were extracted using a 1:5 (w/v) fresh sample:extractant ratio with 1 M KCl (Zhong and Makeschin, 2003). Nitrate and ammonium were determined using a San⁺⁺ segmented flow analyzer (Skalar Inc., Norcross, GA). Olsen P was extracted using 0.5 M NaHCO₃ and a ratio of 1:20 (w/v) fresh sample:extract and determined using the method of Murphy and Riley (1962). K was extracted using 1:5 (w/v) fresh sample:extractant ratio with 1 M ammonium acetate (Helmke and Sparks, 1996) and analyzed using a Sherwood 410 flame photometer (Sherwood Scientific, Cambridge, UK).

Table 6.1: Compost feedstock properties. All values in mg kg⁻¹ dry matter (*n* = 6) unless otherwise stated.

| Variable | Green waste | Catering waste | Shredded paper |
|--|-------------|----------------|----------------|
| Moisture content (%) | 47.2±1.5 | 63.7±2.5 | 7.6±0.7 |
| Organic matter (%) | 64.5±5.2 | 95.0±1.0 | 77.6±3.4 |
| pH | 7.13±0.09 | 4.58±0.32 | 8.72±0.12 |
| EC ^a (µS cm ⁻¹) | 1126±101 | 7263±788 | 303±56 |
| Total C (%) | 26.6±2.1 | 49.6±1.8 | 35.5±1.4 |
| Total N (%) | 0.85±0.04 | 1.90±0.30 | 0.02±0.01 |
| KCl extractable NO ₃ ⁻ | 3.3±0.3 | 1.9±0.5 | 21.0±3.2 |
| KCl extractable NH ₄ ⁺ | 114±8 | 521±149 | 18±6 |
| Olsen P | 214±10 | 500±60 | 31.2±15.1 |
| NH ₄ OAc extractable K | 6100±264 | 7910±818 | 129±59 |
| Total Cd | 0.13±0.03 | 0.10±0.02 | 0.03±0.03 |
| Total Cu | 20.3±0.8 | 3.5±0.7 | 10.8±7.9 |
| Total Ni | 15.0±3.4 | 1.3±0.5 | 0.9±0.1 |
| Total Pb | 51.9±6.9 | 4.3±1.9 | 3.1±1.1 |
| Total Zn | 88.6±17.6 | 6.2±3.5 | 5.9±5.2 |

^a EC = Electrical conductivity

6.3.3 Growth trial composts

Chemical properties of all compost mixtures used in the growth trials are presented in Table 2. Commercially available peat-free (PF) and peat-based (PB) composts were used as delivered from 80 litre sacks (B&Q peat-free garden compost, B&Q PLC, Eastleigh, Hampshire, UK and John Innes peat-based potting compost, Humax Horticulture Ltd., Gretna, Cumbria, UK). Green waste and food waste compost (GF) was produced in the EcoPOD[®] experiment outlined in section 6.3.1, and used after storage for 6 months in open bags.

6.3.4 Plant growth trials

To test the performance of the food waste-based compost as a potential peat replacement, we set up a pot trial in 10 l pots with 6 different blends of food waste and commercially-available peat-based composts as follows: 100% PB (100PB), 75% PB / 25% GF (75PB), 50% PB / 50% GF (50PB), 25% PB / 75% GF (25PB), 100% GF (GF), and a control treatment of 100% commercially-available peat-free compost (PF). The GFP compost was not used in the growth trials as preliminary analysis revealed that it gave no benefits over the GF compost. Compost mixtures were blended mechanically, and then placed into six pots to give six replicates. The treatments were split into six randomised blocks with one replicate of each per block and were grown for a period of 12 weeks in a heated greenhouse with a photoperiod of 16 h, maintained at 25°C daytime, 20°C night, augmented when necessary by 400 W Sun SON-T horticultural lamps.

Sunflower seeds were germinated in John Innes No. 1 compost for one week, after which growth stage 1 (Meier, 1999) was reached, and the seedlings transplanted to the pots. To assess growth performance, plant height was measured fortnightly until harvest (week 12 - equivalent to growth stage 9). At harvest, total above ground dry mass, seed dry mass and flower head diameter were determined.

6.3.5 Statistical analysis

All data were inputted into SPSS v14.0 (SPSS Inc., Chicago, IL), and one-way ANOVAs were carried out with Tukey's HSD or Least Significant Difference (LSD) post hoc procedures to assess differences between growth features and compost blend characteristics. All graphs were produced in SigmaPlot v10.0 (Systat Software Inc., San Jose, CA). All values are expressed on a dry weight basis.

6.4 Results

6.4.1 Composting of food waste

The results presented in Figure 6.1 illustrate that compost feedstocks containing food waste were successfully composted using the EcoPOD® in-vessel composting system. There was no difference in the C:N ratio of the GF and GFP composts after 112 d of composting, however, the GFP compost had a significantly lower ($P = 0.048$) C:N ratio (16 ± 1) than the green waste only compost (22 ± 2). Compost GF was not significantly different to either G or GFP composts in this respect. The initial pH of the green waste compost was neutral, whereas the pH of the composts containing food waste were both acidic. The pH in these treatments rose rapidly over the first 8 d to level out at around pH 8, at which point the pH of all three composts became similar.

Table 6.2: Chemical properties of substrates used for growth trial. PB = commercially available peat-based compost, GF = Green waste and food waste compost. Different letters indicate that substrates are significantly different ($P < 0.05$) according to Tukey's HSD for that variable. All values in mg kg^{-1} dry matter ($n = 6$) unless otherwise stated.

| Variable | Peat-free | 100 % GF | 25 % PB | 50 % PB | 75 % PB | 100 % PB |
|---------------------------------------|------------|------------|------------|------------|-------------|------------|
| Moisture content (%) | 41.4±1.5ab | 37.9±1.2a | 48.0±0.9b | 43.7±0.5ab | 45.1±1.4b | 53.5±0.4c |
| Organic matter (%) | 47.5±1.0b | 35.2±1.4a | 55.6±1.0b | 55.2±4.0b | 48.6±3.5b | 75.4±0.6c |
| pH | 6.70±0.01b | 7.73±0.03a | 5.85±0.04d | 6.14±0.02c | 5.95±0.09cd | 4.67±0.02e |
| EC* ($\mu\text{S cm}^{-1}$) | 2365±72b | 4462±472a | 2217±81b | 2522±217b | 2111±119b | 957±51c |
| KCl extractable NO_3^- | 64.9±0.9d | 77.6±3.5ab | 74.3±1.8bc | 67.9±2.6cd | 79.1±1.9ab | 86.6±0.5a |
| KCl extractable NH_4^+ | 25.3±1.0cd | 32.7±1.0b | 31.3±1.7bc | 37.5±1.8ab | 39.7±2.1a | 24.2±1.4d |
| Olsen P | 348±33a | 283±11a | 464±102a | 417±89a | 296±33a | 355±9a |
| NH_4OAc extractable K | 4424±176b | 5265±219a | 3504±155c | 3841±179bc | 3367±248c | 1130±26d |

* EC = Electrical conductivity

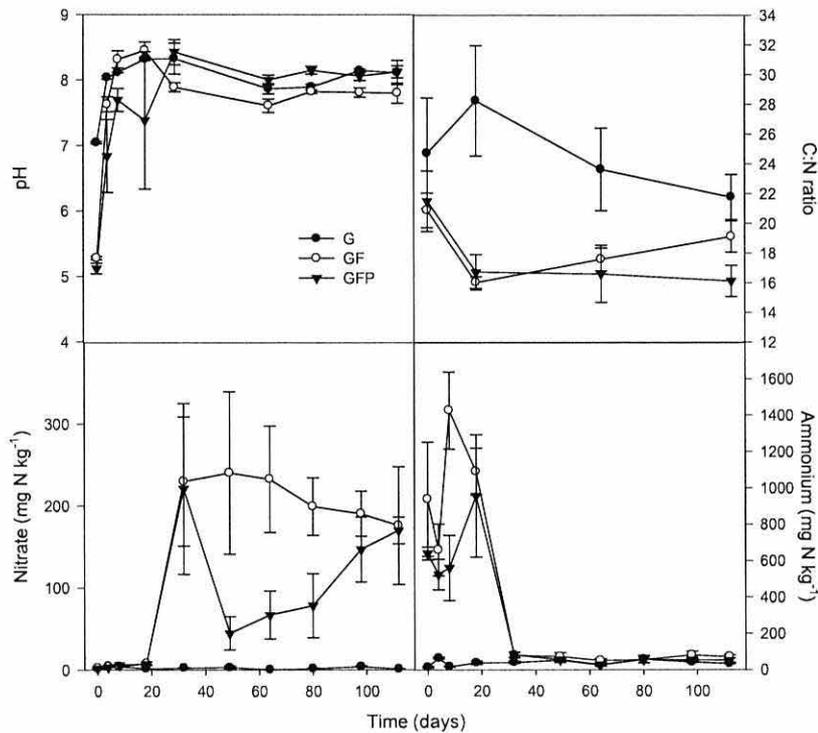


Figure 6.1: Changes in compost pH, C:N ratio, nitrate-N and ammonium-N over the composting period. Composting ceased on day 112, when temperatures (Fig. 2) had reached ambient. Closed circles = green waste only (G), open circles = green waste and catering waste (GF), inverted triangles = green waste, catering waste and shredded paper (GFP). Values represent means \pm SEM ($n=3$).

Ammonium levels started off high for both composts containing food waste and fell sharply after 32 d, remaining stable for the remainder of the composting period. By contrast, NH_4^+ in the green waste-only compost remained low throughout the duration of the composting trial. Nitrate levels were initially low in all three composts but rose rapidly between 18 and 32 d in the GF and GFP composts, whilst levels in compost G remained low. Whilst the high levels of nitrate in compost GF were maintained with slight decline after the initial rise for the duration of the remaining composting period, levels fell sharply again in compost GFP by 49 d, and slowly rose again by day 112. By day 112 the temperature of the compost inside the vessel had returned to background levels (Fig. 6.2). The stable pH, low C:N ratio, and high $\text{NO}_3^- : \text{NH}_4^+$ ratio of the food waste containing composts suggested that composting was complete and that the resultant product was ready for bagging and maturation.

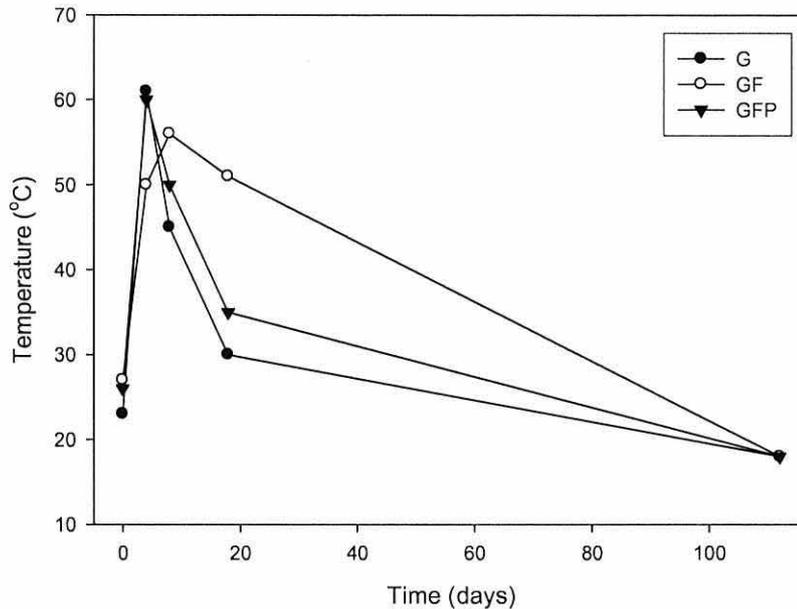


Figure 6.2: Temperature changes throughout composting. Closed circles = green waste only, open circles = green waste and catering waste, inverted triangles = green waste, catering waste and shredded paper.

6.4.2 Compost mixture properties

The chemical properties of the composts and compost mixtures used in the growth trial are listed in Table 6.2. Individually, 100% compost GF contained significantly ($P < 0.05$) less organic matter and moisture, whilst possessing a significantly higher pH, K, electrical conductivity (EC), and ammonium concentrations than the 100% peat-based compost treatment (PB). There were no significant differences between the Olsen-P values of any of the composts or compost mixtures ($P > 0.05$). The commercially purchased peat-free compost (PF) contained less nitrate than the two other composts or their mixtures, but did have a significantly higher pH than compost PB, and 50% less soluble salts than compost GF. The three mixtures of GF and PB composts (25, 50 and 75% v/v) were statistically similar to each other ($P > 0.05$) for all variables with the exception of nitrate and ammonium, where the 25% PB treatment had significantly more ammonium ($P < 0.05$) than the 75% PB treatment, and the 50% PB treatment had significantly less nitrate ($P < 0.05$) than the 75% PB treatment. It is clear from these results that the PB compost is significantly different in several respects to the GF compost, but with the exception of potassium (where

compost GF has a five-fold increase over compost PB), they contained similar nutrient concentrations, whilst the physical parameters of organic matter and moisture content were 100 and 50% higher respectively in compost PB.

6.4.3 Plant growth

After two weeks growth from the date of transplanting, there were no significant differences between the height of *H. annuus* in each treatment ($P = 0.358$). However, after four weeks growth, the plants were significantly shorter in the 100% GF compost in comparison to the other treatments ($P = 0.007$). After six weeks growth, both GF and PF composts had produced significantly shorter plants than any of the mixtures containing PB compost ($P = 0.003$). This trend continued for the remainder of the growth period (Fig. 6.3).

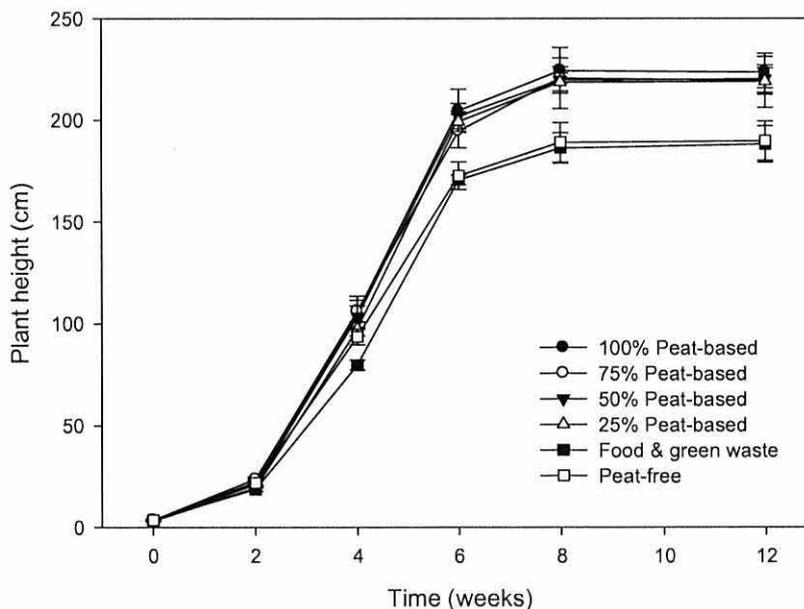


Figure 6.3: Effect of different compost blends on the height gain of sunflowers from seedling transplant at principal growth stage 1 (Meier, 1997) to final harvest at principal growth stage 9 (12 weeks). ● = food and green waste compost (GF); ○ = 100 % commercially available peat-based compost (PB); ▼ = 75 % PB / 25 % GF; △ = 50 % PB / 50 % GF; ■ = 25 % PB / 75 % GF; □ = commercially available peat-free compost (PF).

Whilst only 100% GF and PF treatments yielded significantly shorter sunflowers, the patterns presented in Figure 6.4 illustrate that only compost PF gave

significantly smaller head diameter ($P = 0.031$), and lower seed dry mass ($P = 0.033$) and total above-ground biomass ($P = 0.018$). From these results, it can be seen that the green waste and food waste-derived compost provided sufficient nutrition and water retention to allow *H. annuus* to grow to its full potential. Both seed mass (for food or biofuel production via oil) and head diameter (for horticultural purposes) were statistically similar to the peat-based compost in all treatment mixtures of GF compost from 100% GF through to 100% PB.

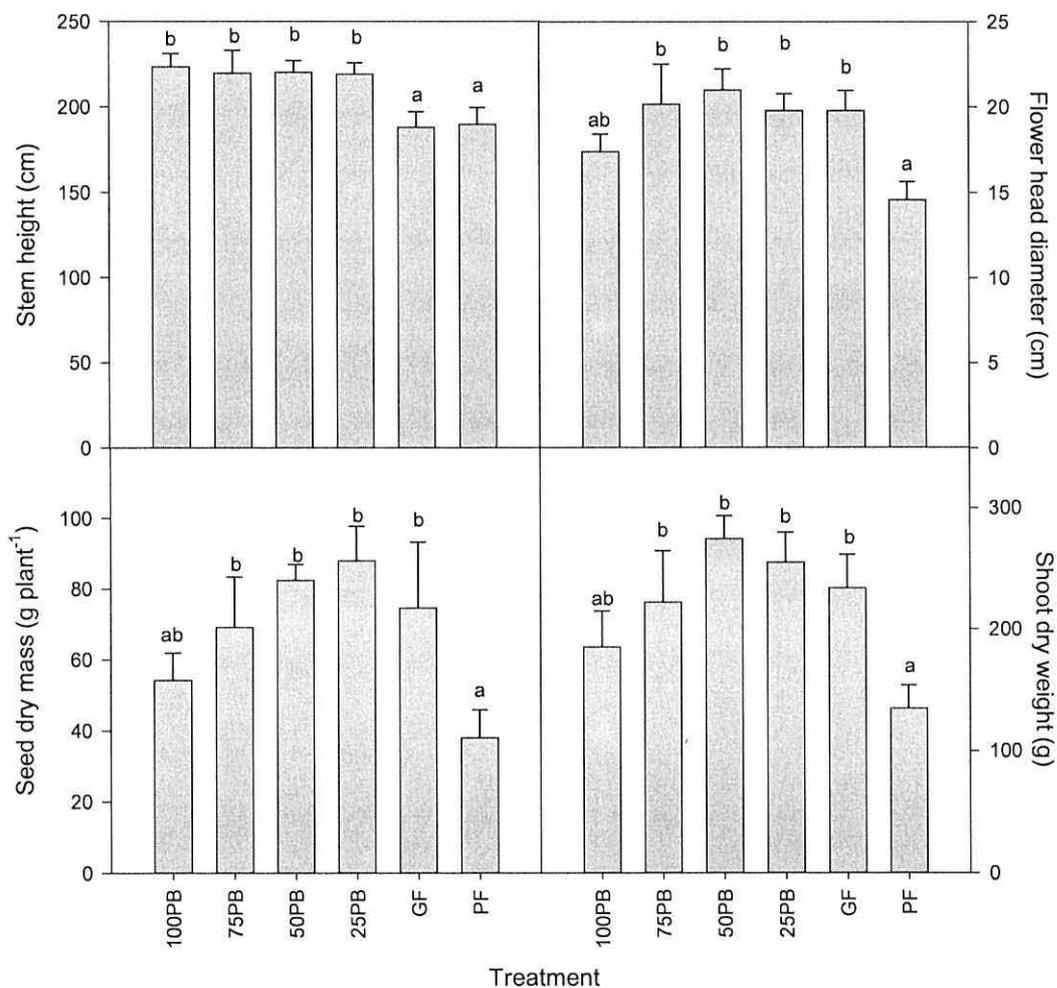


Figure 6.4: Effects of different compost blends on key growth parameters for sunflowers at harvest (12 weeks). Different letters denote statistically significant differences between treatments according to the Least Significant Difference (LSD) test ($P < 0.05$). 100PB = 100% peat-based compost, 75PB = 75% peat-based compost and 25% green waste and food waste-derived compost, 50PB = 50% peat-based compost and 50% green waste and food waste-derived compost, 25PB = 25% peat-based compost and 75% green waste and food waste-derived compost, GF = 100% green waste and food waste-derived compost, PF = 100% commercially available peat-free compost.

6.5 Discussion

6.5.1 Composting of food waste

We have demonstrated that low C:N ratio food waste can be successfully co-composted with green waste either in the presence or absence of shredded paper. The rise to a stable pH and low C:N ratio (Sharma *et al.*, 1997) have illustrated that the thermophilic stage of the process was completed satisfactorily for all three feedstocks. The green waste-only compost contained very low levels of nitrate and ammonium, and these exhibited little variation throughout the composting period. However, both feedstock mixes containing food waste exhibited typical changes of successful aerobic composting (Benito *et al.*, 2003), resulting in a high $\text{NO}_3^- : \text{NH}_4^+$ ratio after 112 days.

