The application of mixed waste organic output (MWOO) to soils: Effects on metal and metalloid concentrations, distribution, bioavailability and mobility in NSW soils

A Thesis submitted by

Sara Bayat

For the award of
Doctor of Philosophy

January 2016
Abstract

Mixed waste organic output (MWOO) has been used as a soil amendment for many years. However, concern regarding the introduction of contaminants to soil ecosystems can potentially restrict its use and there is growing need to fully understand the risk associated with utilizing this potentially beneficial resource, in particular with regard associated metal and metalloid contamination.

The aim of this project was to examine the impact of MWOO application on concentration, distribution, bioavailability and mobility of seven targeted priority pollutants including As, Cd, Cr, Cu, Ni, Pb and Zn on different soils of NSW. MWOO is frequently used for different purposes such as agricultural or rehabilitation of the minesite in NSW and it is specifically regulated for this. Hence the soils studied were collected from different, mainly agricultural, areas within NSW, Australia. One of the soils used was collected from a NSW coal mine rehabilitation site. This was achieved through a sequence of experiment that progressed from method development, investigating the impact of MWOO application rate and method on concentration and down soil profile distribution of these contaminants, evaluating their distribution in different soil fractions by a sequential extraction and a leaching batch experiment to estimate the leachability and mobility of targeted metals and metalloids to achieve better estimation of the potential bioavailability and soil water contamination resulted from MWOO application to soils.

As a precursor comprehensive method evaluation was carried out for determination of total concentration of metals and metalloids in MWOO and MWOO amended soil. An ultrawave microwave digestion using aqua regia extractant with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis showed the optimum extraction efficiency and precision, and was used for further analysis of total metals and metalloids.
A glasshouse column experiment over 18 months was established to evaluate and compare the accumulation and distribution of the targeted metals and metalloids with MWOO amendment in ten different NSW soils. The MWOO was both surface applied and incorporated (to 15 cm) at three different rates (20, 50 t ha\(^{-1}\) and 140 t ha\(^{-1}\)) to the soils that encompassed a range of pH, texture and organic matter. Soil samples were collected at 6, 12 and 18 months to 70 cm depth. Total concentration of some the elements studied in MWOO contact depths, (which were 0–5 cm depth in surface applied treatments and 0–15 cm depth in incorporated applied treatments, was increased in soils). The significance of this, however varied depending on the element, soil type, initial concentration in MWOO and in background soils, application method and rate. Generally, Cu, Pb and Zn, with the highest concentration in MWOO, (180.8 ± 40.4, 275.1 ± 35.5 and 411.1 ± 16.3 mg kg\(^{-1}\), respectively), showed the greatest increase in MWOO contact application depths. These three elements also showed significant increases at depths below MWOO contact application in some of the sandy soils, silt loams and one of the clays, most significantly at the depth immediately below the MWOO contact zone. The elements As, Cd, Ni and Cr were present at lower concentrations (5.3 ± 0.5, 2.2 ± 2.1, 40.2 ± 10.8 and 85.4 ± 12.2 mg kg\(^{-1}\), respectively) in MWOO and slight but significant increases were only observed in MWOO contact depths in the sandy soil and silt soils, but also for depths below MWOO application As, Cd, Cr were in higher concentrations in some sandy soils and for Ni in the silty loams. In the high organic matter content soil, however, no change in metal or metalloid concentration was observed below MWOO contact depth for any of the elements, nor for As, Cd, Cr in the silty loams and clay soils. This experiment has evaluated the metal and metalloid concentration in different soil types from NSW for the first time and has demonstrated that MWOO additions can result in metal and metalloid accumulation that persists and usually maintained to 18 months and can cause down profile movement especially in sandy soils.

