

The characterisation of some South African water treatment residues and glasshouse pot experiments to investigate the potential of two residues for land disposal

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Declaration

I hereby certify that the research reported in this thesis is the result of my own investigation, except as acknowledged herein, and that it has not been submitted for a higher degree at any other university or institution.

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Abstract

Water treatment residues (WTRs) are the by-product from the production of potable water. They consist mainly of the precipitated hydrous oxides of the treatment chemicals, and materials removed from the raw water. This study investigated the range of treatment processes and residues produced in South Africa, and two WTRs were selected for testing on selected soils and mine materials.

A questionnaire was developed and sent to water treatment authorities across South Africa. Information on the treatment chemicals, dosages, volumes and current disposal practices, and a sample of WTR from each treatment plant were requested. Eleven, of 21 authorities, returned completed questionnaires, representing 37 water treatment facilities. Organic polymers were the most commonly used treatment chemical, with most plants also using lime. Other less frequently used chemicals and additives were $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3$, FeCl_3 , sodium aluminate, activated silica, activated charcoal, CO_2 and bentonite. Information given regarding residue thickening and disposal was poor. Samples from Rand Water, Umgeni Water (Midmar), Midvaal Water Company, Amatola Water and Cape Metropolitan Council (Faure) were received or collected. An additional sample from Faure was also received, representing a change in the treatment process. These samples were analysed for a range of chemical and physical characteristics. These analyses showed that the WTRs had the potential to supply some plant nutrients (Ca, Mg, Fe, S) but that metal toxicity may be a problem, in particular Mn in the Faure WTR, and that P adsorption may be severe. The samples selected to test the potential for land disposal were from Rand Water and Faure.

A pot experiment tested the growth of *Eragrostis teff*, *Cenchrus ciliaris* and *Digitaria eriantha* in mixtures of Rand WTR and material from a coal mine i.e., a sandy soil material, spoil material and coal combustion ash, at rates of 0, 50, 100, 200 and 400 g kg⁻¹ with a uniform fertiliser treatment applied to all mixtures. The grass was harvested on three occasions and the mean total yield (dry mass) determined, as well as nutrient uptake. The pots were leached after each harvest and the pH and electrical conductivity determined. The soil, spoil and ash were characterised and pH, EC and water retention characteristics of the mixtures determined. Growth of the grasses in the ash treatments was poor and these were terminated. *Eragrostis teff* grown in the soil showed a decrease in mean total yield with increasing WTR application rate, but yield was good up to the 200 g kg⁻¹ treatment at the first

harvest, declining substantially by the second harvest. In general *C. ciliaris* and *D. eriantha* grown in the soil showed a decrease in mean total yield for all harvests with increasing WTR application. The yield of *E. teff*, grown in the spoil, increased up to 100 g kg⁻¹ WTR addition, but decreased thereafter. *Digitaria eriantha* showed a decrease in yield, and *C. ciliaris* an increase, with increasing WTR application rate, but for all treatments the differences were non-significant. The pH and EC of the leachates generally increased with increasing WTR addition. The concentration of nutrients in the grasses did not indicate any deficiencies or toxicities.

As the growth of grass was poor in the ash treatments, another pot experiment was established to test the growth of two creeping grass species grown in the Rand WTR as a cover over the ash material. *Cynodon dactylon* and *Stenotaphrum secundatum* were grown in 20, 40 and 60 mm layers of Rand WTR, with and without a fertiliser treatment. Both species performed best in the 60 mm layer with fertiliser, and *C. dactylon* performed better than *S. secundatum*. The former species was more tolerant of the high pH, but both have potential as cover vegetation on the ash dumps when these are covered with Rand WTR.

