

**Heavy metal extractability and  
plant bioavailability from two  
sacrificial biosolids soils as  
influenced by intensive liming**

by

**Johan Hilgard van der Waals**

Submitted in partial fulfilment of the  
requirements for the degree of

Doctor of Philosophy

In the Faculty of Natural and Agricultural Sciences  
Department of Plant Production and Soil Science

University of Pretoria

Pretoria

June 2005

## **DECLARATION**

I, the undersigned, declare that the thesis, which I hereby submit for the degree of Doctor of Philosophy at the University of Pretoria, is my own work, except where acknowledged in the text, and has not previously been submitted for a degree in any form at this or any other tertiary institution.

Johan Hilgard van der Waals

June 2005

Dedicated to Jacquie.

You complete me!

## ACKNOWLEDGEMENTS

The **Water Research Commission (WRC)** and **ERWAT** for the funding of the project,

**Professor Andries Claassens** for guidance, support and a lot of patience,

**Dr Heidi Snyman** for support, motivation and funding for the project,

Personnel (**Willem Kirsten, Charl Steyn** and **Elise Herselman**) from the ISCW for information on heavy metal testing and aspects related to heavy metals in South African soils,

**Personnel** from the **Department of Plant Production and Soil Science's** soil testing laboratory for help in conducting numerous tests,

**Colleagues** in the **Department of Plant Production and Soil Science** for lending their ears and giving advice and moral support,

**My parents** for supporting me through major career changes that led to this study,

**My parents in-law** for supporting me as their “new son” in this endeavour,

**My wife Jacquie** for believing in me and a lot of support through the tough times and early mornings,

**My son Andrew** for being his wonderful (and energetic) self and for his hug in the mornings after a late night's work and little sleep,

**My Lord and Saviour Jesus Christ** for life, the ability and the opportunity to discover His creation.

**Heavy metal extractability and plant bioavailability from two sacrificial biosolids soils as influenced by intensive liming**

By

**Johan Hilgard van der Waals**

Supervisor: Prof. A.S. Claassens  
Department: Plant Production and Soil Science  
Degree: Doctor of Philosophy

**Abstract**

The influence of pH on metal extractability from two sacrificial soils that received large amounts of biosolids was studied in four separate trials. The soils (Soil 1: gravelly sandy loam; Soil 2: sandy clay loam) were collected from different water treatment plants in Gauteng. Both soils had undergone significant changes in physical (organic carbon content) and chemical characteristics (pH, metal and nutrient content) due to the prolonged disposal of biosolids.

A preliminary pot trial was conducted where large quantities of lime were added to the soils. Results indicated that the soils had high pH buffer capacities due to low pH and high organic matter content. An unexpected increase in the metals extracted with  $\text{NH}_4\text{EDTA}$  after intensive liming lead to the performing of three further trials to shed light on the phenomenon.

In the second trial lime was added to the soils at four rates (0, 12, 24, 36 tons  $\text{ha}^{-1}$ ). An increase in most  $\text{NH}_4\text{EDTA}$  extractable metals was found and this was correlated with increasing absorbance values (at 465 nm) of the extracting solutions (indicating increased extractability of organic matter). In the third trial limed (27 ton  $\text{ha}^{-1}$ ) and unlimed samples were incubated over a period of 20 weeks with regular sampling intervals. The  $\text{NH}_4\text{NO}_3$  extractable metals decreased significantly in the lime treated soils but the  $\text{NH}_4\text{EDTA}$  extractable metals generally increased.

A fourth trial was conducted due to concern regarding the increased EDTA extractable metals after liming and a possible correlation with plant metal bioavailability. The soils were incubated in pots with four lime rates (0, 12, 24, and 36 ton  $\text{ha}^{-1}$ ) and wheat and spinach grown for two months. Although similar trends as for

the previous trials were obtained in terms of metal extractability, plant metal content was best correlated with  $\text{NH}_4\text{NO}_3$  extraction levels.

The results indicate that liming is a safe option for sacrificial soils and that  $\text{NH}_4\text{NO}_3$  extractable and plant metal levels decrease with liming. The use of EDTA in metal guidelines or in soil metal content studies is discouraged due to its increased metal extractability with liming and poor correlation with plant metal content.