It is well accepted that total metal and metalloid concentration in MWOO provides limited information about actual risk to biological receptors and this may be better assessed by determining the bioavailability of these elements in amended soils.
Hence, the speciation and distribution of the metals and metalloids was determined in the exchangeable fraction (acid soluble), reducible fraction (associated with soil Fe and Mn oxides), oxidisable fraction (associated with soil organic matter) and residual fraction was determined for the controls and MWOO amended soil by the three step BCR (Community Bureau of Reference of the European Commission) sequential extraction method. To compare the impact of soil texture and low pH content on the availability and speciation of the metals and metalloids following MWOO amendment, the acidic sandy loam and clay soils used in the glasshouse experiment with acidic pH were chosen for this experiment. The proportion of metals in MWOO in the exchangeable fraction followed the sequence: Zn > As > Cd > Ni > Cu > Pb > Cr. This was, however < 20% of total concentration. The highest proportion of metals and metalloids studied was in the residual fraction (> 45.5%) in all the controls and MWOO amended soil samples. The impact of MWOO application on element distribution was most important for those elements with the highest concentrations in the MWOO i.e. Zn, Cu and Pb, and was relative to soil background concentrations. Following application of MWOO to the soils, the greatest increase in the exchangeable fraction was observed for Zn in the sandy loam, reaching 20% of total soil Zn concentration. Application of MWOO to the soils also mostly increased the proportion of the elements in the reducible or oxidisable fractions. Both these fractions are considered relatively unavailable under consistent soil conditions, and in our study were largely stable during the 18 month study period. The result demonstrates that generally low risk if compliant MWOO applied at moderate rates. The fraction of the elements of greatest concern in terms of risk to soil systems is the exchangeable fraction, and Zn showed the greatest increase in exchangeable forms with MWOO addition in the sandy loam, approximately 6 mg kg\(^{-1}\). Cations such as Zn in MWOO are high risk for plant uptake or availability for other organisms, however, the concentration in this exchangeable form following amendment with NSW MWOO for 50 t ha\(^{-1}\) application seems to present little risk.

A number of studies have reported increases in metals leached from soils that have been amended with MWOO which can be of concern in regards to ground water contamination or their availability to the plants and other soil organisms. Hence, the
impact of MWOO application on the metals and metalloids leachability in acidic sandy loam soil was subsequently examined with three agents; deionised water, 0.01 M CaCl₂ and 0.05 M EDTA over 48 hours in a batch experiment. The application of MWOO to the acidic sandy loam soil significantly increased the concentration of most of the metals and metalloids in all three extractants. Generally, concentrations of Zn, Pb and Cu were the greatest in all extractants, which can be explained by their high concentrations in MWOO and also formation of soluble organic complexes following MWOO application. Even though only a low % of total soil metal was extracted (< 4 % in both water and 0.01 M CaCl₂), extractant concentrations indicate potential risks for water contamination following MWOO application, with the greatest concern being for Zn in leachate. Of the three extractants, EDTA extracted the largest concentration of all elements (up to 7.48 mg kg⁻¹ for Zn), indicating potentially higher risk for plant availability, but only if EDTA can in fact be confirmed as a good measure of this.

The results from the EDTA extraction in the batch experiment were applied in a kinetic model using first order kinetic study with both two step and one step first order models to predict the lability of the elements studied. The data showed a good fit for the one step first order model, suggesting that either the desorption of the labile and non-labile element components were similar, or, more likely, that the labile fraction was too small to be easily identified in the model. This is quite probable in this well matured MWOO amended system. Overall, Zn, Cd and Pb showed the fastest desorption whereas As and Cr were slowest. Sequential extraction of the residue showed that effects of MWOO application were evident in the soil 48 hours after leaching. Zinc showed the highest proportion in the exchangeable fraction (in water and 0.01 M CaCl₂, 26 and 25 %, respectively) and Pb showed the highest proportion in the reducible fraction (26 % and 21 %, respectively). The proportion of these elements in the exchangeable fraction and the reducible fraction increased in MWOO amended samples compared to controls. This shows the impact of MWOO application in increasing the availability especially of Zn. The largest proportion of all the elements studied was still in the residual fraction (> 44.6 %) which is considered not available to plant and soil organisms.
In conclusion, MWOO application can significantly increase contaminant concentrations when applied to soils, with the increase most significant for those contaminants present at higher concentrations in MWOO, notably Cu, Pb and Zn. Further, these effects persist for at least 18 months and some down profile movement can occur, to the greatest extent in sandy soils. The effects of MWOO are evident also in increased potential bioavailability of contaminants such as Zn and Pb and also increased contaminant in the aqueous phase. However, the risks for soil systems in NSW seem to be low if MWOO meets the current NSW General Exemption Guidelines and is used for soil application at rates suitable for plantation forestry, broad acre agriculture and non-contact agriculture (< 50 t ha\(^{-1}\)). Concern is greater if MWOO is applied at higher rates and/or in repeat applications.
I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis and all sources used have been acknowledged in this thesis.