Currently, most composts produced from large scale composting facilities are relatively rich in nutrients (Roberts *et al.*, 2007). The substitution of green waste for food waste in our study at a rate of 30% doubled the nitrogen content of the finished compost after 112 d, suggesting that the co-composting of catering waste with green waste provides an effective a means of improving the quality of composts destined for use in the horticulture industry. Catering wastes contain high levels of proteins from waste foods, and it is these compounds that have been found to control the rate of composting, providing easily accessible nitrogen and carbon for microbial respiration and growth (Chang and Hsu, 2008).

The sharp drop in nitrate concentration observed in compost GFP between days 32 and 49 after the sharp initial rise between days 18 and 32 may be attributable to thermophilic denitrification or immobilisation (Roberts *et al.*, 2007), indicating that the addition of paper increased the temperature of the pile above optimum temperatures. Given the nature of forced aeration composting, gaseous nitrogen losses in the form of nitrous oxide, ammonia and nitrogen gas may be greater than conventional windrow composting due to airflows forcing gases outwards (de Guardia *et al.*, 2007). Whilst the losses of nitrogen in themselves represent a lost resource in terms of nutrient depletion of the finished compost, N_2O has major implications for global warming, being 296 times more potent than CO_2 as a greenhouse gas (IPCC, 2001), and as such, significant emissions of N_2O somewhat negate the composting

process as an environmentally suitable waste management technique. It is therefore of utmost importance both for compost quality and the overall sustainability of the operation that feedstock mixes, oxygen levels and temperatures be regulated appropriately to mitigate against gaseous losses of nitrogen (Fukumoto *et al.*, 2003; Roberts *et al.*, 2007). In the present study, the addition of shredded paper (planned to address potential issues of high nitrogen levels) had little effect on the chemistry of the final product, and with the exception of the aforementioned dip in nitrate levels, no significant effects on nitrogen dynamics within the compost vessel were observed.

6.5.2 Use of food waste compost as a peat replacement

Despite initial indications (Fig. 6.3), our results clearly demonstrate that conventional green waste only peat-free compost gave the joint-poorest results for sunflower height. By twelve weeks, all treatments containing peat-based compost had grown significantly higher than either the peat-free control, or the 100% GF treatment. There is little indication from the chemical properties presented in Table 6.2 to signify why this may be. Pearson's correlation carried out on plant growth characteristics and the substrate properties highlight positive correlations with moisture content ($P = 0.014$) and organic matter ($P = 0.022$) – indicating that the physical characteristics of the substrate may be the major factor governing plant growth rate. Of the chemical factors, only pH ($P = 0.006$), electrical conductivity ($P = 0.012$) and potassium ($P = 0.033$) showed significant negative relationships with plant height. It is difficult to distinguish between cause and effect with these results. Indeed, the negative correlation of potassium with sunflower height can be attributed to the strong positive correlation ($P < 0.001$) between electrical conductivity and potassium, indicating a negative plant response to excess salinity, as demonstrated by Turhan *et al.* (2008), as opposed to excess potassium *per se*.

From Figure 6.3, we demonstrate two differing patterns in growth characteristics of *H. annuus*. Height was influenced by the addition of peat-based media i.e. treatments 100PB, 75PB, 50PB, and 25PB gave significantly greater vertical growth, whilst head diameter, seed biomass and total above-ground biomass appeared to be governed to a greater extent by the presence of GF compost. This

paradoxical result is not easily explained, however, whilst stem height may be a useful indicator by which to measure plant growth experimentally, head size and seed mass are the most useful indicators for horticultural purposes. Of the three macronutrients measured, only potassium and ammonium-N were present in significantly greater concentrations in compost GF over compost PB. There were no significant correlations between any of the growth media properties measured and either head diameter, seed mass or aboveground biomass, again giving little indication as to why the PF composts (and to a lesser extent the PB compost) gave poorer yield and head diameter.

6.5.3 Conclusions

We have demonstrated that food wastes can be successfully co-composted with green waste, and that the addition of shredded paper was unnecessary for improving the process. From the sunflower growth trials, we found that whilst the addition of peat is necessary to produce the tallest sunflowers, its inclusion in the growth media had no significant effect on flower size or seed yield – the two quality indicators chosen to assess growth. A study by Herrera *et al.* (2008) suggested that provided peat constituted more than 50% of the mixture of growth medium, a mixed waste compost could replace at least some of the peat requirement for the growth of tomatoes. The overarching concerns from three studies investigating the feasibility of composts for peat replacement are the relatively high electrical conductivity and pH levels of composts compared to peat (Garcia-Gomez *et al.*, 2002; Benito *et al.*, 2005; Herrera *et al.*, 2008). In the case of *Helianthus annuus* and the green waste / food waste compost used in our study, these concerns have proved to be unfounded. Taking into account the lower organic matter and moisture content of the GF compost (and the effect these physical characteristics may have on the water holding capacity of the compost), we suggest that up to a 75% substitution of peat by catering waste – derived composts would be suitable for unaffected growth. This should not unduly increase the irrigation requirement, however, where water resources are not an issue, 100% replacement of peat by catering waste derived composts may be possible. We conclude that catering wastes make a positive contribution to the nutritive value of waste-derived composts, and that the production and marketing of

such composts should be encouraged to reduce the burden of the gardening and horticulture industries on the finite resources of *Sphagnum* peat.

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CHAPTER 7: MIGRATION OF HEAVY METALS IN SOIL AS INFLUENCED BY ORGANIC AMENDMENTS

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7.1 Abstract

Soils contaminated with heavy metals can pose a major risk in the sustained protection of freshwaters and food chains. The success of organic and inorganic intervention strategies to alleviate toxicity in a highly acidic soil heavily contaminated with As, Cu, Pb and Zn was evaluated over 4 months. Amelioration of metal toxicity was assessed by measuring changes in soil solution chemistry, metal leaching, plant growth and foliar metal accumulation. Both green waste- and MSW-derived composts increased plant yield and rooting depth, reduced plant metal uptake, and raised the pH and nutrient status of the soil. At lower depths, composts increased soil solution Pb and Cu concentrations which were attributed to displacement from cation exchange sites in the topsoil by the high salts present in the compost. We conclude that composts are well suited to aiding the revegetation of contaminated sites, however, care must be taken to ensure that very short term pulses of heavy metals leached are not of sufficient magnitude to cause contamination via leaching.

7.2 Introduction

Alternative long-term sustainable strategies to the disposal of municipal solid waste (MSW) in landfill are being sought in most industrialised nations worldwide. It is imperative, however, that these strategies have a low environmental, social and economic footprint (Adani *et al.*, 2000). Methane emitted from landfill sites is the largest source of greenhouse gas (GHG) produced by the waste management sector, and treatments such as composting have been employed to mitigate against this (IPCC, 2007). European Union (EU) Council Directive 1999/31/EC (EC, 1999) on the landfill of waste has set down strict mandatory targets to reduce the amount of Biodegradable Municipal Waste (BMW) entering landfill. This EU Directive also states that no waste may be deposited in landfill without it first being treated to reduce its subsequent environmental footprint. Mechanical Biological Treatment (MBT) can be used to pre-treat residual mixed wastes after recyclates have been removed to ultimately produce a quasi-stabilised, compost-like substance (Binner and Zach, 1999). Whilst according to EC (1999), this is suitable for landfill, it is desirable to find alternative uses for this mixed waste compost. This position is supported by Bockreis and Steinberg (2005) who demonstrated that MBT-treated wastes still have a large potential to produce methane in an anaerobic landfill environment. As soil organic matter levels have declined to critical levels in many regions of the world compromising their ability to deliver ecosystem services (Bellamy *et al.*, 2005), it is advantageous to recycle this 'waste' organic matter to land. However, this land spreading must occur without unduly increasing the loading of inorganic and organic contaminants onto previously uncontaminated soils. One proposed use for mixed waste composts is in the remediation of heavy metal contaminated sites, where the addition of heavy metals may not pose such a problem, provided they are added in non-labile forms.

Soil-borne heavy metals must be either removed or stabilised into a less environmentally available form for successful remediation (Kiikkilä *et al.*, 2001). The former is generally carried out "ex situ", causes soil structure deterioration and comes at high economic cost, limiting its use on vast contaminated areas. Biostabilisation techniques tend to be carried out "in situ" and are less expensive, more time consuming and prone to uncertainty. Soils can naturally reduce mobility and

bioavailability of heavy metals as they are retained in soil by sorption, precipitation and complexation reactions (Pérez-de-Mora *et al.*, 2005). This natural attenuation process (natural remediation) can be accelerated by the addition of organic amendments (Bolan and Duraisamy, 2003). Brown *et al.* (2003) concluded in their study that biosolids could promote plant growth on a former mine site in Idaho, whilst Kiikkilä *et al.* (2001) found that an application of an organic mulch to a heavy metal contaminated forest soil decreased the toxicity of soil solution to bacteria. Traditionally, liming and covering with non-toxic topsoil or inert mineral material was the most common remediation method. In this strategy, lime application can induce precipitation of non-toxic metal-carbonates while plant establishment can restore ecosystem services whilst simultaneously reducing water ingress and leaching (Krebs *et al.*, 1998; Lee *et al.*, 2004).

Organic and inorganic stabilisation techniques such as these do, however, raise some concerns, primarily that the metals present, although bound by amendments, have not been removed from the site. Further, unless regular re-application of lime or organic wastes takes place, it has been hypothesised that metals may increase in availability with time, as the organic matter to which they are bound is degraded by soil microbes (Nwachukwu and Pulford, 2008). Additionally, regular re-application of contaminated wastes may lead to a progressive accumulation of other potentially toxic elements not initially contributing to the pollution on site (Pérez-de-Mora *et al.*, 2006). Amendments are usually applied to the surface layer of contaminated sites or incorporated to the top 10 cm of soil (Pérez-de-Mora *et al.*, 2007a), and pot trials such as those of van Herwijnen *et al.* (2007a) fail to address possible mobilisation effects due to leaching of soluble organic matter through the vertical plane. Indeed, local remediation works have been shown to produce a complex effect on pollutant flux at a catchment level (Blake *et al.*, 2007).

Preliminary work by Bishop *et al.* (2006) demonstrated that differing organic wastes have different effects on the leachability of different elements, and van Herwijnen *et al.*'s (2007b) study concluded that general metal availability can be either increased or decreased by compost addition, depending on the type of amendment used. The aim of this study is to investigate the effect of two contrasting

types of compost, and a conventional inorganic treatment on the chemistry and heavy metal mobility within a highly acidic heavy metal contaminated soil.

Table 7.1: Chemical properties of the soil and compost (GWC and MSWC) substrates used in the plant growth trials. All values in mg kg⁻¹ dry matter unless otherwise stated.

| Variable | Soil | GWC | MSWC |
|--|-----------------|-----------|-----------|
| Moisture content (%) | 13±1 | 41±3 | 57±2 |
| Organic matter (%) | 2.5±0.1 | 25.2±2.9 | 42.2±3.7 |
| pH | 2.27±0.03 | 8.11±0.18 | 7.28±0.03 |
| EC ^a | 2.98±0.06 | 0.73±0.16 | 3.59±0.80 |
| Total C (%) | 0.7±0.3 | 13.2±0.9 | 24.6±4.3 |
| Total N (%) | BD ^b | 0.62±0.06 | 0.97±0.17 |
| KCl-extractable NO ₃ ⁻ | 1.7±0.1 | 1.2±0.5 | 21.9±11.8 |
| KCl-extractable NH ₄ ⁺ | 12.9±1.1 | 32.5±2.1 | 29.0±6.4 |
| Olsen P | 3±1 | 119±5 | 132±32 |
| NH ₄ OAc-extractable K | 9±1 | 1113±230 | 2925±382 |
| Total As | 77.6±5.4 | BD | 17.1±7.5 |
| Total Cd | 1.02±0.09 | BD | 0.78±0.46 |
| Total Co | 11.9±0.9 | 25.2±6.7 | 14.5±13.3 |
| Total Cr | 8.3±0.6 | 37.4±2.8 | 48.1±13.3 |
| Total Cu | 2474±77 | 66.4±39.5 | 329±83 |
| Total Mo | 16.2±0.7 | BD | 9.4±0.6 |
| Total Ni | 1.7±0.2 | 31.3±2.3 | 87.2±19.2 |
| Total Pb | 6703±247 | 40±2 | 906±324 |
| Total Zn | 194±11 | 57±3 | 505±216 |

^a Electrical conductivity (mS cm⁻¹), ^b BD = Below limit of detection.

7.3 Materials and methods

7.3.1 Substrate characteristics

Chemical characteristics of the soil and composts used in the experiment are listed in Table 7.1. Soil (ca. 400 kg) was collected from Parys Mountain, Anglesey, North Wales (53°23'22"N, 4°20'54"W) and sieved to 1 cm before use. Parys Mountain was extensively mined for copper ore from the 18th to the 20th century. The site covers an area of 200 ha and is covered with very large areas of unvegetated heavy metal contaminated mine spoil (ca. 100-200 years-old), dominated by sulphide minerals including pyrite, chalcopyrite, sphalerite and galena, with lesser amounts of other minerals (Walton and Johnson, 1992).

The MSW-derived compost (MSWC) was produced using a commercially available CT-5[®] and EcoPOD[®] in-vessel composting system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA) at the Ffridd Rasmus Waste Treatment Facility located at Harlech, Gwynedd, North Wales (52°52'59"N, 4°06'43"W). The in-vessel composter was filled with a CT-5[®] feed hopper (3 m³ feedstock volume) which uses a hydraulic ram to push the material through a filling chamber and into an extended 1.5 m diameter green plastic EcoPOD[®] vessel at a fill rate of approximately 3 m³ min⁻¹. At the same time as filling the EcoPOD[®], a rigid perforated (7.62 cm diameter pipe with 1.59 mm slits) plastic aeration pipe is inserted into the base of the vessel to provide forced aeration. The aeration regime can be closely controlled by means of a timed fan (Ag-Bag International Ltd, Warrenton, OR, USA) running at a flow rate of 137 l min⁻¹ (Roberts *et al.*, 2007). The timed aeration regime was managed manually in order to maximise the rate of composting. In the initial 18 d, aeration was managed in order to maintain high temperatures and therefore optimal sanitation conditions (typically air pumped through the vessel for 2 min every 10 min). This was changed to on 4 min on, 6 min off to compensate for the relatively wet feedstocks on day 18. This continued until day 83, when the vessel was opened, and the compost was matured in static piles for a further 62 d before bagging for storage and use. The green waste-derived compost (GWC) was obtained from a commercial open windrow green waste composting facility near Aberystwyth, mid Wales (49°46'28"N, 7°32'57"W). For the inorganic treatment, analytical grade CaCO₃, NH₄NO₃, P₂O₅ and KCl (VWR, Lutterworth, Leicestershire, UK) were used as supplied and mixed with the top 10 cm treatment layer. Lime requirement of the soil was assessed using the method of Sims (1996) giving a treatment of 70 g m⁻², and N, P and K were applied at rates of 8, 2 and 4 g m⁻² respectively. Compost treatments were added at 40% (v/v) to the top soil (0-10 cm), whilst a control treatment of 10 cm untreated soil was also used.

7.3.2 Experimental design

Six replicates of each treatment giving a total of 24 columns were constructed using 16 cm diameter plastic drain piping 45 cm in length. The bottoms of these

columns were closed using plastic blanking plates, which were drilled to allow drainage. Sieved soil was mechanically homogenised, before being packed untreated into the columns to 30 cm depth, with the remaining 10 cm being hand-mixed with the appropriate treatment as described in section 7.3.1. Each column was placed in an individual saucer on a 3 cm off-cut of pipe to collect leachate whilst ensuring that the column did not come into contact with standing water. The columns were arranged in a fully, randomised block design experiment in a heated greenhouse with a photoperiod of 16 h, maintained at 20°C daytime, 18°C night, augmented when necessary by 400 W Sun SON-T horticultural lamps. Treatments were allowed to equilibrate for two days before *Agrostis capillaris* L. (common bent grass) was sown in all columns at a density of 4 g seed m⁻², and was grown for 112 d before harvest. Soils were maintained at 70% field capacity by watering three times weekly with artificial rainwater fed via a multi-nozzle array to ensure uniform coverage (Stevens *et al.*, 1986).

7.3.3 Sampling and analysis

Standard chemical analyses were carried out in triplicate on the soil and compost substrates used in the trial. Moisture content was determined by drying samples at 80°C for 24 h and organic matter content was determined as loss-on-ignition at 450°C overnight. pH (Hanna Instruments pH 209 pH meter) and electrical conductivity (EC) (Jenway 4010 EC meter) were determined after mixing for 1 h. Total C and N were determined using a CHN2000 analyser (LECO Corp., St Joseph, MI). Prior to total elemental analysis, substrates were air dried (25°C, 14 d) and plant samples dried at 80°C before being ground in a T1-100 vibrating sample mill (Heiko Co Ltd., Fukushima, Japan) equipped with tungsten grinding vessels. Subsamples of the ground material were then digested using HNO₃ (Havlin and Soltanpour, 1980). Nitrate and ammonium were extracted using a 1:5 (w/v) fresh sample : extractant ratio with 1 M KCl, shaken for 1 h on a reciprocating shaker at 250 rev min⁻¹ (Zhong and Makeshin, 2003). Olsen P was extracted using 0.5 M NaHCO₃ and a ratio of 1:20 (w/v) fresh sample : extractant and shaken for 1 h on a reciprocating shaker at 250 rev min⁻¹. Available K was extracted using 1:5 (w/v) fresh sample : extractant ratio of

1 M NH₄OAc, buffered to pH 7.0, shaken for 1 h on a reciprocating shaker at 250 rev min⁻¹ (Helmke and Sparks, 1996). Nitrate and ammonium were determined using a San⁺⁺ segmented-flow analyser (Skalar Inc., Norcross, GA). K was analysed using a Sherwood 410 flame photometer (Sherwood Scientific, Cambridge, UK). Heavy metals were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Fissions PlasmaQUAD II Turbo ICP-MS. Phosphate was determined colourimetrically using the method of Murphy and Riley (1962).

Soil solution was collected from each column overnight at each sampling interval using 10 cm Rhizon-MOM[®] in situ soil solution samplers (Rhizosphere Research Products, Wageningen, The Netherlands), and was analysed using the same methods as detailed for the extracts from the substrate samples. Total dissolved nitrogen and dissolved organic carbon (DOC) in soil solution were analysed using a TOCV-TN analyser (Shimadzu Corp., Kyoto, Japan).

7.3.4 Statistical analysis

All data were inputted into Microsoft Excel 2003 (Microsoft Corp., Redmond, WA). Statistical analyses were carried out in SPSS v14.0 (SPSS Inc., Chicago, IL), and data graphically presented using SigmaPlot v10.0 (Systat Software Inc., San Jose, CA). A one-way ANOVA with Tukey's Honestly Significant Difference (HSD) post hoc test was used to differentiate between the treatments for plant growth and tissue metal concentration. Repeated measures GLM procedures were carried out to assess the effects of time, depth and treatment on soil solution chemistry over the 112 days of the trial. Where sphericity was not met, the Huynh-Feldt correction was applied to allow univariate results to be used. Spearman's Rho was used to assess correlation between soil solution variables. All nutrient and heavy metal content values are expressed on a dry weight basis, except where soil solution data are quoted.

7.4 Results

7.4.1 Compost and soil properties

The soil was highly acidic whereas both composts were mildly alkaline (Table 7.1). The electrical conductivity of the MSWC was five-fold higher than that of the GWC, and 15% higher than the soil. This high level of soluble salts in the MSWC can be attributed to high levels of soluble nutrients such as potassium; however, this was not the case for the soil, with over 300-times less NH_4OAc extractable K present. Olsen-extractable P was also very low in the soil, typically 30-times lower than that of either compost. Total nitrogen in the soil was below limit of detection by the dry combustion method, however, appreciable levels of nitrate and ammonium were detected.

From the suite of nine potentially toxic elements (PTEs) tested, it was demonstrated that the GWC was a very clean compost, with total metals levels well within British PAS100 standards (BSI, 2005). The soil was heavily contaminated with copper and lead, and contained moderate levels of arsenic and zinc. Whilst heavy metal contamination of the MSWC was an order of magnitude lower than the soil for Cu and Pb, the amount of Zn was 2.5 times higher in the MSWC compared to the soil, and Ni was 75% higher than that permitted in the PAS100 compost quality guidelines. In contrast, Cd and Cr were both below PAS100 guideline levels.

7.4.2 Plant growth and metal uptake

Despite the expected toxicity of the untreated control soil, *A. capillaris* germinated and grew in all treatments, although root biomass was unmeasurable in the control treatment (Fig. 7.1). Whilst the inorganic treatment gave a significant ($P < 0.05$) increase in above-ground biomass over the untreated control, both compost treatments gave statistically higher yields ($P < 0.05$), with the GWC giving the greatest above-ground biomass ($P < 0.05$). Root growth in the 0 and 10 cm soil layer was recorded for all three treated columns, with MSWC giving the greatest root biomass, being statistically higher than the inorganic treatment ($P < 0.05$). Only the compost-treated columns gave root growth below the 10 cm treated depth of soil, with no

significant difference in root biomass found between the two compost treatments ($P > 0.05$).