<b>TABLE OF CONTENTS</b>	<b>Page</b>
List of Tables	ix
List of Figures	x
<b>CHAPTER 1: General Introduction</b>	<b>1</b>
1.1 Introduction	1
1.2 Critical Research Questions	3
1.3 Broad Aim of the Study	4
1.4 Communication of Results of the Study	4
1.4.1 Publications in Peer Reviewed Journals	4
1.4.2 Submitted Manuscripts for Peer Review	4
1.4.3 Conference Presentations	4
1.4.4 Awards	5
<b>CHAPTER 2: Literature Review on the Effect of Liming on Heavy Metal Mobility in Acid Soils After Long-term Biosolids Disposal – A South African Perspective</b>	<b>6</b>
2.1. Introduction	6
2.2 Background	9
2.2.1 Degradation of Biosolids in Soil	10
2.2.2 Organo-metalic Complexes	11
2.2.3 Fulvic and Humic Material and its Influences on Metal Mobility	14
2.2.4 Iron and Manganese in Biosolids	16
2.3 Soil Characteristics Determining Metal Mobility	16
2.3.1 Soil pH and Cation Exchange Capacity (CEC)	16
2.3.2 Clay Content and Type	18
2.3.3 Time Elapsed After Metal Application	19
2.3.4 Partition Coefficient	19
2.3.5 Crop Used and Total Soil Metal Content	19
2.4 The Effect of Liming and Increased pH on Organic Material Solubility and Metal Mobility	20
2.5 EDTA Extractability of Metals and Organic Matter After Liming	21
2.6 Concluding Remarks	22
2.7 Aim of the Study	23
<b>CHAPTER 3: Soil Description</b>	<b>24</b>
3.1 Introduction	24
3.2 Materials and Methods	28
3.2.1 Soil pH and Organic Carbon	29
3.2.2 Extractable Heavy Metals	29
Effective Cation Exchange Capacity (ECEC) and	
Extractable Cations	30
3.3 Results and Discussion	31
3.3.1 Organic Carbon and pH	31
3.3.2 Extractable Heavy Metals	31
3.4 Conclusions and Recommendations	34

<b>CHAPTER 4: Increase in Metal Extractability After Liming of Sacrificial Sewage Sludge Disposal Soils</b>	<b>35</b>
4.1 Abstract	35
4.2 Introduction	35
4.3 Materials and Methods	36
4.4 Results and Discussion	37
4.5 Conclusions and Recommendations	40
<b>CHAPTER 5: The Influence of Increasing Lime Rates on Ammonium EDTA (NH<sub>4</sub>-EDTA) Extractable Metals and Organic Matter from Two Acid Long-term Biosolids Disposal Soils</b>	<b>42</b>
5.1 Abstract	42
5.2 Introduction	42
5.3 Materials and Methods	44
5.4 Results and Discussion	45
5.5 Conclusions and Recommendations	53
<b>CHAPTER 6: Changes in Ammonium Nitrate (NH<sub>4</sub>NO<sub>3</sub>) and Ammonium EDTA (NH<sub>4</sub>EDTA) Extractable Metals from Two Long-Term Biosolids Disposal Soils due to Intensive Liming and Incubation</b>	<b>54</b>
6.1 Abstract	54
6.2 Introduction	54
6.3 Materials and Methods	56
6.3.1 Incubation With and Without Lime	56
6.3.2 Soil Analysis	57
6.4 Results and Discussion	58
6.4.1 Change in pH Upon Incubation	58
6.4.2 NH <sub>4</sub> NO <sub>3</sub> Extractable Metals	59
6.4.3 NH <sub>4</sub> EDTA Extractable Metals	60
6.5 Conclusions and Recommendations	60
<b>CHAPTER 7: Heavy Metal Uptake by Wheat from Two Sacrificial Biosolids Disposal Soils at Differential Liming Rates</b>	<b>70</b>
7.1 Abstract	70
7.2 Introduction	70
7.3 Materials and Methods	71
7.4 Results and Discussion	72
7.4.1 Soil pH and Dry Matter Yield	72
7.4.2 Wheat Metal Content	73
7.4.3 Soil Metal Levels	75
7.4.4 Correlation Between Plant and Soil Metal Levels	77
7.5 Conclusions and Recommendations	78
<b>CHAPTER 8: Concluding Remarks and Recommendations</b>	<b>80</b>
<b>References</b>	<b>82</b>

<b>LIST OF TABLES</b>	<b>Page</b>
Table 3.1. Maximum metal content in soil (Water Research Commission, 1997), and suggested preliminary threshold values for NH <sub>4</sub> -EDTA (pH 4.5) extractable heavy metals for the soils of South Africa (Bruemmer and van der Merwe, 1989)	29
Table 3.2. Organic carbon and pH values for the two soils (standard deviation indicated in brackets)	31
Table 3.3. EPA 3050 extractable metal levels (mg kg <sup>-1</sup> ) for Soils 1 and 2 (values in brackets indicate the standard deviation – n = 4)	32
Table 3.4. NH <sub>4</sub> -EDTA extractable metal levels (mg kg <sup>-1</sup> ) for Soils 1 and 2 (values in brackets indicate the standard deviation – n = 4)	33
Table 3.5. NH <sub>4</sub> NO <sub>3</sub> extractable metal levels (mg kg <sup>-1</sup> ) for Soils 1 and 2 (values in brackets indicate the standard deviation – n = 4)	34
Table 4.1. Soil 1 and 2 pH values before and after liming (n = 4)	38
Table 4.2. The effect of liming on BaCl <sub>2</sub> extractable metals (mg·kg <sup>-1</sup> soil; n = 4; values in brackets denote the standard deviation)	39
Table 4.3. Effect of liming on NH <sub>4</sub> -EDTA-extractable metals (mg·kg <sup>-1</sup> soil; n = 4; values in brackets denote the standard deviation)	39
Table 7.1. The pH (CaCl <sub>2</sub> ) of the two soils at four liming rates (n = 4; values in brackets denote the standard deviation)	73
Table 7.2. Plant metal content (mg kg <sup>-1</sup> wheat dry matter) and regression equations for the lime treatments and soils	75
Table 7.3. NH <sub>4</sub> NO <sub>3</sub> extractable metal levels and regression equations for the two soils (mg kg <sup>-1</sup> , n = 4, the values in brackets denote the standard deviation)	76
Table 7.4. NH <sub>4</sub> EDTA extractable metal levels and regression equations for the two soils (mg kg <sup>-1</sup> , n = 4, the values in brackets denote the standard deviation)	77
Table 7.5. Regression equations of plant metal content (mg kg <sup>-1</sup> dry matter) versus NH <sub>4</sub> NO <sub>3</sub> and NH <sub>4</sub> EDTA extractable metal levels (mg kg <sup>-1</sup> soil) respectively	78