Signature                      Date       30/11/2015
Acknowledgements

Firstly, I would like to express my sincere gratitude to my principal supervisor Dr Susan Wilson for the continuous support of my PhD study and related research, for her patience, motivation, and immense knowledge. I would not have been able to complete it without her support and assistance, which went above and beyond what I had expected and hoped for. From the beginning of this wonderful journey, finding financial support, designing the experiments, setting up in particular the glasshouse column experiment, sample collection, preparation, analysis, working with new laboratory devices and finally towards the end, data set analysis, interpretation and writing up would not have been possible without her amazing supervision, guidance and dedication. I could not have imagined having a better supervisor and mentor for my PhD study.

Besides my principal supervisor, I would like to thank the rest of my supervision team, Associate Professor Brian Wilson and Associate Professor Paul Kristiansen, not only for their generous support in field work, sampling and statistical analysis but also for insightful comments, encouragement which gave me incentive to widen my research from various perspectives.

I also appreciate the great help and support of soil and plant laboratory personnel, Ms Leanne Lisle, Mr Garry Cluey and Ms Gabrielle Ray for their technical guidance and advice and Mr Ewan Peterson and Ms Kirsten Drew for assisting with sample collection, preparation and analysis.

I owe a huge thanks to Ms Chris Fife for all her generously time and support for editing my thesis and her positive and friendly attitude.

I would like to thank the NSW Office of Environment and Heritage for providing the financial support for this project, without which, I would not have been able to carry on my PhD candidature.
I would like to thank my parents, brother and sister for supporting me spiritually, throughout writing this thesis and my life in general.

Finally and most of all, a massive thanks to my husband, Iman Samaee, for unselfishly supporting me financially, emotionally, technically, spiritually and giving me the courage to continue my education to higher degrees even with having a baby during the years of PhD and believing in me to be able to finish this huge responsibility.

I would like to dedicate this thesis which is the result of years of hard work and study to my daughter, Elena who has come to this world along with this project and I do certainly believe that she is capable of being a successful scientist full of motivation, talent and determination.
# Table of Content

**List of Tables** ........................................................................................................................................................................... ix  
**List of Figures** ............................................................................................................................................................................... xi  

## Chapter 1  
**Introduction** ........................................................................................................................................................................... 1  
1.1 Mixed Waste Organic Outputs (MWOO) production and management ................................................................. 1  
1.2 Process of MWOO production ........................................................................................................................................... 2  
1.3 Mechanical preprocessing .................................................................................................................................................. 2  
1.4 Biological treatment ............................................................................................................................................................ 3  
1.5 Factors affecting the quality of the MWOO product ...................................................................................................... 3  
1.6 Australian regulation of MWOO application: NSW General Exemption ............................................................... 4  
1.7 Thesis aims and structure .................................................................................................................................................. 5  

## Chapter 2  
**The impact of MWOO application on total metal and metalloid concentration, speciation, bioavailability and leaching in soil with associated risks: a review** ......................................................................................... 7  
2.1 Introduction ........................................................................................................................................................................... 7  
2.2 Sources of metals and metalloids in MWOO and effect of production process on concentrations ........................................................................................................................................................................... 7  
2.3 Total metal and metalloid concentrations in MWOO and maximum limit values .............................................................. 9  
2.4 Available fractions of metals and metalloids in MWOO .................................................................................................. 11  
2.5 Factors influencing risk for MWOO amended soils ....................................................................................................... 15  
2.5.1 MWOO effects on metal and metalloid retention in soils ....................................................................................... 15  
2.5.2 Impact of MWOO application on total metal and metalloid accumulation and distribution in MWOO amended soil ........................................................................................................................................................................... 16  
2.5.3 Impact of MWOO application on available fractions of metals and metalloids associations in MWOO amended soils ........................................................................................................................................................................... 21  
2.5.4 Metal and metalloid leachability and mobility in MWOO amended soils ................................................................. 22  
2.5.5 Simulation of metal availability and mobility ........................................................................................................... 24  
2.6 Plant uptake, animal and human exposure .......................................................................................................................... 25  
2.7 Conclusions and research needs ................................................................................................................................. 28  