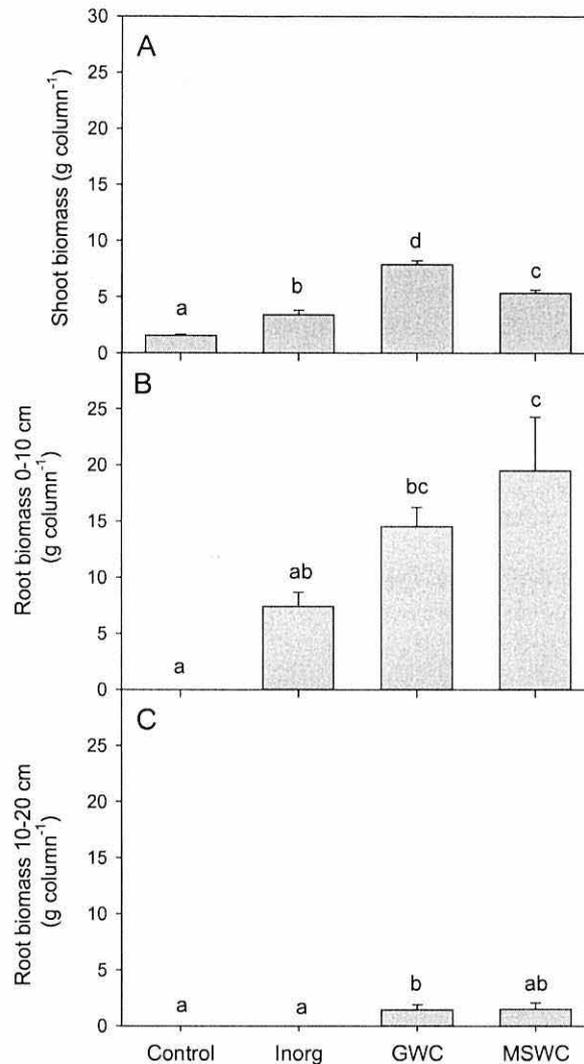


Figure 7.1: Biomass production of *A. capillaris* after growth in a contaminated soil amended with nothing (control), inorganic fertiliser (Inorg), green waste-derived compost (GWC) and MSC-derived compost (MSWC). Panel A illustrates shoot biomass, Panel B illustrates root biomass between 0 and 10 cm depth, and Panel C illustrates root biomass between 10 and 20 cm depth. No root growth was observed below 20 cm, and no measurable root growth was observed for the control treatment at any depth. Different letters within each panel denote significant differences after ANOVA and Tukey's HSD of $P < 0.05$. Values represent mean \pm SEM ($n = 6$).

Of the nine PTEs assessed in this experiment, mixed patterns in foliar metal accumulation were observed between elements (Fig. 7.2). For As, Cd, Cu and Pb, the control treatment gave significantly greater tissue concentrations than all other treatments ($P < 0.05$). In addition to this, the two compost treatments reduced metal

uptake compared to the inorganic treatment as well as that of the control for As and Cu. The GWC treatment gave the lowest leaf concentrations for As, Co, Cr, Cu, Ni, Pb and Zn, although it was never statistically different from at least one other treatment across these elements ($P > 0.05$). Interestingly, the MSWC resulted in the least uptake of Cd out of the four treatments, whilst giving rise to the highest plant tissue concentrations of Mo, Ni and Zn. In the case of Ni and Zn, the greater concentrations of elements when compared to the soil (cf. Table 7.1) can be attributed to this fact. Even though the MSWC contained 50 times the concentration of Ni compared to the soil as a raw substrate, there was no significant difference in foliar Ni accumulation between these two treatments. With this taken into consideration, it is surprising that the GWC treatment did not also give rise to elevated Ni tissue concentrations, give its 20-fold increase in substrate Ni concentration compared to the soil.

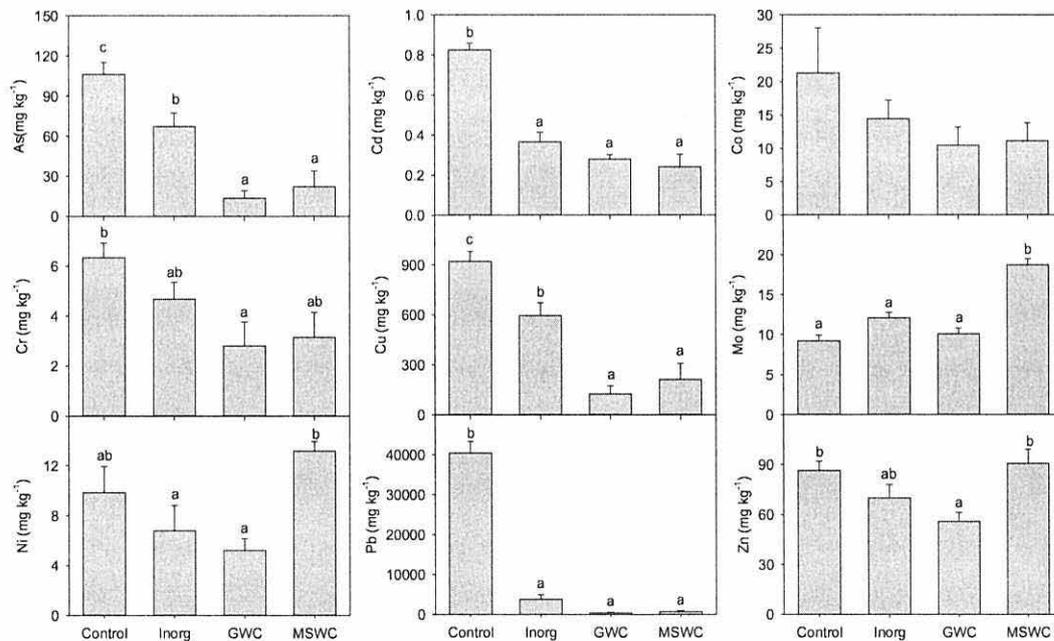


Figure 7.2: Heavy metal concentration of *A. capillaris* after growth in a contaminated soil amended with nothing (control), inorganic fertiliser (Inorg), green waste-derived compost (GWC) and MSC-derived compost (MSWC). Different letters within each panel denote significant differences after ANOVA and Tukey's HSD of $P < 0.05$. Note no significant differences between treatments for Co. Values represent mean \pm SEM ($n = 6$).

Despite the order-of-magnitude differences in concentration of both Cu and Pb between the composts and the soil, only Pb was taken up at a rate reflecting this in the control over the treated soils. There was a one order-of-magnitude reduction between the control and the inorganic treatment, and a two orders-of-magnitude between the control and both compost treatments.

7.4.3 Changes in soil solution chemistry

All the variables measured in soil solution changed over the duration of the experiment (Figs 7.3 & 7.4, Table 7.2, $P < 0.001$), with most metals decreasing, and only pH and DOC increasing. Spearman's Rho correlations were carried out allowing the identification of strong negative correlations ($P < 0.001$) for all three metals against pH, strong positive correlations of all three metals against EC ($P < 0.001$), but mixed correlations between the metals and DOC (Cu, $r = -0.099$, $P = 0.828$; Pb, $r = -0.288$, $P < 0.001$; Zn, $r = 0.150$, $P < 0.001$). The highest levels of soil solution Cu, Pb and Zn were observed at the start of the trial, with these being leached out over time. We ascribe this leaching to the positive correlations ($P < 0.001$) between the three elements and NO_3^- , NH_4^+ and TDN, which were also leached rapidly from the columns. Of particular note, was the high level electrical conductivity for MSWC, with our data clearly showed leaching of high levels of soluble salts from the MSWC down the soil profile, with progressive peaks seen to occur with increasing depth over time.

The MSWC treatment resulted in the highest pH levels at the surface layer, and this was also significantly higher than the control at 10-20 cm. DOC was highest at the surface layer for the GWC treatment, although MSWC also resulted in an increase over the control and inorganic treatments, with levels peaking at 24 d and decreasing thereafter. Ammonium levels were not significantly affected by depth, or the treatment \times depth interaction ($P > 0.05$), however, the time \times treatment, time \times depth and time \times treatment \times depth interactions were all significant ($P < 0.01$), indicating that NH_4^+ levels decreased at differing rates, and that overall, these rates differed when treatment, time and depth were considered together. Nitrate levels changed at a similar rate across all depths, hence the lack of a significant interaction effect ($P > 0.05$).

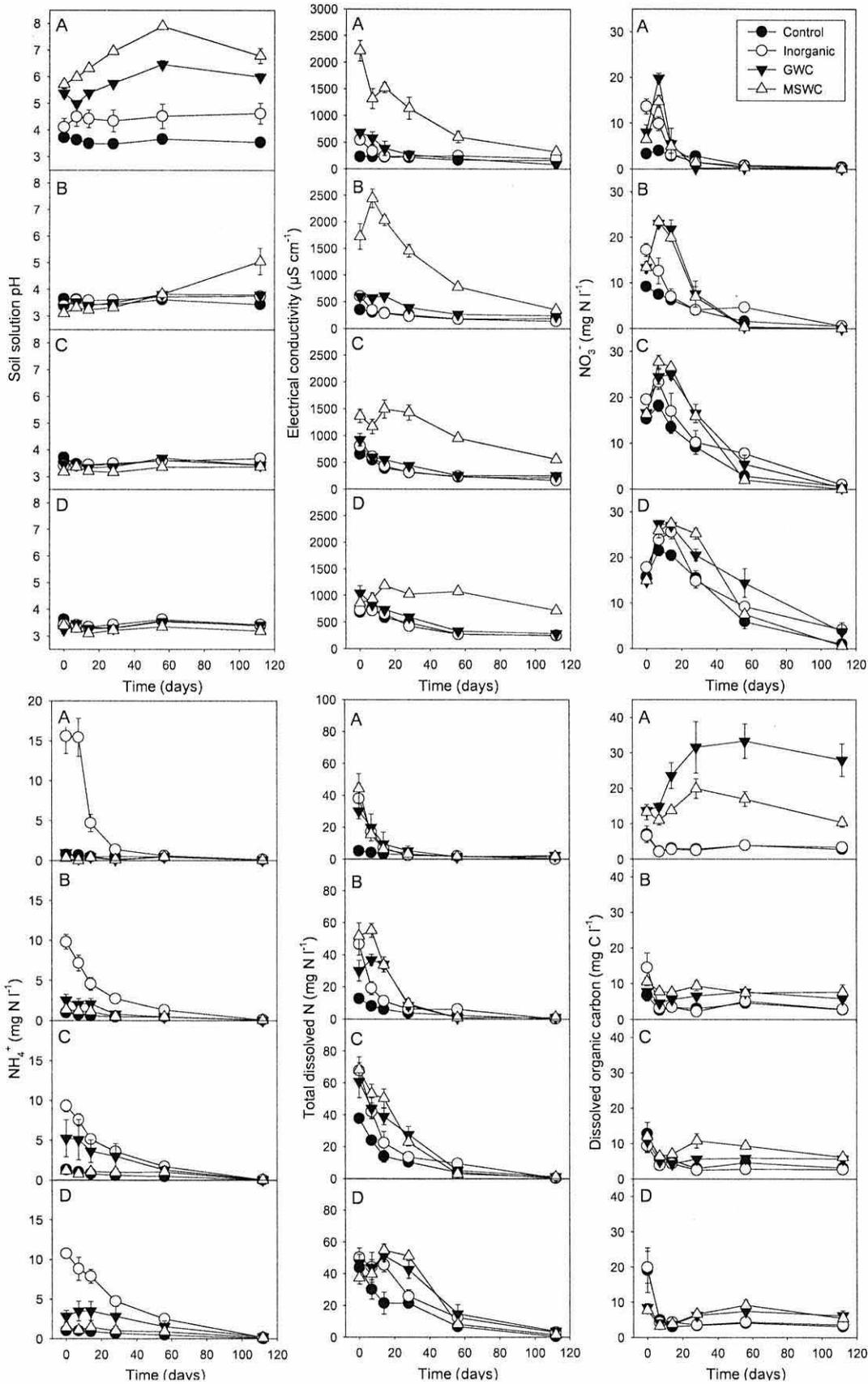


Figure 7.3: Soil solution chemistry over the 112 days of the trial. Within each variable, Panels A, B, C and D represents the 0-10 cm, 10-20 cm, 20-30 cm and 30-40 cm soil layers respectively. Repeated

measures ANOVA results are presented in Table 7.2. The legend is the same for all panels. Values represent mean \pm SEM ($n = 6$).

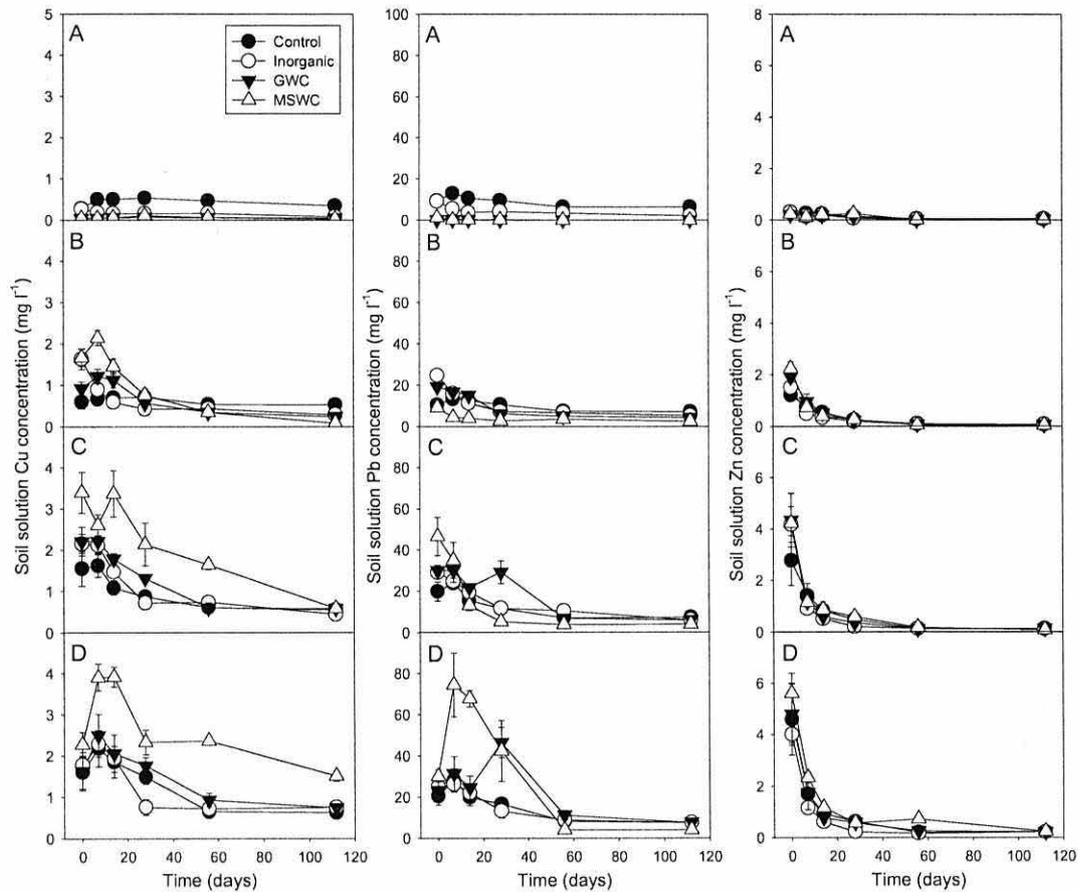


Figure 7.4: Soil solution heavy metal concentration over the 112 days of the trial. Within each variable, Panels A, B, C and D represents the 0-10 cm, 10-20 cm, 20-30 cm and 30-40 cm soil layers respectively. Repeated measures ANOVA results are presented in Table 7.2. Values represent mean \pm SEM ($n = 6$).

Table 7.2: Results from repeated measures ANOVA analysis on changes in soil solution chemistry over time and depth, as affected by soil amendment treatment.

| Factor | F value (asterisks indicate significance of result: * < 0.05, ** < 0.01, *** < 0.001) | | | | | | | | |
|---------------------------|---|---------|------------------------------|------------------------------|---------|---------|---------|---------|---------|
| | pH | EC | NO ₃ ⁻ | NH ₄ ⁺ | TDN | DOC | Cu | Pb | Zn |
| Time | 56.0*** | 236*** | 672*** | 144*** | 330*** | 34.3*** | 117*** | 72.7*** | 191*** |
| Treatment | 28.6*** | 263*** | 26.3*** | 61.1*** | 23.6*** | 28.8*** | 29.7*** | 2.7 | 1.8 |
| Depth | 200*** | 6.0** | 146*** | 2.1 | 52.6*** | 24.6*** | 163*** | 137*** | 38.5*** |
| Tr \times D | 37.3*** | 10.1*** | 0.8 | 1.8 | 0.9 | 19.0*** | 9.3*** | 17.7*** | 0.6 |
| Tr \times Ti | 14.1*** | 25.8** | 24.4*** | 61.5*** | 11.4*** | 8.7*** | 6.1*** | 4.7*** | 1.6 |
| Ti \times D | 15.6*** | 7.2*** | 34.0*** | 3.1** | 17.0*** | 7.9*** | 19.4*** | 16.5*** | 29.9*** |
| Ti \times Tr \times D | 8.6*** | 14.9*** | 5.3*** | 4.2*** | 4.2*** | 2.3** | 2.4*** | 5.1*** | 0.6 |

As discussed earlier, all three heavy metals measured in the soil solution were strongly related to pH, yet *all* three demonstrated different patterns when investigated by repeated measures ANOVA, indicating that pH alone is not a good predictor of heavy metals, and that each element must be considered individually. Soil solution Cu was significantly affected by treatment, whereas neither Pb or Zn showed a significant effect. Despite this, a significant interaction was observed for treatment×depth, treatment×time and treatment×depth×time for Pb, whereas no significant interactions involving treatment were observed for Zn. At $t = 0$, Zn levels were highest at 30-40 cm, after which, a sharp decrease in concentration was observed with time. This pattern also applied to the two depths above this, but no differences were observed in soil solution Zn concentration at the 0-10 cm depth. Soil solution Pb levels remained below 20 mg l^{-1} for all treatments in the 0-10 cm layer, however, higher levels were observed after 0, 7 and 14 d at 20-30 and 30-40 cm depths respectively for the MSWC treatment. A later spike in Pb concentration was observed at both 20-30 and 30-40 cm depths after 28 d, although this then decreased in line with the MSWC treatment concentration to below 20 mg l^{-1} after 56 d. Copper concentrations were always below 1 mg l^{-1} in the surface layer for all treatments, although higher levels were observed in the control than the treated columns. Below the surface layer, MSWC addition caused an increase in soil solution Cu initially, which subsided to match other treatments after 112 d in all depths apart from 30-40 cm, where concentrations double that in the other treatments were observed.

7.5 Discussion

7.5.1 *Effect of treatments on soil solution chemistry*

It has been demonstrated by several authors that the addition of organic substrates to a contaminated soil significantly raises the pH of the soil, and increases its organic matter and moisture content (Kiikkilä *et al.*, 2001; Pérez-de-Mora *et al.*, 2007a). Organic matter reduces the effects of soil acidity in several ways: increasing the pool of Ca^{2+} ions present in the soil solution thereby displacing Al^{3+} and H^+ ions, and binding Al^{3+} ions tightly to form insoluble Al^{3+} complexes (Brady and Weil, 2002). As sulphide minerals dominate the Parys Mountain geology (Walton and Johnson,

1992), this gives stability to the soil chemistry, reducing the risk of large pH shifts due to rainfall events that may leach sulphides into the soil solution causing increased protonation of the variable-charge surfaces on soil particles, reducing the sorption efficiency due to increased positive charge (Barrow and Whelan, 1998). The presence of a rhizosphere (facilitated by the improved soil characteristics such as compost or lime addition) can alter the pH of a soil (Pérez-de-Mora *et al.*, 2007a), with the initial soil pH contributing to both the direction and magnitude of this shift (Jones *et al.*, 2004).