A further glasshouse study investigated the effect of Faure WTR mixed with a nutrient poor sandy soil on the nutrient uptake and seed yield of common dry beans (*Phaseolus vulgaris*). The WTR was added to the soil at 0, 50, 100, 200 and 400 g kg⁻¹ each with five levels of fertiliser (0, 25, 50, 100 (recommended optimum) and 150 %). Bean pods were harvested once the plants had senesced. The number of pods and mass and number of seeds per treatment were determined. The seeds were analysed for nutrient uptake. Interveinal chlorosis and necrotic lesions were evident on cotyledonous and new leaves in the WTR treated soils, the severity of the symptoms increasing with increasing rate of WTR. Additional pots were established at the 400 g kg⁻¹ rate (without fertiliser) and leaf material collected for chemical analysis. This showed that Mn toxicity was the cause, with leaf concentrations about 12 times the recommended 100 mg kg⁻¹ upper limit. However, mass of bean seed was highest in the 400 g kg⁻¹ Faure WTR treatment with 150 % fertiliser. Nutrient translocation to the seed seemed to be relatively consistent regardless of treatment, with little accumulation of Mn.

The data collected illustrated the range of conditions and types of WTRs produced in South Africa, and that in some instances these residues have favourable characteristics for land application. The use of the Rand WTR showed that it could be applied to the spoil medium at relatively high concentrations without severely negatively impacting on grass growth, but that

more caution should be used when applying this material to the soil medium. While the grass did not grow in the ash treatments, it would seem that with suitable species the Rand WTR could be beneficially applied to ash material as a cover layer. The use of the Faure WTR on a sandy soil seemed to potentially improve the yield of the indicator crop, but caution should be exercised due to the possibility of Mn toxicity. The use of additional fertiliser would seem to be essential. Further research would require that field scale investigation of both WTRs be conducted, as well as further studies of application rates and techniques in laboratory and glasshouse investigations.

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Table of Contents

Declarationi

Abstractii

Acknowledgementsv

Table of Contentsvii

List of Tables.....xi

List of Figuresxv

List of Platesxvii

List of Appendicesxviii

Introduction.....1

Chapter 1

Water treatment residue: a review of the literature3

1.1 Introduction3

1.2 The water treatment process and residue production3

1.3 Past disposal practices and current trends.....5

1.4 Properties and characteristics of water treatment residues.....6

 1.4.1 Physical properties.....7

 1.4.2 Chemical properties9

 1.4.3Phosphorus studies.....12

1.5 Effects on plant growth.....13

1.6 Codisposal with biosolids.....16

1.7 Discussion and conclusions.....17

Chapter 2

Characterisation of South Africa’s water treatment residues19

2.1 Introduction19

2.2 Materials and methods.....19

 2.2.1 Questionnaire.....19

 2.2.2 Chemical and physical analyses.....20

2.3 Results and discussion22

 2.3.1 Questionnaire22

| | |
|---|-----------|
| 2.3.2 Chemical characteristics..... | 24 |
| 2.3.3 Physical characteristics | 25 |
| 2.3.4 Nutrient concentrations | 26 |
| 2.3.5 Other analyses..... | 27 |
| 2.3.6 Phosphorus adsorption | 30 |
| 2.4 General discussion and conclusions | 33 |

Chapter 3

Land application of Rand Water's water treatment residue to selected mine

material and coal combustion ash: laboratory and glasshouse investigations.....36