## Chapter 3  
**An examination of hot plate and microwave extraction methodology with ICP-OES analysis for multi-elemental determination of metals and metalloids in MWOO and soils** ......................................................................................................................... 30  
3.1 Abstract ................................................................................................................................................................. 30  
3.2 Introduction ................................................................................................................................................................. 31  
3.3 Materials and methods .................................................................................................................................................. 34  
3.3.1 Apparatus ................................................................................................................................................................. 34
3.3.2 Certified reference material, MWOO and reagents ........................................ 35
3.3.3 Experimental protocols and digestion methods ........................................... 36
3.3.4 Quality assurance and quality control ......................................................... 39
MDL = method detection limit ................................................................................... 39
3.3.5 Statistical analysis ....................................................................................... 39
3.4 Results .............................................................................................................. 40
3.4.1 Preliminary assessment of hot-plate and Milestone ETHOS Plus microwave digestion systems (Experiment 1) ............................................................... 40
3.4.2 Preliminary assessment of the Milestone Ultrawave Microwave digestion on the certified reference soils (Experiment 2) ......................................................... 47
3.4.3 Comparison of the Milestone Ultrawave Microwave digestion system and hot-plate digestion for different MWOO samples (Experiment 3) ....................... 50
3.5 Discussion ........................................................................................................ 55
3.5.1 Assessment of hot-plate and microwave-assisted digestion methods for soil certified reference materials ................................................................. 55
3.5.2 Assessment of hot-plate and microwave-assisted digestion methods for MWOO samples .............................................................................................. 59
3.6 Conclusions .................................................................................................... 60

Chapter 4 Effects of MWOO application on metal and metalloid accumulation and distribution in ten different NSW soils after 6, 12 and 18 months ........................................ 62
4.1 Abstract .......................................................................................................... 62
4.2 Introduction .................................................................................................... 64
4.3 Materials and methods .................................................................................. 67
4.3.1 Soil and MWOO samples ........................................................................ 67
4.3.2 The glasshouse column experiment ...................................................... 68
4.3.3 Physico-chemical analysis of soils and MWOO .................................... 71
4.3.4 Statistical analysis .................................................................................. 72
4.4 Results ............................................................................................................ 72
4.4.1 Soil and MWOO characterization ............................................................. 72
4.4.2 MWOO application effects on soil metal and metalloid concentrations and distribution ........................................................................................................... 75
4.4.2.1 Sandy soils – S1, S2, S3 ..................................................................... 75
4.4.2.2 Silty Loam soils -SL1, SL2, SL3 ......................................................... 95
4.4.2.3 Clay soils - C1, C2, C3 ..................................................................... 112
4.4.2.4 High organic content soil - OM1 ..................................................... 126
6.1 Abstract .................................................................................................................. 177
6.2 Introduction ........................................................................................................... 178
6.3 Materials and Methods ....................................................................................... 180
   6.3.1 MWOO and soil characteristics .................................................................. 181
   6.3.2 The glasshouse soil column experiment .................................................... 181
   6.3.3 Physico-chemical analysis of soils and MWOO ...................................... 182
   6.3.4 Batch extraction experiment .................................................................. 183
   6.3.5 Sequential extraction of leached residue ................................................. 184
   6.3.6 Statistical analyses ................................................................................... 185
6.4 Results .................................................................................................................... 185
   6.4.1 MWOO and soil characterisation ............................................................... 185
   6.4.2 Desorption of metals and metalloids from MWOO amended soil ........... 186
   6.4.3 Kinetic modelling of desorption using EDTA .......................................... 193
   6.4.4 Fractionation of metals and metalloids in MWOO amended soil residue after leaching ................................................................. 198
6.5 Discussion .............................................................................................................. 201
   6.5.1 Desorption of metals and metalloids from MWOO amended soil .......... 201
   6.5.2 Kinetic modelling of desorption using EDTA .......................................... 203
   6.5.3 Fractionation of metals and metalloids in MWOO amended soil residue after extraction ................................................................. 205
6.6 Conclusions .......................................................................................................... 205