We observed in our study that Cu, Pb and Zn all decreased in concentration in the soil solution over the duration of the experiment. This method of metal availability assessment was proposed as a good measure of the plant-available metal pool within a soil (Nolan *et al.*, 2005). It is interesting to note that whilst levels remain essentially constant in the top 10 cm of soil, the sub-surface layers exhibited higher concentrations towards the start of the trial, and progressively declining after 112 d. Whilst no treatment effects were observed for Zn, both Cu and Pb were present in higher concentrations in the sub-surface soil solutions treated with MSWC than the other treatments. This is despite the fact out of the three elements studied in the soil solution, only Zn was present in greater total concentrations in the compost than those contributed to the pool by the soil (Table 7.1). Heavy metals are known to bind to organic matter, although binding efficiencies are known to differ between elements (Alloway, 1990). Nwachukwu and Pulford (2008) found in a study investigating the ability of various organic substrates to sorb metals that the order of strength of binding was $Pb > Cu > Zn$, implying that of the three elements, the Zn bound to the MSWC could have been expected to be more loosely bound and easily leached. As there was no treatment effect on the soil solution Zn concentration, it is evident that the Zn present in the MSWC was not easily leachable, and was well bound within the compost matrix. However, it is also evident that none of the amendments reduced the leachability of Zn from the soil. Despite the low levels by the end of the trial, up to 6 mg l^{-1} Zn were recorded in the soil solution at 30-40 cm at the start of the trial. Kiekens (1990) stated that average total Zn concentrations were 50 mg kg^{-1} in an unpolluted soil, leading to soil solution concentrations in the range of $4\text{-}270 \text{ } \mu\text{g l}^{-1}$; however, in highly acidic soils, concentrations in excess of 7 mg l^{-1} have

been observed due to the solubility increase of Zn with acidity. In addition, ZnSO_4 is highly soluble, and given the pyritic nature of the parent material at Parys Mountain (Walton and Johnson, 1992), zinc-sulphur compounds are likely to be dominant. We propose that coupled with the antagonistic effect of Cu and Pb competing for sorption sites (Nwachukwu and Pulford, 2008), that this explains why the addition of compost had less effect on Zn than Cu and Pb at the surface layer.

The absence of a peak at the start of the trial at the surface layer for the three heavy metals, whilst higher levels were observed further down the profile can be explained by rapid leaching of the extremely labile pool of metals down the column as the soil equilibrated. As we observed the Rhizon[®] samplers taking several hours to extract soil solution, preferential flow channels within the columns may have allowed the leached metals to pass through the surface layer before sufficient soil solution could be collected. The high soluble salt content of the MSWC allows a general insight into the dynamics of leachable compounds from the compost, with the peak at 0 d at the surface layer, 7 d at 10-20 cm, 14 d at 20-30 cm and 56 d at 30-40 cm, illustrating the leaching of compounds from the amendments over time. Whilst both Cu and Pb are elevated in the MSWC-treated columns at a lower depth, it is difficult to interpret whether these metals can be directly attributed to those borne by the compost or as a result of changes in pH and chelation by soluble organic compounds. A study by van Herwijnen (2007b) also ascribed increases in leachability of heavy metals under some types of composts to a mixture of pH change and possible increases in the formation of soluble metal chelates due to organic matter leaching from the compost. Kaschl *et al.* (2002) studied the leaching of trace metals from a compost, and concluded that the majority of leached fractions were due to organo-metallic complexes, and that these were easily leached below the rooting zone, however in heavier soils (such as the clay-loam in our study), leaching was noticeably reduced, and they concluded that even under simulated storm events, groundwater was not at risk. In our study, however, Pb and Cu in soil solution at 20-30 cm and 30-40 cm were negatively correlated with DOC, but EC was found to increase at lower depths over time. Increases in salinity have been shown to increase the availability of heavy metals due to displacement on exchange sites, solubilisation of OM and formation of soluble metal-chloride compounds (Wahla and Kirkham, 2008); we propose that the leaching

of salts from the MSWC resulted in the increases in soil solution Cu and Pb at lower depths for this treatment. Several studies (Pérez-de-Mora *et al.*, 2007b; van Herwijnen, 2007ab; Tandy *et al.*, in press) have found contrasting effects of the addition of organic compounds on the availability of heavy metals, demonstrating not only reductions but also increases in available fractions of metals to the addition of organic matter and pH change. It is therefore evident that whilst overall, addition of organic matter can be expected to increase the pH of acidic soils and decrease metal leaching, caution must be taken to ensure that any initial burst such as that observed in our study does not have a detrimental effect on sub-surface soil and water quality (Blake *et al.*, 2007).

7.5.2 Plant growth and metal uptake

The increase in both above- and below-ground biomass over the control treatment was expected in line with many similar studies on the effects of organic matter addition to acidic, heavy metal contaminated soil, demonstrating the ability of organic materials to alleviate phytotoxicity of such soils, and improve the nutrient and physical structure of the material (Pérez-de-Mora *et al.*, 2006; van Herwijnen *et al.*, 2007b). The growth of roots from both the compost-treated columns below the surface layer was encouraging, indicating that the application of composts can improve sub-surface layers sufficiently to allow root growth, further stabilising the soil matrix and leading to successful long-term restoration (Bradshaw, 1997).

The phytoavailability and therefore plant uptake of heavy metals from the soil is governed by many interacting factors (Alloway, 1990), and although the nine elements investigated were found in varying quantities in the soil and organic composts, these trends did not necessarily predict plant tissue concentration. For the most part, however, our results agreed with those in the literature (Pérez-de-Mora *et al.*, 2006; Tandy *et al.*, in press) that compost addition decreases plant uptake of heavy metals. Whilst the extremely high levels of total Pb within the soil led to tissue concentrations in excess of 40 g kg⁻¹ Pb in the control treatment, the reduction in uptake when 40% of the soil was substituted for either compost is far greater than the reduction that could be expected from the substitution alone, especially when

roots were observed below the 10 cm treated layer. This reduction in phytoavailability can be ascribed to direct interactions between increases in soil pH and organic matter content (van Herwijnen, 2007b), and indirect interactions between increases in soil fertility, causing nutrient ions to successfully out-compete metal ions for uptake transporters (Tandy *et al.*, in press). However, as we described above, there appears to be some discrepancy between the highly labile pool of heavy metals that was leached down the columns within the first few days of the trial, and plant uptake. This flush will have been removed below the reach of the grass roots (Fig. 7.1) before sufficient growth had occurred to take up any significant amount of metals.

Of the other major polluting elements studied, Cu and As were significantly reduced in plant tissue concentration for all treatments, with the composts giving greatest reductions. Both As and Cu are strongly bound by organic matter, and therefore largely removed from the phytoavailable pool (O'Neill, 1990; Baker, 1990; Pérez-de-Mora *et al.*, 2006; Krysiak and Karczewska, 2007). A significant reduction in tissue Zn concentration relative to the control was only observed under the GWC treatment, with both the inorganic and MSWC treatments having no significant effect. Whilst the increase in pH and OM content may have reduced Zn availability (Pérez-de-Mora *et al.*, 2006), the high level of Zn present as a contaminant of the MSWC may have negated any reduction in soil-borne Zn availability, with the same applying for Cr and Ni. Molybdenum exists as an anion, and as such increases in solubility with increased pH (Jones *et al.*, 1990), therefore we attribute the sharp increase in tissue Mo concentration to the increased pH as a result of MSWC addition, and the fact that MSWC also contained 9.4 mg kg^{-1} Mo compared to no Mo addition in either the inorganic or GWC treatments.

7.5.3 Conclusions

We have demonstrated that the addition of composted wastes to an acidic, heavy metal-contaminated soil greatly increases soil pH and plant growth, whilst greatly reducing the uptake of key pollutants present in the soil. Despite the high Zn content, there was no increase in uptake of Zn from the MSWC-treated columns

relative to the control treatment, although levels were significantly elevated compared to the GWC-treated columns. Soil solution levels of heavy metals showed a high initial pulse of soluble metals through the column, with a time lag effect observed for Pb and Cu with depth in the MSWC treatment. Whilst no correlation was observed with DOC, we conclude that this increased leaching was a result of leached salts from the MSWC competing with the heavy metals for exchange sites lower down the soil profile. Whilst below the rooting depth, this has potential implications for groundwater quality and wider effects on a catchment scale (Blake *et al.*, 2007) – an issue not well studied in biostabilisation trials.

Another potential problem with the addition of organic materials to stabilise *in situ* heavy metal contamination is the risk of future releases of pollutants from the site as the organic matter (to which the metals predominantly bind) is degraded. Frequent reapplication would solve this, and also provide a useful sink for organic wastes with a view to both carbon storage and waste management issues. However, the frequent reapplication of contaminated composts could increase the available metal loadings over time. Further work therefore needs to be carried out to assess the bioavailability of amendment-borne contamination after its incorporation into soils. We conclude that in the short term, the addition of compost significantly increased yield and reduced metal availability, and that the MSWC treatment performed well in terms of plant growth and metal uptake reduction.

7.6 References

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CHAPTER 8: MICROBIAL DIVERSITY AND ACTIVITY ARE INCREASED BY COMPOST AMENDMENT OF METAL CONTAMINATED SOIL

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8.1 Abstract

Unlike organic pollutants, heavy metals cannot be degraded and can constitute a persistent environmental hazard. Here we investigated the success of different remediation strategies on promoting microbial diversity and function with depth in an acidic soil heavily contaminated with Cu, Pb and Zn. Remediation involved the incorporation of either a high or low quality compost, or inorganic fertiliser into the topsoil and the monitoring of microbial activity and diversity with soil depth over a 4 month period. While changes in topsoil microbial activity were expected, the possible effects on the sub-surface microbial community due to downwards movement of metals, nutrients and / or soluble organic matter has not previously been examined. The results showed that both compost additions, especially the low quality compost, resulted in significantly increased bacterial and fungal diversity (as assessed by TRFLP) and activity compared to the inorganic and control treatments in the topsoil. Although phospholipid fatty acid profiling (PLFA) indicated that compost

addition had promoted enhanced microbial diversity in the subsoil, no concomitant increase in subsoil microbial activity was observed suggesting that amelioration of the heavy metals remained localised in the topsoil. We conclude that although composts can successfully immobilise heavy metals and promote ecosystem diversity / function, surface incorporation has little remedial effect below the surface layer.

8.2 Introduction

Mitigating against anthropogenic pollution of soils is of global concern for the preservation of ecosystem functioning (Dawson *et al.*, 2006). Heavy metals have been released into the soil as a result of mining activities since before Roman times, and they constitute a particularly difficult hazard due to their long-term toxic effects (Alloway, 1990). Unlike organic pollutants they cannot be degraded, and therefore must be either physically removed (e.g., by phytoremediation; Tandy *et al.*, 2006), or stabilised *in situ* (Pérez-de-Mora *et al.*, 2006). It has long been established that heavy metals have a deleterious effect on the soil microbial community (Brookes and McGrath, 1984; Bardgett and Saggar, 1994). Several studies have demonstrated that addition of inorganic and organic amendments such as composts to contaminated soils can improve their chemical properties, as well as inducing an increase in microbial biomass, functionality and diversity (Chander and Joergensen, 2002; Pérez-de-Mora *et al.*, 2006).

There is an increasing need to develop sustainable end-uses for organic based waste products such as those produced by Mechanical Biological Treatment (MBT) of municipal waste (Binner and Zach, 1999). Given the progressive decline in soil organic matter (Bellamy *et al.*, 2005), it is preferable to find alternative land-based disposal routes for this mixed waste 'compost'. However, many MBT-derived wastes often contain potentially toxic elements (PTEs) making disposal to agricultural land problematic. One potential disposal route for mixed waste composts is in the remediation of heavy metal contaminated sites where an additional burden of inorganic PTEs is of less concern provided that the PTEs are added in non-labile forms.

As compost contains a wealth of organic substrates, in addition to its intrinsic microbial community, it is not surprising that its addition to soil induce changes in microbial community structure (Pérez-Piqueres *et al.*, 2006). Further, the microbial

community present within compost could potentially improve ecological function by amelioration of the substrate and provision of services which were previously not present (Chander and Joergensen, 2002). In addition, organic biowastes may also relieve contamination by binding PTEs, rendering them non-toxic. Ensuring the continued long-term success of passive remediation treatments is one of the big challenges that faces industry, as failure of remediation schemes is not a socially or environmentally acceptable outcome (Kalin *et al.*, 2006). One critical aspect of this is whether surface remediation treatments can exert a positive remediative effect on the underlying soil (e.g. through downward migration of microorganisms, complexing ligands, alkalinising agents etc). We aim to directly test this by comparing the effectiveness of conventional inorganic remediation technologies for heavy metals (i.e. lime application) with two alternative organic amendment strategies (composts). A key variable to be measured will be by microbial community structure and function.

Several PCR-based techniques are now widely used to assess soil microbial diversity, including Denaturing Gradient Gel Electrophoresis (DGGE) and Terminal Restriction Fragment Length Polymorphism (TRFLP). TRFLP in particular has proven to be highly robust and reproducible (Osborn *et al.*, 2000). One advantage of such fingerprinting techniques is that the data may be suitable for interpretation using traditional ecological diversity indices such as Shannon-*H* for both bacterial and fungal data (Brodie *et al.*, 2003; Hill *et al.*, 2003; Fierer and Jackson 2006). However, such interpretations must be conducted cautiously since resolved peaks in TRFLP analysis do not necessarily correspond to microbial taxa (e.g., some peaks may be shared by several species) whilst other unquantifiable biases may also be present (e.g., from DNA extraction or PCR amplification; Avis *et al.*, 2006; Blackwood *et al.*, 2007). Hill *et al.* (2003) conclude however, that when used correctly, Shannon-*H* is a useful means of presenting in an interpretable form the multivariate data obtained by TRFLP.

Alongside molecular fingerprinting techniques, the chemical composition of phospholipid fatty acids (PLFAs) within microbial cell membranes can also be used to quantitatively estimate bacterial diversity (Frostegård and Bååth, 1996). Whilst this technique provides a lower level of taxonomic resolution than DNA-based approaches, it is highly useful when a broad sweep of microbial community structure is required (Drenovsky *et al.*, 2008). However, PLFA analysis is quantitative and

independent of the biases that may affect TRFLP, and can thus provide useful ratios such as stress indicators (e.g. trans:cis ratios of monoenoic PLFAs) or correlated directly with environmental data (Leckie, 2005). These analyses become more powerful if combined with long-established biomass and functional assays.

Preliminary work by Bishop *et al.* (2006) demonstrated that organic wastes differ in their effects on the leachability of particular metals, and we hypothesise that soil amendments will alter microbial activity not only at the soil surface but also deeper within the soil.

The purpose of this study was to combine a range of experimental approaches to investigate the surface and sub-surface effects of contrasting remediation strategies on the microbial community of an acidic soil heavily contaminated with Cu, Pb and Zn.

8.3 Experimental procedures

8.3.1 Substrate characteristics

Top soil (ca. 400 kg) was collected from the remains of an old (> 50 years old) mine spoil tip at Parys Mountain, Anglesey, North Wales (Anglesey Mining Ltd., Parys Mountain, Amlwch, UK; 53°23'22"N, 4°20'54"W), homogenised and then sieved to pass 1 cm before use. Parys Mountain was extensively mined for copper ore from the 18th to the 20th centuries and covers an area of 200 ha, much of the site being covered with heavy metal contaminated mine spoil, dominated by sulphide minerals including pyrite, chalcopyrite, sphalerite and galena, with lesser amounts of other minerals (Walton and Johnson, 1992).

The municipal solid waste-derived compost (MSWC; < 38 mm fraction of a mixed waste pulverisation plant output) was produced over a five month period at Ffridd Rasus Landfill Site, Harlech, North Wales (52°52'59"N, 4°06'43"W) using a commercially available CT-5[®] and EcoPOD[®] in-vessel composting system (ORM Ltd, Canterbury, Kent, UK and Ag-Bag International Ltd, Warrenton, OR, USA), as described in Roberts *et al.* (2007). The MSW compost had the following characteristics: pH of 7.28 ± 0.03 , EC of 3.6 ± 0.8 mS cm⁻¹, and organic matter of $42.2 \pm 3.7\%$. The green waste derived-compost (GWC) was obtained from an open

windrow, commercial green waste composting facility near Aberystwyth, mid Wales (49°46'28"N, 7°32'57"W), and had the following characteristics: pH of 8.11 ± 0.18 , EC of $0.7 \pm 0.1 \text{ mS cm}^{-1}$ and organic matter of $25.2 \pm 2.9\%$. The green waste feedstocks comprised predominantly municipal hedge trimmings, weeds and grass cuttings. For the inorganic remediation treatment, analytical grade CaCO_3 , NH_4NO_3 , P_2O_5 and KCl (VWR, Lutterworth, Leicestershire, UK) were mixed with the top 10 cm soil layer at rates equivalent to $70 \text{ g CaCO}_3 \text{ m}^{-2}$, 8 g N m^{-2} , 2 g P m^{-2} and 4 g K m^{-2} to reflect standard remediation practices, and soil lime requirement was assessed following Sims (1996). In the two compost remediation treatments, each compost was added at a rate of 40% v/v to the top 10 cm of the soil. The control treatment received no amendment.

8.3.2 Experimental design

Six replicates of each treatment giving a total of 24 soil columns were constructed using 16 cm diameter plastic pipe 45 cm in length. The bottoms of these columns were closed using plastic blanking plates, which were drilled to allow drainage. Sieved soil was homogenised using a cement mixer, before being packed untreated into the columns to 30 cm depth, with the remaining 10 cm being hand-mixed with the appropriate treatment as described above. Each column was placed in an individual saucer on a 3 cm off-cut of pipe to collect leachate whilst ensuring that the column did not come into contact with standing water. The columns were arranged in a randomised block design in a climate-controlled greenhouse with 16 h photoperiod, day/night rhythm of 20/18°C and augmented with 400 W Sun SON-T horticultural lamps. After amendment of the topsoil, the cores were allowed to equilibrate for 48 h before *Agrostis capillaris* L. (Common bent-grass) was sown in all columns at a density of 4 g seed m^{-2} . Soils were gravimetrically maintained at 70% field capacity by watering three times weekly using drip-feed containers suspended above the columns with artificial rainwater representing that of North Wales (values given in Stevens *et al.*, 1997). The experiment was ended and aboveground vegetation harvested after 112 d.

8.3.3 Sampling and analysis

Standard chemical analyses were carried out on soil samples taken from the columns after 112 d. Soil characterisation included moisture content determined by drying samples at 80°C for 24 h and organic matter content determined as loss-on-ignition at 450°C overnight. Soil solution was collected from each column overnight (day 112) using pre-installed 10 cm Rhizon-MOM® *in situ* soil solution samplers (Rhizosphere Research Products, Wageningen, The Netherlands) (Vulcan *et al.*, 2000; Tiensing *et al.*, 2001). pH (Hanna Instruments pH 209 pH meter) and electrical conductivity (EC) (Jenway 4010 EC meter) were determined in the soil solution. Nitrate was determined colourimetrically by the Cu-Zn-hydrazine reduction method of Downes (1978) and ammonium by the salicylate-hypochlorite procedure of Mulvaney (1996). Heavy metals were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a Fissions PlasmaQUAD II Turbo ICP-MS. Dissolved organic carbon (DOC) in soil solution was analysed using a Shimadzu TOCV-TN analyser (Shimadzu Corp., Kyoto, Japan).

8.3.4 Microbial analyses

Soil basal respiration was measured on 30 g fresh samples for 24 h at 20°C using an automated multi-channel infra-red gas analyser (PP-systems Ltd, Hitchin, UK). Microbial C was estimated using the chloroform fumigation-extraction procedure of Vance *et al.* (1987), analysed using a Shimadzu TOCV-TN analyser. Glucose and amino acid mineralisation rates were assessed using ¹⁴C-uniformly labelled glucose and amino acids following Jones (1999). Briefly, 5 g fresh soil was weighed into a gas-tight container, and 500 µl of either 50 mM glucose or 10 mM amino acid mixture (3.7 kBq ml⁻¹) added to the soil. A 4 ml scintillation vial containing 1 ml 1 M NaOH trap was then placed inside the container and the container hermetically sealed for 1 h, after which, the NaOH trap was recovered. The ¹⁴CO₂ trapped in the NaOH was determined by liquid scintillation counting with Scintisafe3 scintillation cocktail (Fisher Scientific, Loughborough, UK) and a MicroBeta TriLux 1450 liquid scintillation counter (Perkin-Elmer, Waltham, MA, USA). Lipids were extracted from 15 g soil samples at all depths and analysed using the method of Clegg *et al.* (2003) and Bardgett *et al.* (1996),

adapted from White *et al.* (1979) and Bligh and Dyer (1959). Individual PLFAs were quantified using an Agilent Technologies 6890N Network gas chromatograph equipped with a 30 m DB-225 methylpolysiloxane column (0.25 mm i.d.), a 5973 Network Mass Selective Detector and a MSD ChemStation D.01.02.16 data analysis suite (Agilent Technologies UK Ltd, Stockport, UK). The 26 individual fatty acids were named according to the nomenclature summarised in Leckie (2005).