<b>LIST OF FIGURES</b>	<b>Page</b>
Figure 3.1. Disposal of an aerobically digested biosolids on land by means of a center pivot irrigation system at Rooiwal.	25
Figure 3.2. Flood irrigation of an anaerobically digested sludge at the Hartebeestfontein water works.	25
Figure 3.3. Accumulated organic matter in the Rooiwal soil with shoeprints of up to 5cm deep due to the spongy nature of the altered soils.	26
Figure 3.4. Weeds growing at the Rooiwal site (with the Rooiwal power station in the background).	26
Figure 3.5. Weeds growing at the Hartebeestfontein site with a tractor ploughing a commercial farming land in the background.	27
Figure 3.6. Maize plants in a field irrigated with biosolids at Hartebeestfontein.	27
Figure 3.7. Informal production of maize on the edge of a center pivot field at the Rooiwal site.	28
Figure 5.1. Change in pH (CaCl <sub>2</sub> ) at four lime application rates after 3 weeks incubation.	46
Figure 5.2. The NH <sub>4</sub> -EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn as a function of pH (CaCl <sub>2</sub> ).	48
Figure 5.3. The NH <sub>4</sub> -EDTA extractability of Al, Mn, and Ni as a function of pH (CaCl <sub>2</sub> ).	49
Figure 5.4. Soil 1 and 2 absorbance values as a function of pH (CaCl <sub>2</sub> ) in NH <sub>4</sub> -EDTA extracts at four lime application rates after 3 weeks incubation.	50
Figure 5.5. The NH <sub>4</sub> -EDTA extractability of Cd, Cr, Cu, Fe, Pb, and Zn as a function of the NH <sub>4</sub> -EDTA solution absorbance at 465 nm.	51
Figure 5.6. The NH <sub>4</sub> -EDTA extractability of Al, Mn, and Ni as a function of the NH <sub>4</sub> -EDTA solution absorbance at 465 nm.	52
Figure 6.1. Change in pH (CaCl <sub>2</sub> ) over the 20 weeks incubation period for the limed and unlimed treatments. Vertical bars indicate + and – standard deviation.	58
Figure 6.2. Aluminium and manganese levels (NH <sub>4</sub> NO <sub>3</sub> ) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH (CaCl <sub>2</sub> ) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation.	61

Figure 6.3. Cadmium and zinc levels ( $\text{NH}_4\text{NO}_3$ ) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ( $\text{CaCl}_2$ ) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation. 62

Figure 6.4. Copper and nickel levels ( $\text{NH}_4\text{NO}_3$ ) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ( $\text{CaCl}_2$ ) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation. 63

Figure 6.5. Chromium and lead ( $\text{NH}_4\text{NO}_3$ ) levels for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ( $\text{CaCl}_2$ ) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation. 64

Figure 6.6. Iron levels ( $\text{NH}_4\text{NO}_3$ ) for Soils 1 and 2 extracted at intervals over 20 weeks with and without liming (a) and correlation between extractability and pH ( $\text{CaCl}_2$ ) for the unlimed treatments (b). Vertical bars indicate + and – standard deviation. 65

Figure 6.7. The EDTA extractability of Al, Fe, and Mn from two soils with and without liming over a 20 week incubation period. Vertical bars indicate + and – standard deviation. 66

Figure 6.8. The EDTA extractability of Cd, Cr, and Cu from two soils with and without liming over a 20 week incubation period. Vertical bars indicate + and – standard deviation. 67

Figure 6.9. The EDTA extractability of Ni, Pb, and Zn from two soils with and without liming over a 20 week incubation period. Vertical bars indicate + and – standard deviation. 68

Figure 7.1. Spinach dry matter yield per pot (vertical bars indicate the standard deviation). 74

Figure 7.2. Wheat dry matter yield per pot (vertical bars indicate the standard deviation). 74