Chapter 7 General discussion, conclusions and recommendations ............................. 207
7.1 Summary of findings and key implications ......................................................... 207
   7.1.1 Method development .............................................................................. 207
   7.1.2 The effects of MWOO application on total metal and metalloid accumulation and distribution in NSW soils across 18 months ...... 208
   7.1.3 Implications for environmental risk and MWOO management .............. 209
   7.1.4 Applied investigation into metal and metalloid availability and distribution in different fractions and comparison with critical phytotoxic concentrations . 212
   7.1.5 Applied investigations into metal leachability and mobility .................... 214
7.2 Conclusions ........................................................................................................... 215
7.3 Recommendations ............................................................................................... 216

Bibliography ................................................................................................................ 218
Appendix A .................................................................................................................. 238
Appendix B1 .................................................................................................................. 244
<table>
<thead>
<tr>
<th>Appendix</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix B2</td>
<td>266</td>
</tr>
<tr>
<td>Appendix B3</td>
<td>288</td>
</tr>
<tr>
<td>Appendix B4</td>
<td>310</td>
</tr>
<tr>
<td>Appendix B5</td>
<td>318</td>
</tr>
<tr>
<td>Appendix C</td>
<td>329</td>
</tr>
<tr>
<td>Appendix D</td>
<td>334</td>
</tr>
</tbody>
</table>
List of Tables

Table 2.1 Summary of metals and metalloid concentrations reviewed in MWOO (Wilson et al. 2014) (data in mg kg$^{-1}$ dry weight). Australian data presented in brackets [ ]. Number of detections presented in parentheses ( ). ................................... 9

Table 3.1 Method details for hot-plate, microwave and ultra-wave digestions ........... 38

Table 3.2 The optimum wavelength and method detection limits for ICP-OES analysis ............................................................................................................................................. 39

Table 3.3 Result of elemental determination in NIST SRM 2711a and SQC001 standard soil materials prepared for ICP-OES analysis using the methods hot-plate aqua regia, hot-plate USEPA 3050B, microwave (nitric, aqua regia reverse and aqua regia) .............................................................................................................................................. 43

Table 3.4 Result of elemental determination in MWOO prepared for ICP-OES analysis using the methods hot-plate aqua regia, hot plate USEPA 3050B, microwave (nitric, aqua regia reverse and aqua regia) ........................................................................................................................................ 46

Table 3.5 Elemental determination for NIST SRM 2711a and SQC001 standard soil materials using the methods ultrawave microwave digestion (nitric acid, aqua regia reverse and aqua regia) .............................................................................................................................................. 49

Table 4.1 Characteristics of MWOO and soils (prior to MWOO amendment) used in the glasshouse trial ............................................................................................................................................. 74

Table 4.2 The correlation parameters between metals and metalloids and EC, pH in CaCl$_2$ and TOC of ten soils studied following MWOO application ......................... 133

Table 5.1 Physical and chemical properties of the background soils and MWOO . 156

Table 6.1 Summary of the sequential extraction method ............................................. 184

Table 6.2 Chemical and physical characteristics of the soil and MWOO .............. 186
Table 6.3 Changes in pH for the three extractants and DOC in the deionised H2O extractant during a 48 hour extraction period .......................................................... 187

Table 6.4 Proportion of six elements leached from the total in soil and the proportion remaining in the residue for controls and MWOO amended soils leached with deionised water, 0.01 M CaCl2 and 0.05 M EDTA ................................................. 192

Table 6.5 Non-linear regression model parameters for one component model ...... 196

Table 7.1 Total metal and metalloid concentration following 50 t ha⁻¹ MWOO application in the 10 soils and 140 t ha⁻¹ in the minesite soil at 0–5 cm depth after 18 months, their maximum allowable concentration in soils and MWOO and the critical toxic concentrations for plants ................................................................................. 211

Table 7.2 Proportion of metals and metalloids studied in four fractions following 50 t ha⁻¹ MWOO application after 18 month compared with critical phytotoxic concentration to plants ........................................................................................................ 213
List of Figures