DNA was extracted from 0.25 g of soil from the top layer (0-10 cm) of the columns using the PowerSoil DNA extraction kit (MoBio Laboratories, Inc., Solana, CA, USA), as directed by the manufacturer. PCR amplification of the fungal internal transcribed spacer (ITS) region of the rRNA locus (ca. 600 bp amplicon) was conducted using primers Cy5-ITS1F (CTTGGTCATTTAGAGGAAGTAA; 5' labelled with fluorophore Cy-5) and ITS4 (TTCTTCGCTTATTGATATGC), whilst the bacterial 16S rRNA locus (ca. 1300 bp) was amplified using primers Cy5-27F (AGAGTTTGATCCTGGCTCAG; 5' labelled with fluorophore Cy-5) and 1389R (ACGGGCGGTGTGTACAAG), PCR (25 μ l) reactions contained 1 μ l DNA, 2.75 mM MgCl₂, 32 μ l BSA, 200 nM of each dNTP, 0.25 nM of each primer, 1 \times GoTaq flexi (Green) buffer and GoTaq DNA polymerase according to the manufacturer's instructions (Promega Inc., Madison, WI, USA). Amplification conditions were as follows: 10 min at 94°C, then 45 cycles 94°C, 51°C and 72°C (1 min each), followed by 10 min at 72°C. For each sample, four replicate PCR reactions were conducted and then pooled. Following agarose gel electrophoresis to confirm the presence of the DNA fragments of the expected size, PCR products were purified using a Qiagen MinElute kit (Qiagen KK., Tokyo, Japan) and digested with five units of HaeIII (Promega Inc.) for 5 h at 37°C. Fluorescently labelled TRFs were separated and quantified using a Beckman-Coulter CEQ-8000 capillary electrophoresis system. Fragments were identified using a Local Southern size calling algorithm with a slope threshold of 10 and relative peak height threshold of 5% for bacteria and 10% for fungi before binning peaks between 100 and 600 RFU within 1.00 bp. Of the 48 samples from both the bacteria and fungi datasets, 10 failed the software's data quality test and were omitted from further analysis. In addition to this, a further extreme outlier was manually removed from the bacteria dataset after identification in exploratory CA analysis.

8.3.5 Statistical analyses

All data were initially collated in Microsoft Excel 2003 (Microsoft Corp., Redmond, WA). Data was normalised against average peak area, and then Correspondence Analysis (CA), Canonical Correspondence Analysis (CCA) and Shannon-*H* diversity indices for PLFA and TRFLP data were computed using MVSP 3.1 (Kovach Computing Services, Anglesey, UK). SPSS v14.0 (SPSS Inc., Chicago, IL) was used to conduct ANOVA analyses on diversity data and Principal Components Analysis (PCA; using varimax ordination after standardisation) on the environmental data. With the exception of the CCA and PCA data, all graphs were produced using SigmaPlot v10.0 (Systat Software Inc., San Jose, CA).

8.4 Results

8.4.1 Soil and soil solution chemical properties

Seeds sown to assess soil phytotoxicity were successfully germinated in all treatments; however plant growth became extremely stunted in the control treatment, whilst greatest growth was observed in the compost-treated columns (Table 8.1). There was a slight moisture gradient within the soil columns from the top to the bottom soil layers in the control and inorganic treatments, whereas both compost-treated soils retained significantly more moisture in the treated 0-10 cm layer than the underlying soil layers (a decrease of 15% and 25% in the municipal solid waste-derived compost (MSWC) and the green waste-derived compost (GWC) treated columns respectively; Table 8.1). Not surprisingly, organic matter was doubled in the soil receiving compost. Whilst the GWC treatment significantly increased the pH of the surface layer by two pH units, only the MSWC treatment significantly affected the pH in the underlying soil layers. At harvest it was apparent that the added lime in the surface soil had become completely neutralised in the inorganic treatment with the topsoil becoming even more acidic than the control treatment. Electrical conductivity (EC) generally increased with depth, and this was particularly evident for the MSWC treatment, with an increase of 122% over the surface layer ($P < 0.05$). This was due to the high intrinsic EC of the MSWC itself.

Table 8.1: Effect of an inorganic (lime and fertilizer; Inorganic) or compost (GWC or MSWC) remediation strategy on grass growth and below-ground soil properties versus depth after 4 months of treatment. All values represent mean \pm SEM.

| | Depth (cm) | Above ground biomass (g column ⁻¹) | Zn (mg l ⁻¹) | Pb (mg l ⁻¹) | Cu (mg l ⁻¹) | NH ₄ ⁺ (mg l ⁻¹) | NO ₃ ⁻ (mg l ⁻¹) | DOC (mg l ⁻¹) | Electrical conductivity (μS cm ⁻¹) | pH | Organic matter (%) | Moisture content (%) |
|-----------|------------|--|--------------------------|--------------------------|--------------------------|--|--|---------------------------|--|-----------------|--------------------|----------------------|
| Control | 10 | 1.58 \pm 0.11 | 0.06 \pm 0.01 | 6.46 \pm 0.29 | 0.35 \pm 0.02 | 0.10 \pm 0.02 | 0.45 \pm 0.07 | 2.8 \pm 0.2 | 164 \pm 10 | 5.55 \pm 0.03 | 2.9 \pm 0.1 | 19.7 \pm 0.4 |
| | 20 | | 0.08 \pm 0.01 | 7.21 \pm 0.22 | 0.53 \pm 0.05 | 0.10 \pm 0.02 | 0.53 \pm 0.05 | 2.7 \pm 0.2 | 187 \pm 10 | 3.44 \pm 0.03 | 2.9 \pm 0.1 | 20.2 \pm 0.2 |
| | 30 | | 0.13 \pm 0.01 | 7.37 \pm 0.22 | 0.55 \pm 0.01 | 0.04 \pm 0.01 | 0.63 \pm 0.03 | 3.1 \pm 0.2 | 217 \pm 8 | 3.43 \pm 0.03 | 3.0 \pm 0.1 | 21.8 \pm 0.2 |
| | 40 | | 0.21 \pm 0.02 | 7.61 \pm 0.28 | 0.62 \pm 0.00 | 0.03 \pm 0.01 | 0.98 \pm 0.04 | 3.1 \pm 0.1 | 246 \pm 5 | 3.39 \pm 0.05 | 2.8 \pm 0.1 | 24.8 \pm 0.4 |
| Inorganic | 10 | 3.42 \pm 0.40 | 0.03 \pm 0.01 | 2.27 \pm 0.48 | 0.08 \pm 0.01 | 0.10 \pm 0.04 | 0.22 \pm 0.01 | 3.4 \pm 0.4 | 196 \pm 21 | 4.62 \pm 0.39 | 2.9 \pm 0.1 | 20.2 \pm 0.2 |
| | 20 | | 0.07 \pm 0.01 | 5.25 \pm 0.29 | 0.29 \pm 0.02 | 0.10 \pm 0.03 | 0.61 \pm 0.05 | 2.8 \pm 0.2 | 138 \pm 8 | 3.75 \pm 0.04 | 2.7 \pm 0.1 | 19.4 \pm 0.6 |
| | 30 | | 0.11 \pm 0.03 | 6.01 \pm 0.93 | 0.48 \pm 0.12 | 0.05 \pm 0.01 | 1.02 \pm 0.19 | 2.6 \pm 0.2 | 166 \pm 27 | 3.68 \pm 0.16 | 2.8 \pm 0.1 | 21.9 \pm 0.3 |
| | 40 | | 0.21 \pm 0.02 | 7.60 \pm 0.14 | 0.75 \pm 0.02 | 0.16 \pm 0.05 | 4.12 \pm 0.47 | 3.5 \pm 0.5 | 254 \pm 7 | 3.43 \pm 0.01 | 2.9 \pm 0.1 | 23.7 \pm 0.3 |
| GWC | 10 | 7.89 \pm 0.34 | 0.04 \pm 0.01 | 0.09 \pm 0.01 | 0.05 \pm 0.01 | 0.05 \pm 0.03 | 0.11 \pm 0.02 | 28.0 \pm 4.6 | 85 \pm 16 | 5.99 \pm 0.14 | 7.7 \pm 1.0 | 27.8 \pm 1.4 |
| | 20 | | 0.07 \pm 0.01 | 4.40 \pm 0.35 | 0.24 \pm 0.05 | 0.04 \pm 0.01 | 0.05 \pm 0.02 | 5.8 \pm 0.2 | 240 \pm 26 | 3.80 \pm 0.07 | 3.0 \pm 0.1 | 20.8 \pm 0.2 |
| | 30 | | 0.13 \pm 0.01 | 6.03 \pm 0.24 | 0.58 \pm 0.05 | 0.05 \pm 0.02 | 0.40 \pm 0.10 | 5.6 \pm 0.3 | 256 \pm 17 | 3.44 \pm 0.03 | 2.9 \pm 0.2 | 22.3 \pm 0.2 |
| | 40 | | 0.21 \pm 0.01 | 7.64 \pm 0.17 | 0.75 \pm 0.06 | 0.24 \pm 0.11 | 3.72 \pm 1.99 | 6.1 \pm 1.4 | 287 \pm 15 | 3.41 \pm 0.02 | 2.9 \pm 0.2 | 23.5 \pm 0.3 |
| MSWC | 10 | 5.36 \pm 0.28 | 0.03 \pm 0.01 | BDL* | 0.02 \pm 0.01 | 0.04 \pm 0.02 | 0.08 \pm 0.02 | 10.3 \pm 1.3 | 324 \pm 42 | 6.79 \pm 0.28 | 6.6 \pm 0.8 | 24.1 \pm 1.4 |
| | 20 | | 0.04 \pm 0.01 | 2.51 \pm 0.43 | 0.09 \pm 0.01 | 0.06 \pm 0.02 | 0.06 \pm 0.01 | 7.6 \pm 2.0 | 352 \pm 46 | 5.05 \pm 0.49 | 3.5 \pm 0.1 | 20.4 \pm 0.4 |
| | 30 | | 0.08 \pm 0.01 | 3.96 \pm 0.26 | 0.58 \pm 0.02 | 0.01 \pm 0.01 | 0.06 \pm 0.02 | 6.2 \pm 0.7 | 561 \pm 40 | 3.37 \pm 0.02 | 3.3 \pm 0.1 | 21.1 \pm 0.2 |
| | 40 | | 0.23 \pm 0.02 | 3.98 \pm 0.12 | 1.51 \pm 0.12 | 0.13 \pm 0.05 | 0.59 \pm 0.14 | 5.4 \pm 0.3 | 720 \pm 40 | 3.19 \pm 0.01 | 3.7 \pm 0.5 | 23.6 \pm 0.4 |

* = Below limit of detection

The greatest increase in dissolved organic carbon (DOC) was found in the GWC-amended columns, with a 10-fold increase over the control treatment in the surface layer ($P < 0.05$), whilst MSWC gave a 3-fold increase ($P < 0.05$). An increase in DOC levels was also apparent at depths of 20-40 cm for the two compost treatments ($P < 0.05$), whereas DOC concentrations in the inorganic treatment was similar to the control at all depths ($P > 0.05$). Levels of ammonium were very low for all treatments ($< 0.3 \text{ mg l}^{-1}$), whilst nitrate levels at 30-40 cm depth were elevated relative to the control in both the inorganic and the GWC treated columns ($P < 0.05$). Nitrate levels in the MSWC columns were significantly lower than the control treatment at all depths ($P < 0.05$).

Cu, Pb and Zn soil showed an increase in solution concentration with depth for all treatments ($P < 0.05$), however, the depth gradient was lowest in the control treatment, whilst the MSWC treatment at 30-40 cm showed a 140% increase in Cu over the control at the same depth. Pb concentrations were significantly reduced by surface MSWC application at all depths ($P < 0.05$), with concentrations being below limits of detection in the 0-10 cm layer. GWC and the inorganic treatment also greatly reduced Pb concentrations relative to the control though this effect was less pronounced in the two lowest soil layers. Zn concentrations showed a 5 to 10-fold increase down the columns for all treatments (30-40 cm compared to 0-10 cm) though levels were below 0.3 mg l^{-1} in all cases.

8.4.2 Soil microbial activity

Microbial biomass C was increased in the surface layers in both compost treatments relative to the control ($P < 0.05$; Fig. 8.1), however, this was not mirrored at any layer below the immediate surface. Similarly, basal respiration was > 10 -fold higher in the upper 10 cm of the compost treated columns relative to the control, though much lower levels of microbial activity ($< 0.2 \text{ } \mu\text{g CO}_2 \text{ g}^{-1} \text{ h}^{-1}$) were found between 20 and 40 cm in all treatments. Basal respiration in the surface layer of the inorganic treatment was intermediate (44% of that observed in the GWC treated column). In the surface soil layers, glucose and amino acid mineralisation rates were similarly elevated in the GWC and MSWC treatments in comparison to the

unamended control soil. In contrast, inorganic amendment failed to stimulate an enhanced turnover of glucose and amino acids relative to the control ($P > 0.05$). However, mineralisation rates were lower in MSWC than GWC (33% and 25% for glucose and amino acids respectively).

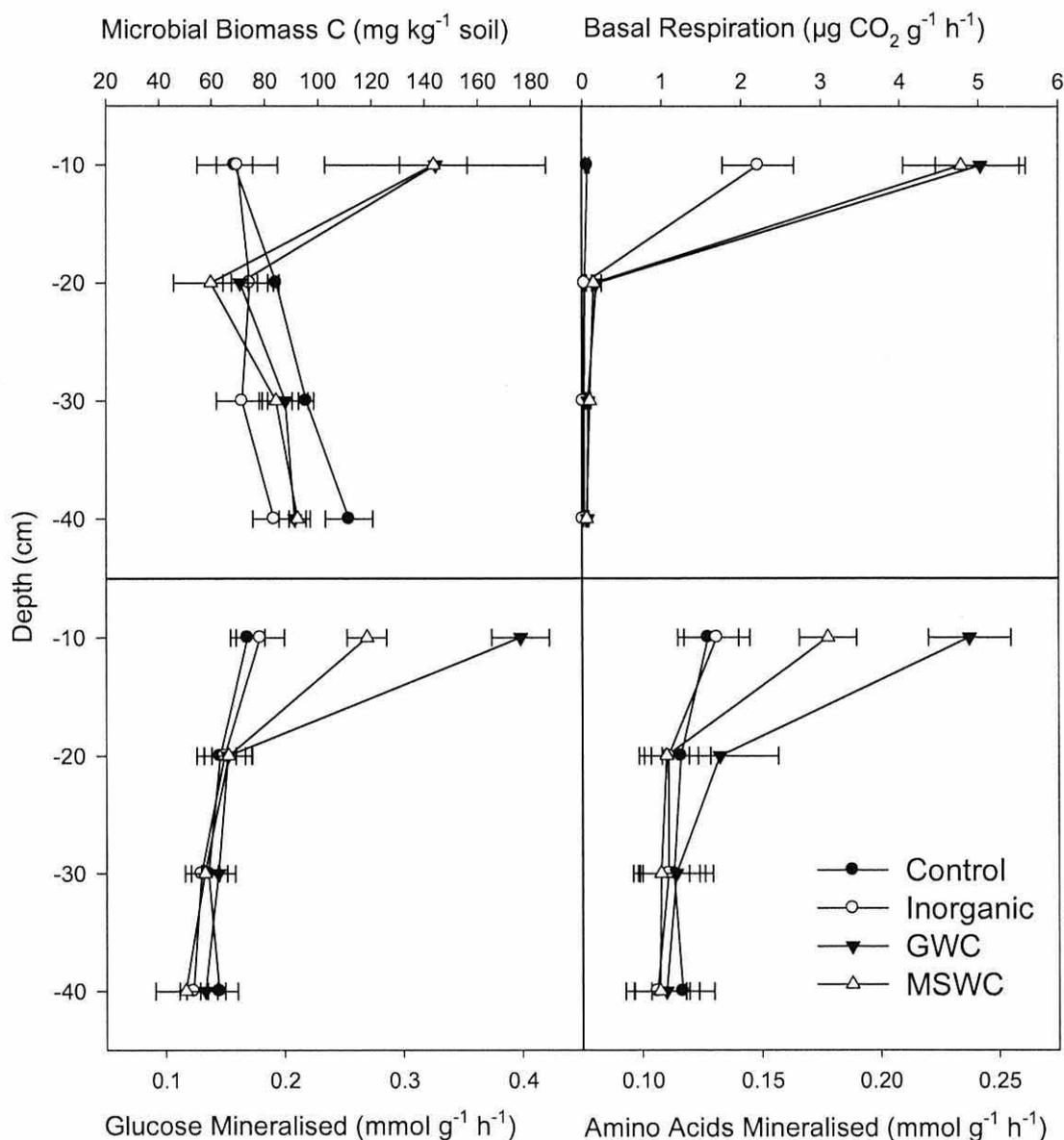


Figure 8.1: Influence of remediation strategy and soil depth on (a) soil microbial biomass-C, (b) basal soil respiration, and (c) ¹⁴C-glucose mineralisation, and (d) ¹⁴C-amino acid mineralisation in samples taken after 112 days growth. GWC = green waste compost, MSWC = MSW compost. Values represent means ± SEM.

8.4.3 Correlations between biological activity and chemical properties

Pearson's correlation coefficients were calculated between biological and chemical variables, and are presented in Table 8.2. pH was a dominant predictor, giving significant correlations between all variables, with EC, Cu, Pb and Zn being significantly negatively correlated ($P < 0.05$), with all other variables being positively correlated ($P < 0.01$). Pore water concentrations of the heavy metals were also strongly negatively correlated with both basal and substrate-induced respiration rates, indicating a strong negative effect ($P < 0.01$) on microbial activity. However, only Pb was negatively associated with microbial biomass carbon ($P < 0.05$).

Table 8.2: Pearson's correlation coefficients between chemical and biological variables across all remediation treatments after 4 months.

| | EC | DOC | Cu | Pb | Zn | MC | OM | Resp | Gluc | AA | Bio-C |
|------|---------|---------|----------|----------|----------|---------|----------|----------|----------|----------|---------|
| pH | -0.213* | 0.578** | -0.605** | -0.764** | -0.522** | 0.308** | 0.690** | 0.812** | 0.655** | 0.538** | 0.366** |
| EC | | -0.144 | 0.610** | -0.1 | 0.377** | 0.029 | -0.051 | -0.2 | -0.327** | -0.247** | -0.02 |
| DOC | | | -0.286** | -0.597** | -0.220* | 0.604** | 0.786** | 0.713** | 0.718** | 0.605** | 0.218* |
| Cu | | | | 0.494* | 0.746** | 0.122 | -0.298** | -0.475** | -0.447** | -0.354** | -0.037 |
| Pb | | | | | 0.562** | -0.205* | -0.657** | -0.722** | -0.592** | -0.495** | -0.211* |
| Zn | | | | | | 0.228* | -0.293** | -0.417* | -0.383** | -0.288** | 0.077 |
| MC | | | | | | | 0.697** | 0.522** | 0.473** | 0.412** | 0.422** |
| OM | | | | | | | | 0.834** | 0.715** | 0.583** | 0.489** |
| Resp | | | | | | | | | 0.766** | 0.617** | 0.482** |
| G | | | | | | | | | | 0.875** | 0.392** |
| AA | | | | | | | | | | | 0.287** |

* = $P < 0.05$, ** = $P < 0.01$,

EC = electrical conductivity, DOC = dissolved organic carbon, MC = moisture content, OM = organic matter, Resp = basal respiration, Gluc = glucose-induced respiration, AA = amino acid-induced respiration, BioC = microbial biomass C

8.4.4 TRFLP analysis of bacterial and fungal communities

Shannon- H diversity indices (Brodie *et al.*, 2003; Hill *et al.*, 2003; Fierer and Jackson, 2006) were derived from TRFLP data for bacterial and fungal communities (Table 8.3). Significant differences ($P < 0.05$) in the number of TRF peaks and Shannon- H indices were observed between the MSWC and control treatments for both bacterial and fungal diversity, though the GWC compost only showed a significant difference for fungal diversity. Twice as many bacterial TRFLP peaks were observed in the MSWC relative to the control, and a 3-fold increase was observed for fungal TRFs.