3.1 Introduction.....36

3.2 Materials and methods.....37

3.2.1 Material collection and preparation.....37

3.2.2 Laboratory materials and methods

3.2.2.1 Chemical analyses.....38

3.2.2.2 Physical analyses.....38

3.2.2.3 Water retention studies.....38

3.2.3 Study 1 - Pot experiment

3.2.3.1 Establishment of the pot experiment

3.2.3.2 Grass harvest

3.2.3.3 Leaching experiment.....41

3.3 Results and discussion

3.3.1 Chemical properties

3.3.1.1 General.....42

3.3.1.2 Nutrient concentrations.....43

3.3.1.3 Saturated paste.....44

3.3.1.4 Elemental concentrations.....45

3.3.1.5 pH and electrical conductivity.....45

3.3.1.6 Phosphorus adsorption.....46

3.3.2 Physical properties.....47

3.3.3 Water retention studies.....48

3.4 Pot experiment

3.4.1 Leaching experiment

| | |
|--|-----------|
| 3.4.2 Yield..... | 52 |
| 3.4.2.1 Soil/RWTR mixtures..... | 58 |
| 3.4.2.2 Spoil/RWTR mixtures..... | 61 |
| 3.4.3 Effect of pH and electrical conductivity on yield..... | 62 |
| 3.4.4 Plant analyses..... | 62 |
| 3.5 General discussion and conclusions..... | 64 |
| 3.6 Study 2: The use of RWTR as a growth medium | |
| over a coal combustion ash..... | 65 |
| 3.6.1 Introduction..... | 65 |
| 3.6.2 Materials and methods..... | 65 |
| 3.6.3 Results and discussion..... | 66 |
| 3.6.4 Conclusions..... | 69 |
| Chapter 4 | |
| The use of a water treatment residue from the Faure Water Treatment Plant | |
| to improve the fertility of a sandy soil | 70 |
| 4.1 Introduction..... | 70 |
| 4.2 Materials and methods | 71 |
| 4.2.1 Material collection and preparation..... | 71 |
| 4.2.2 Laboratory investigations..... | 71 |
| 4.2.3 Pot experiment..... | 71 |
| 4.2.4 Harvesting | 74 |
| 4.3 Results and discussion..... | 74 |
| 4.3.1 General characteristics | 74 |
| 4.3.2 Phosphorus adsorption..... | 76 |
| 4.3.3 pH and electrical conductivity..... | 76 |
| 4.3.4 Water retention characteristics | 77 |
| 4.3.5 Pot experiment | 77 |
| 4.3.5.1 Leaf analysis..... | 77 |
| 4.3.5.2 Yield..... | 79 |
| 4.3.5.3 Nutrient uptake by bean seed..... | 84 |
| 4.3.5.4 Mn toxicity alleviation..... | 85 |
| 4.4 Conclusions | 86 |

Chapter 5

General conclusions.....88

Chapter 6

Further research92

References95

Appendices104

List of Tables

Table 1.1 Typical elemental composition and selected chemical properties of water treatment residues (adapted from Basta, 2000).....10

Table 1.2 Some chemical characteristics of 17 water treatment residues and typical soil levels (adapted from Dayton and Basta, 2001).....11

Table 1.3 Summary of water treatment residue studies that examined the effects of water treatment residues on plant growth.....14

Table 2.1 Summary data of the types and quantities of various water treatment chemicals used by the treatment facilities that returned adequately answered questionnaires.....23

Table 2.2 Some chemical properties of the water treatment residues from five of South Africa’s water treatment facilities.....24

Table 2.3 Some physical properties of the water treatment residues from five of South Africa’s water treatment facilities.....25

Table 2.4 Nutrient concentrations of the water treatment residues from five of South Africa’s water treatment facilities.....26

Table 2.5 DTPA and TCLP extractable metals (mg kg⁻¹) of the water treatment residues...28

Table 2.6 Five step fractionation of water treatment residues from five of South Africa’s water treatment facilities. Results from Elliott *et al.* (1990b) are given for comparative purposes.....29

Table 2.7 The amount of P sorbed by the Rand, Faure 1, Midmar, Amatola and Midvaal water treatment residues and a Hutton and a Westleigh topsoils to achieve residual P concentrations of 0.05, 0.20 and 1.00 mg L⁻¹32

| | |
|---|----|
| Table 3.1 Some chemical characteristics of the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery..... | 42 |
| Table 3.2 Some nutrient concentrations of the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery..... | 43 |
| Table 3.3 Saturated paste analysis of untreated ash, spoil, soil and the Rand water treatment residue | 44 |
| Table 3.4 Plant available metals (DTPA extractable) for the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery..... | 45 |
| Table 3.5 pH and electrical conductivity (mS m^{-1}) of the ash, spoil and soil treated with 0, 50, 100, 200 and 400 g kg^{-1} of Rand water treatment residue..... | 46 |
| Table 3.6 Some physical properties of the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery..... | 48 |
| Table 3.7 Summary ANOVA statistics for mean total yield for <i>Eragrostis teff</i> , <i>Digitaria eriantha</i> and <i>Cenchrus ciliaris</i> grown in either the soil and spoil material treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg^{-1} | 52 |
| Table 3.8 Mean ($\pm\text{SE}$, $n=3$) above ground dry yield (g pot^{-1}) for <i>Cynodon dactylon</i> and <i>Stenotaphrum secundatum</i> grown in three different Rand water treatment residue layers over a coal combustion ash, for both the fertilised (Fert) and unfertilised treatments (Unfert). $\text{LSD}_{5\%}$ comparisons for mean yield over the different Rand water treatment residue layers are also given..... | 67 |
| Table 3.9 Mean ($\pm\text{SE}$, $n=3$) root dry yield (g pot^{-1}) for <i>Cynodon dactylon</i> and <i>Stenotaphrum secundatum</i> grown in the three different Rand water treatment residue layers for both the fertilised (Fert) and unfertilised treatments (Unfert)..... | 68 |