Figure 3.1 Concentrations of seven targeted priority pollutants detected in four different MWOO samples (C1, C2, C3, C4) using three methods: hot-plate digestion with aqua regia (HAQ) and ultrawave microwave digestion with either aqua regia (UWAQ) or aqua regia reverse (UWAR) extractants. Raw data is shown (○) with means and 95% confidence intervals. .............................................................. 54

Figure 4.1 The soil glasshouse column experiment set-up and sampling .................... 70

Figure 4.2 Ni and Zn concentration in S1 soil 6 months after MWOO application at 0 (Control), 20 and 50 t ha⁻¹ = application rates. Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals .............................................................................................................. 77

Figure 4.3 As, Cr, Ni, Cu and Pb concentration in S2 soil 6 months after MWOO application at 0 (Control), 20 and 50 t ha⁻¹ = application rates. Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals .............................................................................................................. 79

Figure 4.4 Cu concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha⁻¹ = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 83

Figure 4.5 Cu concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha⁻¹ = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 84

Figure 4.6 Cu concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha⁻¹ = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 86
Figure 4.7 Pb concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals .......................................................... 87

Figure 4.8 Pb concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 89

Figure 4.9 Pb concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 90

Figure 4.10 Zn concentration in S1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 92

Figure 4.11 Zn concentration in S2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 94

Figure 4.12 Zn concentration in S3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................... 95

Figure 4.13 Ni concentration in SL2 soil following MWOO application at 18 months, 0, 20, 50 and 140 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................................................................... 97
Figure 4.14 Cu concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ................................. 99

Figure 4.15 Cu concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 101

Figure 4.16 Cu concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 102

Figure 4.17 Pb concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 104

Figure 4.18 Pb concentration in SL2 soil following MWOO application during three period of time (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 105

Figure 4.19 Pb concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 107

Figure 4.20 Zn concentration in SL1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 109
Figure 4.21 Zn concentration in SL2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 111

Figure 4.22 Zn concentration in SL3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 112

Figure 4.23 Cu concentration in C1 soil following MWOO application during three period of time (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 115

Figure 4.24 Cu concentration in C2 soil following MWOO application during three period of time (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 116

Figure 4.25 Cu concentration in C3 soil following MWOO application during three period of time (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 117

Figure 4.26 Pb concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 119

Figure 4.27 Pb concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ............................................. 120
Figure 4.28 Pb concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence interval ........................................121

Figure 4.29 Zn concentration in C1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................123

Figure 4.30 Zn concentration in C2 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................124

Figure 4.31 Zn concentration in C3 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................125

Figure 4.32 Cu concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................128

Figure 4.33 Pb concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................129

Figure 4.34 Zn concentration in OM1 soil following MWOO application over three periods (6, 12 and 18 months), 0, 20 and 50 t ha\(^{-1}\) = application rates, Incorp = Incorporation applied treatment, Surf = Surface applied treatment, Raw data is shown (○) with means and 95% confidence intervals ........................................130
Figure 5.1 Percentage of various metals in MWOO fractions detected by BCR sequential extraction ................................................................................................. 157

Figure 5.2 Changes in metal distributions in control and 50 t ha$^{-1}$ MWOO amended sandy loam and clay soils over three sampling periods (T1=six months, T2=12 months, T3=18 months), EXCH = Exchangeable fraction, REDU = Reducible fraction, OXI = Oxidisable fraction, RESI = Residual fraction ........................................ 164

Figure 6.1 Concentration of seven metals and metalloids leached by deionised water, 0.01M CaCl$_2$ and 0.05M EDTA from controls and MWOO amended soil across 48 hours (all the concentrations are in logarithmic scale) ................................................. 191

Figure 6.2 Non linear regression curves for one component model of metals and metalloids extracted by 0.05 M EDTA over 48 h. Experimental data (black dots); one component model fit (black line); 1 standard error (dark grey area); 2 standard errors (light grey area), 0 = control, 50 = incorporated applied 50 t ha$^{-1}$ treatment. 196

Figure 6.3 Distribution of the elements in controls and 50 t ha$^{-1}$ MWOO amended soil after extraction with deionized water, 0.01M CaCl$_2$ and 0.05M EDTA, EXCH = Exchangeable fraction, REDU = Reducible fraction, OXI = Oxidisable fraction, RESI = Residual fraction ........................................................................................................ 200