Table 8.3: Effect of inorganic and organic (GWC and MSWC) based remediation treatment on the mean total TRFs and Shannon-*H* diversity indices from fungal and bacterial TRFLP data (mean \pm SEM). Different letters denote significant differences ($P < 0.05$) within each table column.

| Treatment | Bacteria | | Fungi | |
|-----------|------------------------------|-------------------------------|------------------------------|------------------------------|
| | Total TRFs | Shannon- <i>H</i> | Total TRFs | Shannon- <i>H</i> |
| Control | 22.0 \pm 3.1 ^a | 2.59 \pm 0.17 ^a | 13.2 \pm 1.4 ^{ab} | 2.16 \pm 0.09 ^a |
| Inorganic | 22.6 \pm 4.3 ^{ab} | 2.68 \pm 0.18 ^a | 11.6 \pm 1.6 ^a | 2.04 \pm 0.15 ^a |
| GWC | 28.2 \pm 5.3 ^{ab} | 3.13 \pm 0.23 ^{ab} | 33.0 \pm 6.1 ^{bc} | 3.24 \pm 0.25 ^b |
| MSWC | 45.5 \pm 7.4 ^b | 3.61 \pm 0.15 ^b | 39.3 \pm 8.8 ^c | 3.41 \pm 0.27 ^b |

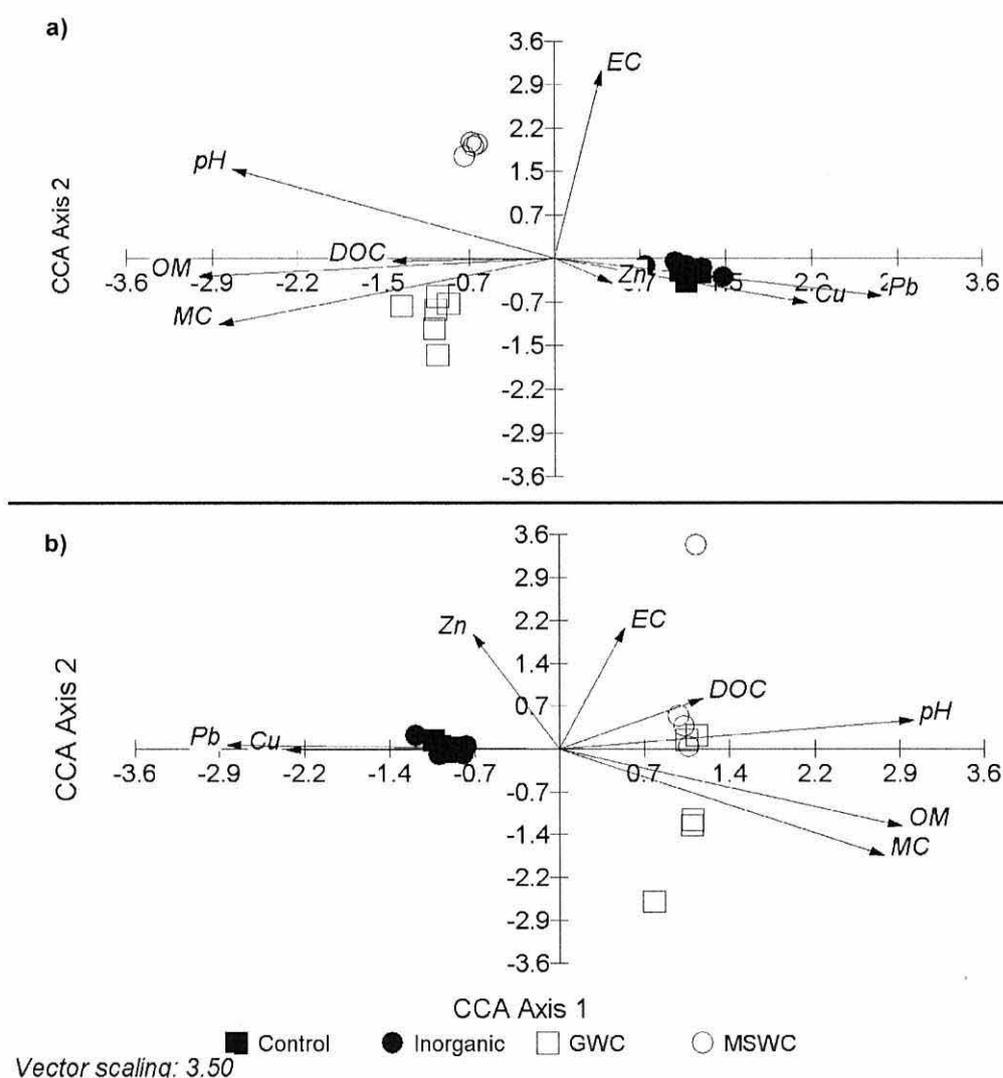


Figure 8.2: Canonical Correspondence Analysis (CCA) of bacterial (Panel A) and fungal communities (Panel B) as influenced by the environmental data. 25.8 and 12.0% of the bacterial variance was explained by axes one and two respectively, and 42.6 and 8.1% of the fungal variance was explained by axes one and two respectively.

CCA was used to investigate the correlation between environmental variables (Tables 8.1 and 8.2) and TRFLP patterns (Fig. 8.2). These indicated a clear divergence between the compost and non-compost treated soils, separated along the first axis (x) by all three heavy metals for both fungal and bacterial diversity, with this axis accounting for 26% and 43% of the variance for bacteria and fungi respectively. The 2nd axis (y) accounted for 12% and 8% of the variation respectively. Electrical conductivity appears to split the two compost treatments for the bacterial diversity data, presumably due to the high EC of the MSWC. The wider spread of data points for the fungi indicates that the fungal communities were more spatially variable than the bacterial communities in the compost-treated soils. Both the bacterial and fungal communities were very similar in the inorganic and control treatments.

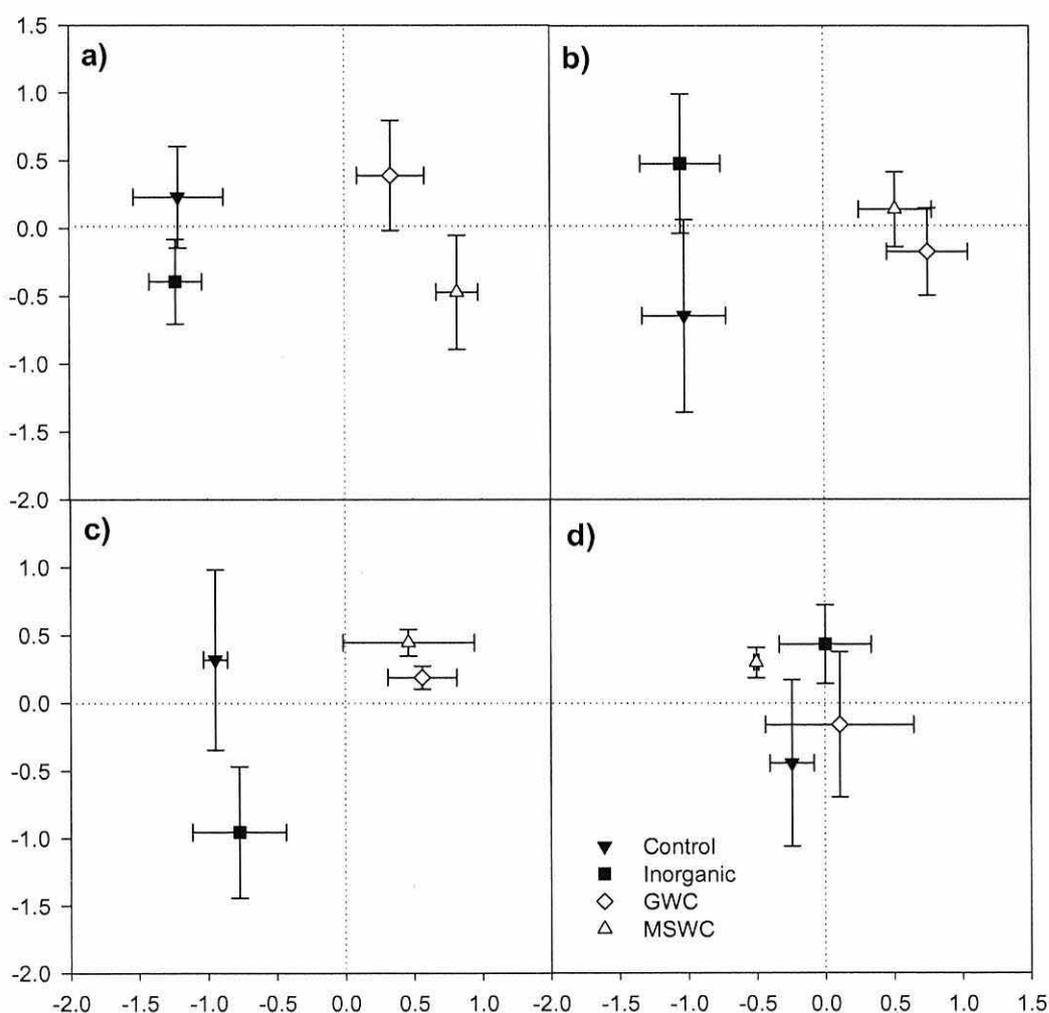


Figure 8.3: Correspondence Analysis (CA) of PLFA data at all four soil depths (mean axis scores \pm SEM) (a = 0-10 cm, b = 10-20 cm, c = 20-30 cm, d = 30-40 cm). GWC = green waste compost, MSWC = MSW compost

8.4.5 PLFA analysis of fungal communities

PLFA analysis of samples from all depths and treatments revealed the presence of 26 identifiable peaks outlined in Leckie (2005). Correspondence analysis (CA) of the PLFA signature data gave good separation of treatments (Fig. 8.3), with the two compost amended soils clearly differing from each other and from the control and inorganic treatments at the soil surface (consistent with the TRFLP data). However, these differences diminished with soil depth, leading to near-convergence of PLFA profiles at 30-40cm. The first two axes of the analysis accounted for 53%, 63%, 68%, and 65% of the variance at each depth respectively.

These changes in community profile were further investigated using CCA to separate the individual PLFA peaks by environmental factors across the whole dataset (Fig. 8.4). Most PLFAs were clustered around the centre of the axes, indicating no effect of any environmental variable on their concentration (Fig. 8.4). However, it is apparent that in particular, the 10Me-branched FAs and 18:1 ω 9c were negatively correlated with soluble heavy metal concentration and electrical conductivity, and positively correlated with high pH, organic matter and moisture content. In contrast, 16:1 ω 7, i17:1 ω 6 and cy17:0 were strongly linked to high heavy metal concentrations and electrical conductivity.

To identify additional relationships between PFLA profiles and chemical concentrations, PCA analysis was carried out on the environmental data to reduce the number of variables, and with the first axis accounting for 50% of the variance this was used as a proxy for all the environmental data (ordination plot presented in Fig. 8.5). PLFA signatures were grouped into actinomycetes, Gram-positive and Gram-negative bacteria, and fungi, and two stress indicators (t18:1 ω 9/c18:1 ω 9 and c16:1 ω 7/cy17:0) according to Leckie (2005). Pearson's correlation analysis (data not shown) highlighted that actinomycetes and Gram-negative bacteria were significantly positively correlated ($P < 0.01$) with PC1 of the environmental data, indicating a tendency away from high concentrations of heavy metals and salts and towards a higher pH and low salinity. No correlations ($P > 0.05$) were observed between fungi, Gram-negative bacteria or either of the stress indicators with PC1, however, both actinomycetes and fungi were significantly negatively correlated ($P < 0.05$) with the trans:cis stress indicator.

8.5 Discussion

8.5.1 Chemical properties and biological activity

Lime addition is a widely used approach to raise the pH of the soil and in an attempt to render heavy metals insoluble and less bioavailable (Alloway, 1990). Here we show that while the conventional inorganic treatment failed to deliver long-term amelioration, addition of composts not only counteracted the acidity of the mine waste but also enhanced soil fertility through an improvement in the substrates chemical, biological and physical characteristics. The positive remedial effects of the compost are consistent their strong buffering capacities (Kiikilä *et al.*, 2001; Mench *et al.*, 2003; Pérez-de-Mora *et al.*, 2007). However, we also observed that the success of the remedial treatment was highly dependent upon compost origin with only the MSW-derived compost capable of inducing a significant change in sub-surface soil properties. We ascribe its greater effect to its higher initial base cation content.

The presence of compost also increased DOC concentrations throughout the soil columns relative to the control and inorganic treatments. Enhanced DOC concentrations have been shown to increase metal solubility and plant uptake from

soil (Khan *et al.*, 2006). However, our plant growth results suggest that this was not apparent here with our results being consistent with the counter-theory that elevated DOC reduces metal bioavailability in soil (Seuntjens *et al.*, 2004; van Herwijnen *et al.*, 2007). This is supported by the observation that both microbial activity and DOC were negatively correlated with soil solution heavy metal concentration. Our results suggested that the leaching of DOC from the added compost promoted soil microbial activity in sub-surface horizons with strong correlations apparent between DOC and microbial biomass-C and all three microbial activity indicator variables (basal respiration, glucose and amino acid SIR). This supply of C in a soluble form from surface horizons is widely recognised as a major C delivery route for subsoil microbes in natural ecosystems (van Hees *et al.*, 2005). The source of the DOC transferred below-ground in the compost treatments, however, remains unknown as it could originate from the compost itself or from plant roots (e.g. via root exudation and turnover) whose growth it promotes. The relative importance of these two processes is worthy of further investigation as this has implications for the long-term supply of DOC belowground.

8.5.2 Microbial community structure

The principal objective of this research was to assess the effects of contrasting organic and inorganic amendments on microbial structure and function in a contaminated soil. Several studies concur with our basic findings that microbial structure or function are affected by organic amendment of contaminated soil (Chander and Joergensen, 2002; Kelly *et al.*, 2003; Pérez-de-Mora *et al.*, 2006). However, our observation that surface-applied organic amendments also significantly affect subsurface microbial communities and induce pedogenesis is to our knowledge novel.

Both the TRFLP and PLFA data are in agreement demonstrating that composts cause large shifts in the structure of the microbial community, and it is interesting to note that whilst the bacterial community is changed by compost type, there is no such separation between the fungal communities of the GWC and MSWC-treated columns at the surface. However, both the Shannon-*H* diversity results and the total

TRFs were found to be statistically similar in both compost-amended soils, indicating that both composts gave equally diverse fungal and bacterial communities.

Using Amplified Ribosomal DNA Restriction Amplification (ARDRA) techniques, Pérez-de-Mora *et al.* (2006) found that different amendments produced differential effects on both fungal and bacterial communities in a metal contaminated soil. However, in our experiment, the inorganic treatment had no effect on the microbial community, implying that such changes were brought about by the direct addition of microbes in the composts alongside those induced by the presence of plant roots (rhizosphere microbial communities). Similarly, organic amendment also increased soil pH and decreased heavy metal concentration which would have allowed proliferation of some highly acid-sensitive microbial groups (e.g., nitrifiers). We propose that these factors would also have a positive feedback effect on the microbial community.

Addition of inorganic amendments has been shown to increase soil microbial activity in non-leached microcosms (Chander and Joergensen, 2002). Whilst the addition of lime and inorganic nutrients promoted plant growth to some extent, this was not, however, reflected below ground and the TRFLP and PLFA profiles of the inorganic treatment were very similar to those of the control soils. Indeed, of the four functional assays employed, only basal respiration was increased in the inorganic treatment relative to the control. Due to our imposed rainfall regime it is possible that the effect of adding soluble inorganic nutrients was short-lived and that the effect of these had dissipated by the end of the experiment. It is notable that, NO_3^- and NH_4^+ levels in the inorganic fertiliser treatment were not significantly different from the control stressing the need to use representative climate conditions in amendment experiments.

Further statistical analysis using CCA and PLFA signature groupings correlated to PCA scores allowed us to attribute the main physicochemical drivers to the observed changes in microbial structure and activity. Figure 8.2 illustrates that the microbial communities in the surface layers of non-compost and compost treated columns cluster quite discretely, and that this is strongly associated with the elevated heavy metal levels associated with the non-compost treatments. This correlated with the reduced levels of respiration and overall microbial biomass in these treatments. It

is well known that heavy metals have a deleterious effect on the soil microbial community (Brookes and McGrath, 1984; Vulcan *et al.*, 2000), and that addition of organic matter has a direct effect on soil microbes (Tiquia *et al.*, 2002; Pérez-Piqueres *et al.*, 2006), as well as indirectly by attenuating concentrations of metals in solution.

From the PLFA analysis presented in figure 8.4 across the four depths, we demonstrate that the fatty acid cy17:0, which is attributed to long periods of stationary growth and stress (Leckie, 2005) is most strongly associated with an increase in Zn. All the 10Me-branched fatty acids as actinomycete indicators (Leckie, 2005) are strongly associated with reductions in heavy metals and increases in pH, organic matter and moisture content. The PLFA 18:1 ω 9c showed the strongest response to pH increase and is mainly attributed to Gram-positive bacteria and eukaryotes (Leckie, 2005), however, many of the other fatty acids quantified in our study are also signatures of Gram-positive bacteria, and due to their scattering across the bi-plot, this blurs overall trends. Despite this, strong positive correlations ($P < 0.001$) were observed between PC1 (Fig. 8.5) of the soil physicochemical data and the Gram-positive and actinomycete PLFA groupings, reinforcing our conclusions drawn from the biplot data. Our results generally agree with Kelly *et al.* (2003), who found that PLFA signatures were significantly affected by remediation strategy, and that actinomycetes and Gram-positive bacteria were negatively correlated with metal loadings in a Zn contaminated site.

It is apparent from our results that compost addition significantly affected microbial community structure up to a depth of 30 cm while at 30-40 cm the microbial communities were unaltered in comparison to the control (Fig. 8.3). In comparison, microbial activity was less affected. Taking this into consideration, and the different outcomes of the TRFLP analysis of bacteria and fungi in the top 10 cm, we hypothesise that there was a high level of functional redundancy evident in the amended soil community. In a field study across a metal contamination gradient, Ramsey *et al.* (2005) found linear responses of microbial biomass and respiration to pollution levels whilst community structure was only observed to change at a threshold pollution level. Further, they concluded that soil function is maintained by functional redundancy mechanisms even when the structure is altered in low to medium contamination levels. Hence in the sub-surface samples in our study, the

separation of treatments observed in the CA plots may be a temporary artefact of either microbes from the composts being physically leached, or alternatively migrating down the profile following leached nutrients.

8.5.3 Conclusions

We demonstrated that composts are suited to biostabilisation of acidic mine spoil due to their high buffering capacity, raising the surface layer pH to circum-neutral. Poorer quality composts such as the MSW-derived compost used in this study are highly suited to this role to both significantly increased bacterial and fungal biodiversity and activity. Stabilisation techniques such as these do however raise some concerns - primarily that the metals present, although bound by amendments, have not been removed from the site. Also, whilst our PLFA results indicated that composts induce a change in sub-surface microbial community structure, no major increases in functional activity were observed. Regular re-application of wastes may overcome this in the medium-long term, however regular re-application of contaminated wastes may lead to the accumulation of other elements not initially contributing to the pollution on site. As the microbial function of soil is essential for nutrient turnover and plant nutrition, further research is required to assess changes in sub-surface microbial activity below biostabilisation works.

8.6 References

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CHAPTER 9: GENERAL DISCUSSION

9.1 Discussion of results

The objectives of this thesis were two-fold:

- To investigate the chemical changes within an in-vessel aerobic composting system using different feedstocks, with particular emphasis on changes in heavy metal speciation throughout the process.
- To identify safe uses for non-PAS100 specification¹ composts. In particular, the avoidance on unnecessary landfilling of these wastes by identifying remediation opportunities for lower-grade composts.

The EcoPOD[®] system performed well for the purposes of this study in that it was possible to set up small industrial-scale composting trials cost effectively, whilst allowing the composting of feedstocks controlled under animal by-products regulations. Both the MSW (Chapter 3) and catering waste (Chapter 6) feedstock mixes composted well, although the MSW-derived composts still had relatively high C:N ratios compared to average figures (see Table 2.2, pg 24). On the other hand, both food-waste containing mixes studied in Chapter 4 had low C:N ratios after 112 days of composting, and despite the paper addition, there was no increase in C:N ratio in the final compost. Whilst heavy metals were of little concern in the catering

¹ Currently, no composts containing any wastes other than green waste e.g. sewage sludge, catering waste etc may pass the PAS100 specification (BSI, 2005), therefore making their marketing very difficult.

waste-derived composts produced in Chapter 6, both Cu and Pb were above UK PAS100 (BSI, 2005) standards for certifiably safe composts in the MSW-derived composts produced in Chapter 2. As the transformations in metal speciation during composting are often complex in nature (Greenway and Song, 2002), the sequential extraction procedure of Mossop and Davidson (2003) was used to elucidate changes in heavy metal availability during the composting of MSW fines material. Of the four elements studied, only Cu demonstrated significant re-partitioning between the four extractants used in the modified BCR method, increasing in fractionation to the oxidisable fraction. As Cu is strongly sorbed by humic substances (Alloway, 1990), and the composting process is widely recognised to increase the humification of organic carbon within the compost (Epstein, 1997; Hsu and Lo, 2001; Amir *et al.*, 2005), it is proposed that the Cu previously loosely bound to simple organic matter within the compost feedstocks was transformed to tightly bound copper within the humic matrix of the composted organic matter.

From initial growth trials carried out in Chapter 3, the MSW-derived compost was found to be particularly suited to promoting plant growth in an acidic, heavy metal contaminated soil from Parys Mountain, the site of an abandoned copper and zinc mine. In agreement with previous studies on degraded sites (Pérez-de-Mora *et al.*, 2006; van Herwijen *et al.*, 2007), compost addition to the contaminated soil raised soil pH, improved the soil's physical structure and increased nutrient availability. In Chapter 4, we investigated this subject in greater detail, testing the MSW-derived compost against a range of other composts, with or without the addition of lime to ascertain if greater reductions in metal uptake and increases in plant biomass could be achieved. Soil solution metal dynamics were also measured over time, with variable effects caused by the addition of composts and lime to the soil. Lime was found to have little effect on either metal uptake or promoting plant growth when applied with compost, however, moderate growth was observed relative to the control treatment when only lime was applied. Of the metals present within the MSW-derived compost, only Zn was found to be of particular concern in terms of increasing plant uptake relative to other compost treatments, therefore suggesting that applying such lower-grade composts to contaminated land would be a

sustainable waste management practice, reducing the amount of waste committed to landfill.

This research theme was carried on though to Chapter 7 and 8, where metals, nutrients and DOC leaching down through the vertical plane were considered. The 40 cm deep mesocosms used in this study facilitated the non-destructive extraction of the soil pore water at regular intervals over the period of the trial, demonstrating a very rapid initial leaching of heavy metals down the soil profile. At depth however, the MSW treatment led to significantly higher levels of Pb and Cu in the soil solution for a longer sustained period of time, and this was ascribed to the leaching of salts down the soil profile from the MSW compost. Processes governed by this include the displacement of metals bound on the exchange sites, the formation and solubilisation of metal-chloride compounds, and the dissolution of organic matter (Wahla and Kirkham, 2008). The variable treatment results shown in Chapter 7 with regard to DOC and salt-induced promotion of heavy metal leaching are not unusual with several authors observing contrasting effects of amendments on a soil metal availability (Pérez-de-Mora *et al.*, 2007; van Herwijnen *et al.*, 2007; Tandy *et al.*, in press).

Chapter 8 investigated the effects of compost amendments on the microbial diversity and function of the contaminated soil, and found that although structural changes (as assessed by PLFAs and TRFLP) were observed, little impact was seen on microbial activity. This implies a high level of functional redundancy within the amended soil community. In a field study across a metal contamination gradient, Ramsey *et al.* (2005) found linear responses of microbial biomass and respiration to levels of pollution, but the structure of the community was only observed to change at a threshold pollution level. Further, they concluded that soil function is maintained by functional redundancy mechanisms even when the community structure is altered in low to medium contamination levels. This is why in the sub-surface samples in this study, the separation of treatments observed in the CA plots in Chapter 8 may be a temporary artefact of either microbes from the composts being physically leached, or alternatively migrating down the profile following leached nutrients. Attributing the PLFA peaks to microbial phenotypes (Leckie, 2005) allowed further investigation into the dominant groups within the community, as affected by the soil chemistry. In agreement with Kelley *et al.* (2003), we demonstrated significant changes in PLFA

signatures as a result of bioremediation, and that PLFA signatures associated with actinomycetes and Gram-negative bacteria were negatively correlated with metal loadings.

The papers presented in this thesis have furthered knowledge useful for the safe and effective use of heavy metal contaminated wastes. In contrast to previous work using sequential extraction methods to assess changes in metal speciation during composting that have focussed on homogenous, uniformly-contaminated wastes such as sewage sludge (Greenway and Song, 2002), our MSW-fines material was extremely heterogeneous, with many point sources of heavy metals such as batteries, as well as homogeneous contamination from printing inks (Richard and Woodbury, 1992). The work has demonstrated that whilst there are concerns about increasing total heavy metal loadings in soil, the extractable levels contained in composts are actually comparably low. Given this fact, the use of low-quality composts for remediation or stabilisation of acidic, metal-contaminated sites is certainly a promising avenue, and certainly preferable to landfilling these mixed wastes, either raw or after some form of aerobic or anaerobic treatment.

In addition to the work on remediation of heavy metal contaminated sites, Chapter 5 investigated the use of S^0 and $Fe(OH)_3$ to control the pH and P availability of two composts (the GF compost produced in Chapter 6, and a green waste, paper pulp and biosolids-derived compost produced by the *Life-Environment* project that ran in the University between 2005-8 [Nason *et al.*, 2007]). Critchley *et al.* (2002) demonstrated that low P availability was a useful indicator of substrate suitability for restoration of nutrient-poor habitats, and exploratory work including initial results from this paper were presented in Nason *et al.* (2006), demonstrating the decrease in pH caused by the addition of S^0 , and the subsequent increase in soil solution P. This was then shown to be decreased by the addition of $Fe(OH)_3$. This experiment focussed on the need to produce a growth substrate for revegetation of inert blocky waste spoil tips that was low in available nutrients, had a low pH, yet could potentially supply nutrients for a long time period without reapplication. We evaluated this by measuring soil solution pH and P over time, whilst growing two competing grass species as a phytoassay to confirm the hypothesis that a reduction in soil solution P increases the competitiveness of a species more commonly found in nutrient-poor

soils (*Festuca ovina*) against one more suited to a nutrient rich environment (*Agrostis capillaris*).

Whilst figures 5.3 & 5.4 demonstrate that the S^0 and $Fe(OH)_3$ treatments had significant effects on soil solution pH and P in both composts, significant amounts of P were lost due to leaching. An increase in pH was also observed in the GS compost towards the end of the trial, indicating that the protonation of the soil solution by addition of S^0 was being counterbalanced by the buffering capacity of this compost, indicating that more than one S^0 application is probably required. Concerns about the forced decrease in pH resulting in an increase in heavy metal availability from the composts or iron hydroxide sludge were unfounded, with plant tissue Zn below the limit of detection in all treatments.

Despite evidence of significant effects on compost pH and P availability, figure 5.2 demonstrates extremely mixed results in terms of vegetation growth and foliar P content. Several studies into *A. capillaris* and *F. ovina* P requirements (Bradshaw *et al.*, 1960; Elias, 1982; McCain and Davis, 1983) highlighted the fact that P levels in plant tissue in our treatments were low in comparison to previous work, indicating that despite the high nutrient availability of the composts used in this study, phytoavailable P was in fact quite low in comparison. This may have led to an up-regulation of plant nutrient stress mechanisms (e.g. organic acid excretion; Johnson and Loeppert, 2006) which enabled roots to desorb P from highly crystalline Fe oxides and partially dissolve poorly crystalline Fe oxides within the iron hydroxide sludge, negating any initial binding. This study has demonstrated that whilst industrial wastes such as S^0 and $Fe(OH)_3$ can be used safely to adjust chemical properties of substrates used in restoration, difficulties in assessing nutrient availabilities and buffering capacities hamper accurate predictions of doses for amendment.

The final proposed use for composts investigated in this thesis was based upon the replacement of peat in the horticulture and market gardening sector. This was investigated in Chapter 6 by firstly producing a nutrient-rich compost from catering and green wastes, and then investigating the growth of *Helianthus annuus* in a substitution experiment with increasing doses of compost GF replacing a commercially purchased peat based compost. Our results demonstrated that whilst peat-based compost is required to obtain the tallest flowers, seed head size and seed

yield were not improved by its inclusion over the GF only treatment. The GF compost produced in this study showed that the concerns of three previous studies into peat replacement (Garcia-Gomez *et al.*, 2002; Benito *et al.*, 2005; Herrera *et al.*, 2008) where the high electrical conductivity and pH inhibiting growth compared to peat, were unfounded. Given the lower organic matter of the GF compost when compared to the PB compost, the results suggest that a 75% substitution rate of PB compost for GF compost would not unduly affect water holding capacity of the growth media and therefore place no extra strain on water resources. Where irrigation is not an issue, however, 100% GF compost could be utilised without unduly affecting growth. Either scenario would lead to a massive reduction on the dependence of the horticulture industry for the finite resources of *Sphagnum* peat, and the nutritive value of food waste-derived composts could be utilised effectively in this manner.

9.2 Further work

This work has demonstrated that different waste streams may be composted effectively, proving that this is an effective management strategy for waste reduction and diversion from incineration and landfill. Whilst stabilisation and remediation of contaminated and denuded land are obvious avenues for utilisation of poorer-quality waste streams, it was also demonstrated that under-utilised waste streams such as catering wastes may be effectively used for both the re-vegetation of highly porous slate waste, and horticultural replacement of *Sphagnum* peat. The horticultural use of wastes gives added value, where the use of poor-quality wastes in remediation may only be seen as a method of waste disposal. It is possible that waste managers may produce several grades of compost suitable for different purposes, with finely graded food waste-derived composts aimed at the lucrative market and home gardening industries. Poorer-grade mixed wastes could be accepted to raise revenues from gate fees, as increasingly stringent EU legislation (EC, 1999) demands reductions in untreated waste to landfill that will be hard to achieve without targeting this waste stream. Their utilisation in the remediation and regeneration markets could make the acceptance of such wastes at composting plants commercially viable. Both these routes (and the processes that take place during thermophilic composting) led to several interesting questions, which are laid out below.

- The first major hurdle to be overcome is the fact that composts derived from mixed wastes, or that do not meet the high standards of the PAS100 specification within the UK, increasingly remain classified as 'wastes', as opposed to 'composts'. This is despite demonstrations of successful maturation and removal of pathogens. Such legal barriers currently prevent the wholesale application of mixed-waste composts in remediation projects.
- Further studies are required into the factors affecting changes in heavy metal fractionation within composts, and whether additives to compost such as paper pulp would decrease or increase metal availability.
- Given the dearth of information on true mixed-waste compost use in remediation, and the fact that MBT-waste processing is ever increasing, it is a fair assumption that the volumes of MSW-derived composts will increase over the next few decades. It is therefore paramount that further *in situ* research be carried out to demonstrate the safe use of these composts in the restoration of contaminated sites. A social acceptability study of their use would also be useful in this context.
- Most standards for compost or biosolids application to land are reported in total metals levels. Whilst these are important for risk assessment where repeated doses may be applied to uncontaminated agricultural land for crop growth, ultimately leading to an increased heavy metal loading, they are a cumbersome method for assessing risk when wastes are applied in remediation projects. Further work is required to assess the availability of heavy metals in composts applied to land, their rate of decomposition when added to contaminated soils, and the effects this will have on eventual increases in metal availability as the organic matter to which the metals are bound becomes degraded.
- One issue touched on in this work was the combination of biostabilisation using composts with the growth of a phytoaccumulator (in this case, *Thlaspi caerulescens* cv. Ganges). Whilst it was used in this instance as a phytoassay for metal availability, it is recommended that biostabilisation trials could be combined with slow-growing phytoaccumulator species to truly remove metals from contaminated sites.

- In addition to the above, the issue of 'bio-energy' has come to the fore in recent years, in both positive and negative light. Whilst it is true that such crops are carbon-neutral, the premise that replacing agricultural food crops with bio-energy species is an environmentally sound practise is increasingly recognised as a fallacy. However, by improving contaminated land to a level where short rotation coppice of *Populus* spp. (Poplar), *Salix* spp. (Willow), or *Miscanthus* spp. can be grown could enable previously uncultivable land to be utilised for energy production. The feasibility of this is demonstrated in Chapter 3, where soil from Parys Mountain amended with MSW compost gave the same *L. perenne* yield as that of the highly fertile Eutric Cambisol obtained from the University Farm.
- Given the results of Chapter 4, where it was demonstrated that there may be a narrow margin of pH between which optimum stabilisation of heavy metals is achieved, further work is required to assess the 'liming potential' of composts to be applied in remediation works. The results of a preliminary study into this are presented in Appendix 1.
- In order to demonstrate the contribution of heavy metals from composts to the burden taken up by plants grown on amended soils, the different isotopic signatures of elements contained within the soil and composts (e.g. Pb) may be used to demonstrate the source of the contamination within the biomass. In Appendix 2, it was demonstrated that the isotopic signature of Pb in *A. capillaris* vegetation grown in the pots was similar to that of digests of the soil, and that the isotopic signature of the MSW was different. Further work is proposed in this field using samples from Chapters 7 & 8 to investigate the contribution of Pb from the MSW compost to the soil solution and how it is fractionated across a sequential extraction of the soils. It is proposed that if this work demonstrates that the Pb from the compost is inert in nature that a further research project could be carried out at a field scale using other Pb-contaminated wastes such as biosolids to investigate the contribution of amendment-based Pb to the overall environmental burden of a site.
- From Chapter 5, we demonstrated that whilst feasible, the manipulation of acidity and nutrient availability of composts for sensitive restoration of

nutrient-poor habitats is a difficult proposition to master, both from accurately predicting phytoavailability of nutrients to plants, and the buffering effects of different composts against the pH reduction. It is recommended that further work be carried out to further explore possibilities in this area.

- While the thesis demonstrates a number of good uses for waste-derived composts there is a need for stakeholder engagement to (1) assess the size of and location of markets relative to waste production volumes and locations, (2) assess the financial viability of using these composts in comparison to alternatives, (3) assess other social barriers to use, and (4) assess the ecological / environmental footprints of the different strategies (i.e. life cycle analysis).
- Finally, in Chapter 6, it was demonstrated that nutrient-rich food waste based composts are highly suitable for peat-replacement in the horticulture industry. One major barrier to this is market acceptance, and further studies are required to demonstrate their benefits for sustainable practises.

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APPENDIX 1: pH BUFFERING CAPACITY OF COMPOSTS

Brief introduction:

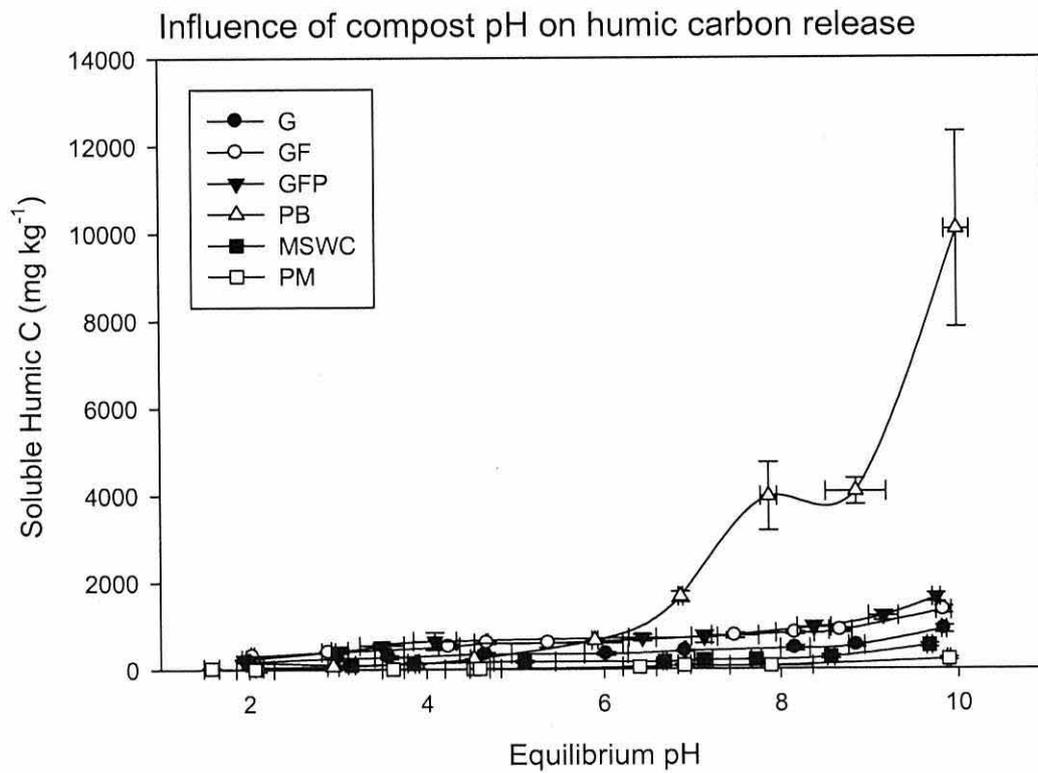
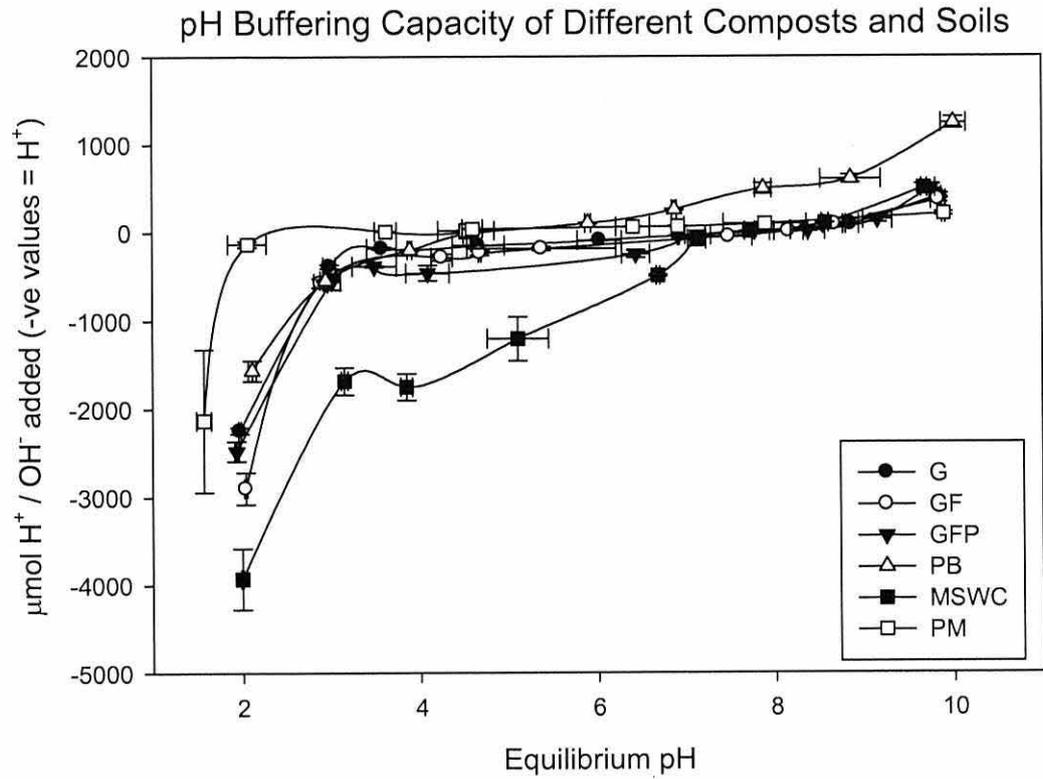
The premise of this experiment was to assess the buffering capacity of the soil and composts used in the growth trial described in Chapter 4. In addition, the release of humic carbon and heavy metals from the substrates was also studied. Knowledge of these factors is paramount in order to accurately predict the effect of forced pH changes on the soils and composts, and the metals contained within.

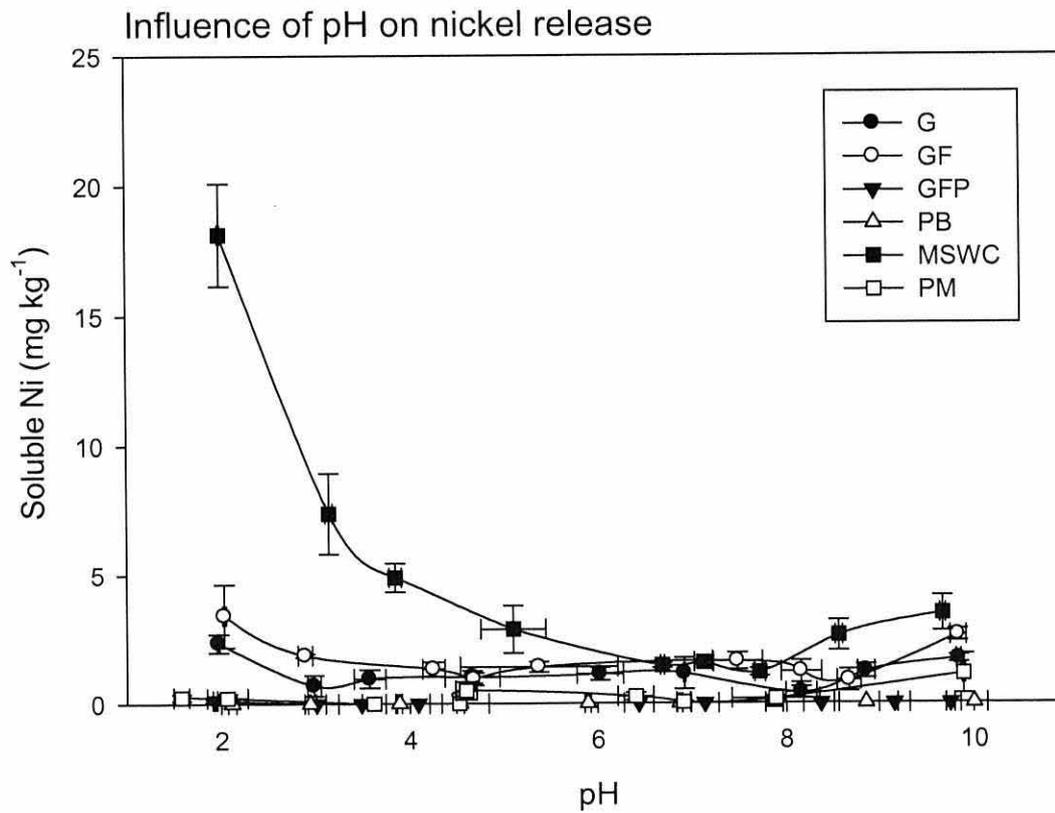
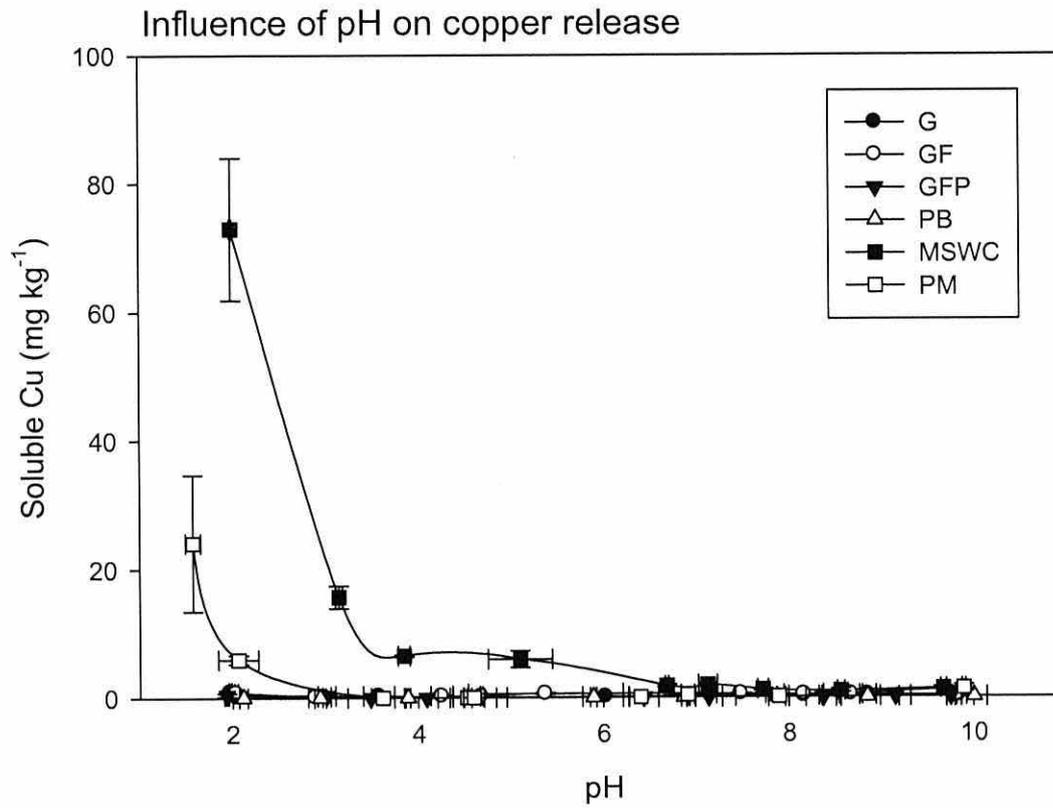
Materials and methods:

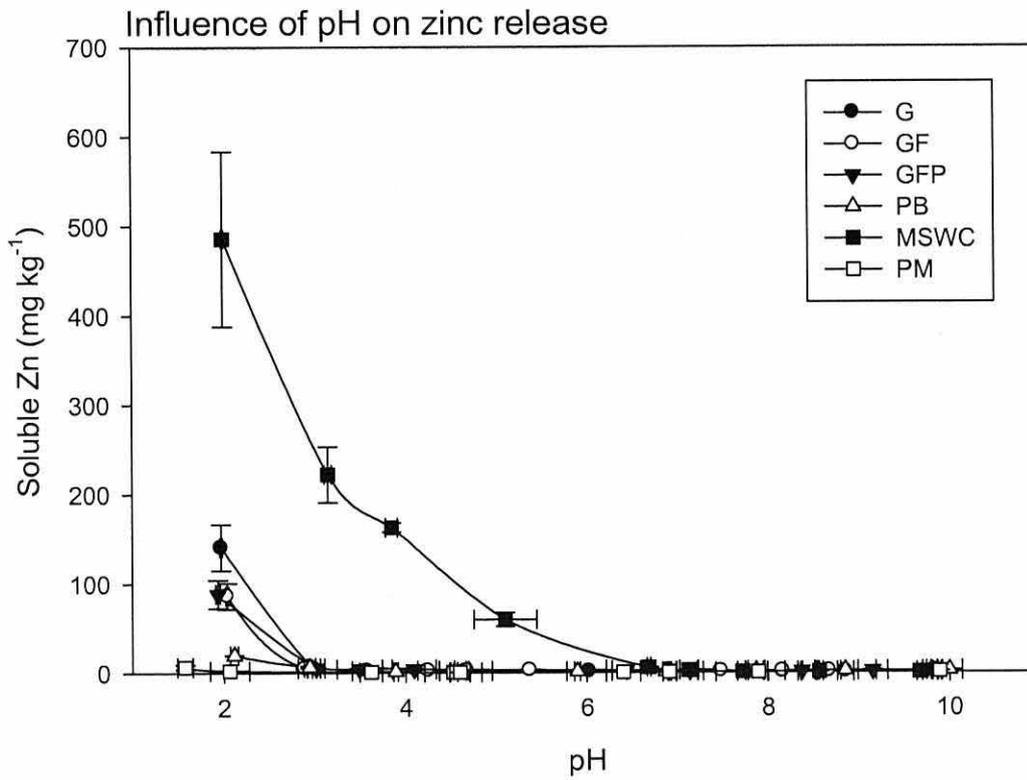
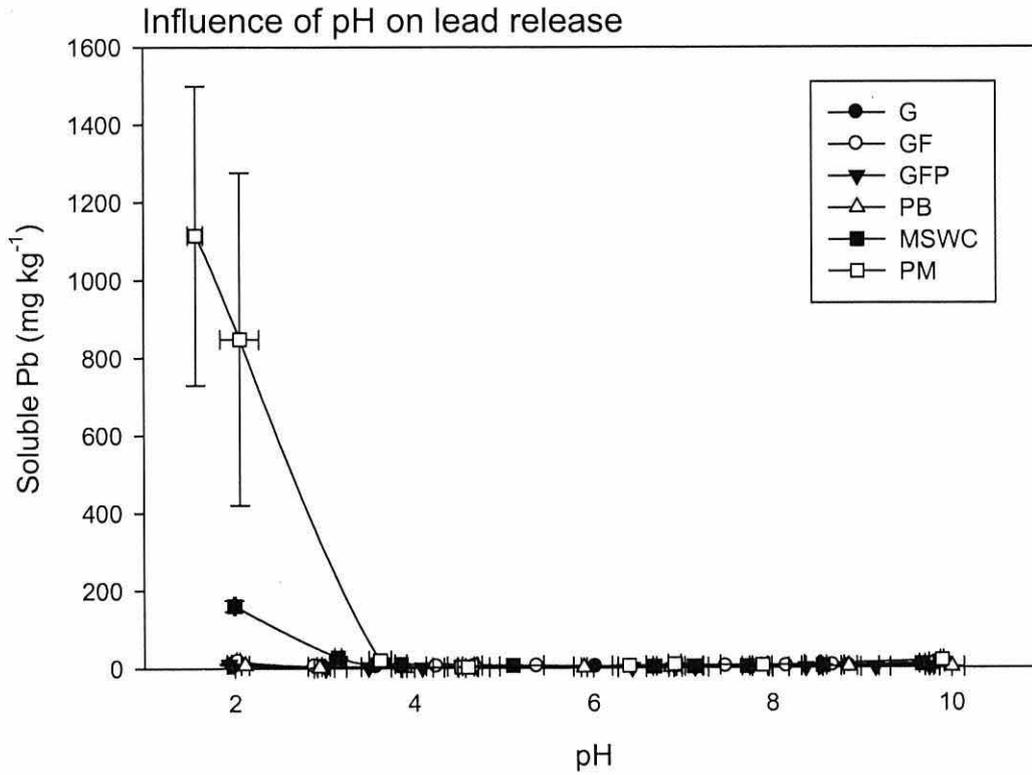
Three g from each of the substrates used in chapter 4 was weighed out in triplicate into beakers for each target pH point, to which 30 ml water was added. Subsequently, 0.1 M or 0.01 M HCl or NaOH was added from burettes to these beakers (dependent on target pH), and the amount of H^+ or OH^- dispensed was recorded. Beakers were equilibrated overnight, and the process was repeated three times, after which time the total volume of solution added and final pH were recorded. Humic C was then measured in these solutions colourimetrically using the absorbance method described in Chapter 4, whilst Cu, Ni, Pb and Zn were measured using a F-AAS (Varian FS220 AAS, Varian Inc., Palo Alto, CA).

Results and discussion:

In terms of pH buffering capacity, the three green waste-derived composts (G, GF and GFP) behaved in a similar manner throughout the pH range, taking a much greater volume of H^+ to lower the pH below 4.







The metal contaminated soil only resisted a drop in pH below 2, indicating a strong buffering capacity around its natural highly acidic pH of 2.27 ± 0.03 . When forcing pH above this, relatively little OH^- was required for the entire target range up to pH 10. The peat-based compost demonstrated similar resistance to pH reduction, but required a greater input of OH^- to raise the pH above 8. Finally, the MSW compost did not exhibit a plateau effect until pH 7-10, with large additions of H^+ being required to reduce its pH from 7.28 ± 0.03 .

All substrates demonstrated an increase in soluble humic carbon as OH^- addition increased, however, this increase was ~5 times higher at pH 10 in the peat based compost, with 10000 mg kg^{-1} soluble humic carbon present. These differences in buffering capacity and humic carbon release illustrate the diverse nature of reactions when pH changes are forced upon a substrate. In the case of assessing liming potential of composts, it can be seen that the MSW-derived compost resisted negative pH change to a much greater extent, demonstrating its potential for remediation of highly acidic soils.

All four elements studied were present in higher concentrations at lower pH levels, with Cu, Ni, Pb and Zn released by the MSW compost, and Cu and Pb released from the metal contaminated soil from Parys Mountain. There was also a small increase in Ni concentration towards pH 10 in the MSW and GF composts. These results demonstrate that care is needed to avoid the leaching of compost-borne metals when applied to highly acidic soils. Meanwhile, there was no obvious increase in metal concentration at higher pH values, demonstrating little correlation with the increase in humic carbon at the high pH end of the trial. This experiment was, however, limited by the dilution of soils into solution to facilitate the accurate addition of acids and bases and pH measurement. In soil solution, it is expected that displacement of heavy metals from solid-phase exchange sites alongside enhanced mineral solubilisation due to metal complexation by soluble carbon compounds may increase their availability at elevated pH levels.

APPENDIX 2: USE OF Pb ISOTOPE SIGNATURES TO TRACE SOURCES OF Pb POLLUTION

Brief introduction:

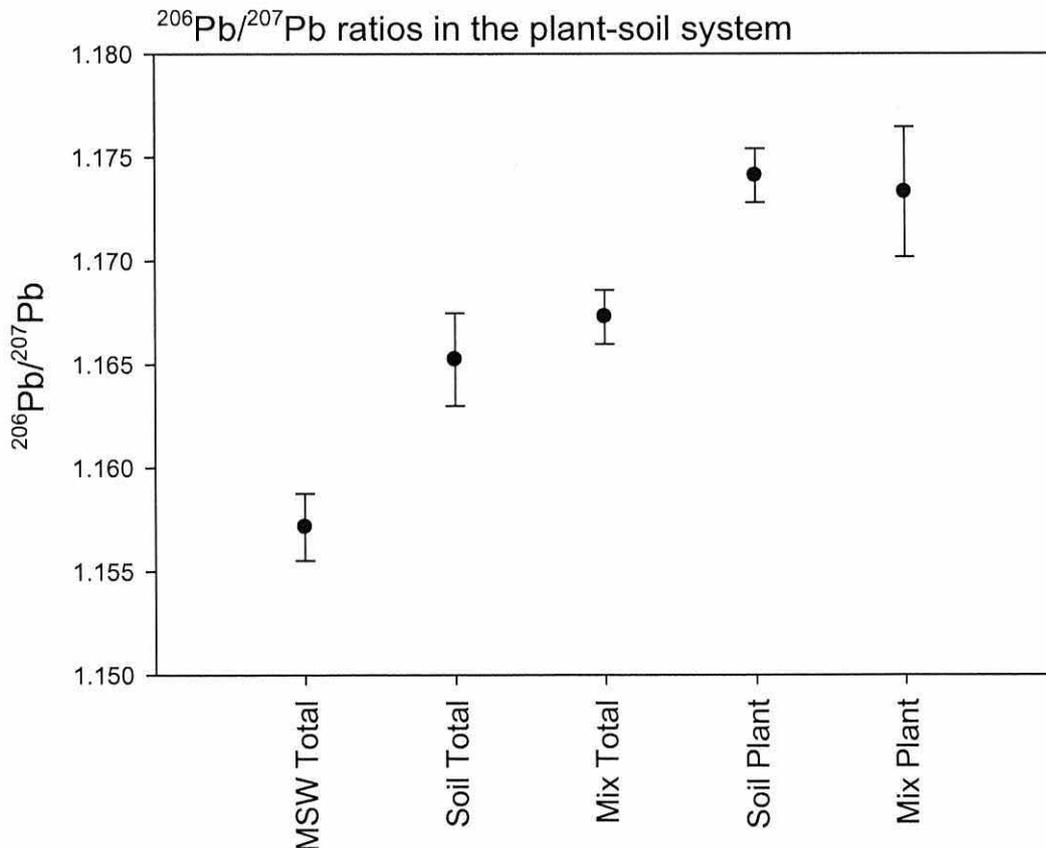
It is widely recognised that different sources of lead in the environment may have differing isotopic signatures. Several studies have investigated sources of lead in the environment using isotopic methods (Teutsch *et al.*, 2001; Bacon *et al.*, 2006; Kylander *et al.*, 2008; Notten *et al.*, 2008), and have demonstrated that it is possible to trace Pb pollution through the environment. In this preliminary study, the Pb isotopic signatures of the soil from Parys Mountain and the MSW compost used in Chapter 4 were analysed, with the Pb signatures of *A. capillaris* leaves also measured to assess the contribution of compost-borne Pb to the overall environmental burden.

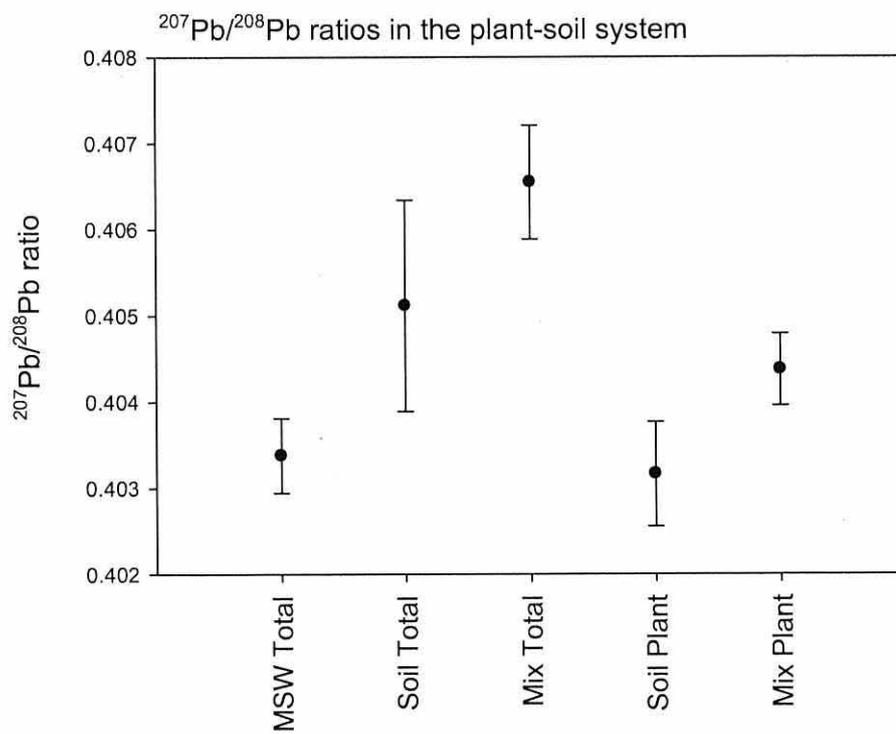
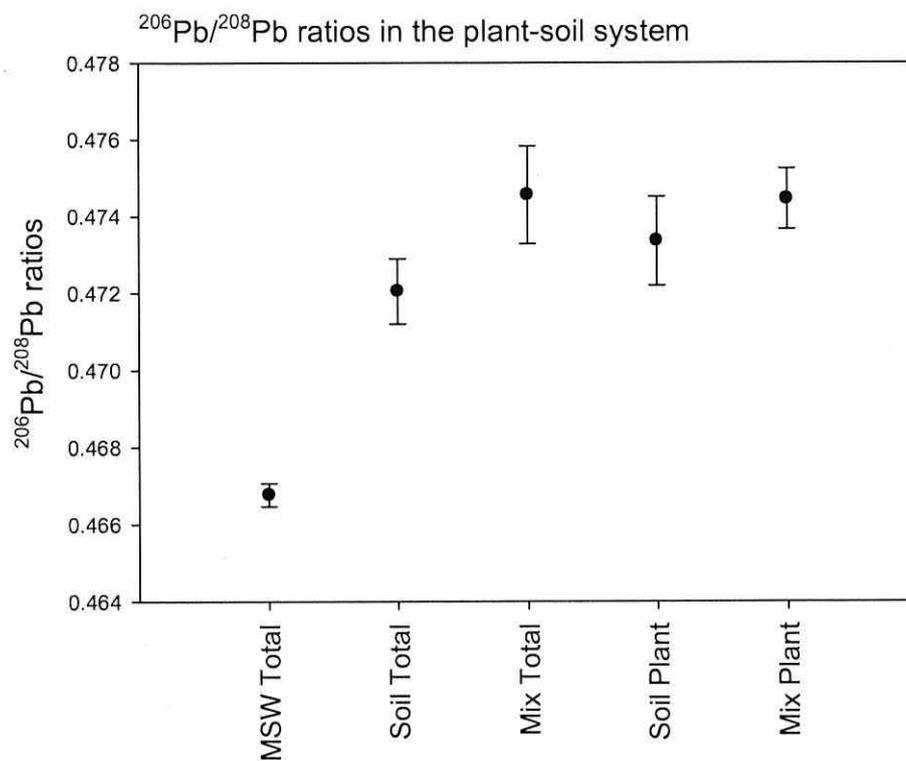
Materials and methods:

Samples used in this preliminary work were digests of the soil, MSW compost, soil and compost mixture, and above ground biomass from *A. capillaris* grown in the lime treated control and MSW compost treatments from the experiments described in Chapter 4. These solutions were diluted to 50 µg l⁻¹ and analysed using a single collector ICP-MS sector spectrometer using reverse Neire-Johnson geometry (Thermo-Finnigan Element2, Thermo Electron Corporation, Waltham, MA), equipped with a standard solution nebulisation system. The instrument was run in low resolution mode to increase count rate and improve peak shape. Ratios between ²⁰⁶Pb/²⁰⁷Pb, ²⁰⁶Pb/²⁰⁸Pb and ²⁰⁷Pb/²⁰⁸Pb were calculated.

Results and discussion:

The results (presented as mean \pm SEM, $n = 3$) demonstrate that the total Pb measured in the MSW compost and contaminated soil had different amounts and ratios of ^{206}Pb , ^{207}Pb and ^{208}Pb . This demonstrated that assessing the contribution of Pb from the MSW compost to the overall available Pb burden in the plant-soil system was possible. From these preliminary results, $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{208}\text{Pb}$ ratios indicate that the Pb present in the plants is sourced mainly from the soil, whereas the $^{207}\text{Pb}/^{208}\text{Pb}$ results make this comparison somewhat less clear. One possible explanation for this is that the sources of Pb within the compost are uncertain, given its highly heterogeneous nature (Richard and Woodbury, 1992). Given the increased error bars observed in this ratio, this is a feasible prospect.





Further work:

This Pb isotopic work is at an extremely preliminary stage, and the tracing of Pb pollution and quantifying a source's effect on the environment is a rapidly expanding field of research. Work further to this is in progress using samples from the mesocosm trial described in Chapters 7 and 8 to assess changes to the isotopic signature of Pb in the soil solution over time and depth, and the fractionation by sequential extraction over depth. Such work should further elucidate Pb sources, especially in the organic fraction of the MSW-treated soil. This would demonstrate the applicability of the method to further field-scale trials for assessing the true impact of amendment-borne lead in biostabilisation work.

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