| | |
|--|----|
| Table 3.10 Mean root dry yield (g pot ⁻¹) for <i>Cynodon dactylon</i> and <i>Stenotaphrum secundatum</i> grown in the three different layers of Rand Water's water treatment residue over a coal combustion ash..... | 68 |
| Table 4.1 Some chemical and physical properties of the Longlands sand from the South African Sugar Association Experimental Station..... | 74 |
| Table 4.2 Some nutrient concentrations of the untreated Longlands sand | 75 |
| Table 4.3 Plant available metals (DTPA extractable) of the Longlands sand..... | 75 |
| Table 4.4 pH and electrical conductivity (mS m ⁻¹) of the Longlands sand treated with 0, 50, 100, 200 and 400 g kg ⁻¹ of Faure water treatment residue..... | 76 |
| Table 4.5 Nutrient concentrations of bean leaves grown in a Longlands sand treated with 400 g kg ⁻¹ Faure water treatment residue, without fertiliser. Recommended nutrient ranges reported by Bennett (1993) and Bergmann (1992) are given for comparison..... | 78 |
| Table 4.6 Summary ANOVA statistics for number of pods and number of seeds for each treatment factor and interactions..... | 79 |
| Table 4.7 LSD _{5%} comparisons of mean seed mass for each treatment factor for dry beans grown in a Longlands sand treated with 0, 50, 100, 200 and 400 g kg ⁻¹ Faure water treatment residue with fertiliser applications of 0, 25, 50, 100 and 150%..... | 81 |
| Table 4.8 LSD _{5%} comparisons of mean number of pods for each treatment factor for dry beans grown in a Longlands sand treated with 0, 50, 100, 200 and 400 g kg ⁻¹ Faure water treatment residue with fertiliser applications of 0, 25, 50, 100 and 150%..... | 81 |

Table 4.9 Summary ANOVA statistics for mass of seeds for each treatment factor and treatment interactions.....81

List of Figures

- Figure 1.1** Block diagram of conventional or typical water treatment process (CSIR, 1985). The term ‘sludge’ refers to the residue produced from the treatment process.....4
- Figure 1.2** A water retention curve of an alum water treatment residue (adapted from Ahmed *et al.*, 1997).....8
- Figure 2.1** Phosphorus adsorption isotherms for the Rand, Midmar, Faure 1, Amatola and Midvaal water treatment residues. Two additional soils (Hutton and Westleigh) are included for comparative purposes.....31
- Figure 3.1** Phosphorus adsorption isotherms for ash, spoil, and soil.....47
- Figure 3.2** Water retention curves for (a) ash, (b) spoil, and (c) soil treated with 0, 100, 200 and 400 g kg⁻¹ Rand water treatment residue (R0, R100, R200 and R400, respectively).....49
- Figure 3.3** Mean total yields (+SE, 3 replicates) for harvests of *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil material treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹. Letters that are different indicate significant differences between treatment means within a grass species (LSD_{5%}: *E.teff* = 4.5, *D.eriantha* = 5.2, *C.ciliaris* = 4.9).....57
- Figure 3.4** Mean total yields (+SE, 3 replicates) for harvests of *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the spoil material treated with Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹.....60
- Figure 4.1** Phosphorus adsorption isotherm of the Longlands sand.....76
- Figure 4.2** Water retention curves for the Longlands sand treated with 0, 100, 200 and 400 g kg⁻¹ Faure water treatment residue (F0, F100, F200 and F400, respectively)....77

- Figure 4.3** Mean (+ SE, 3 replicates) number of (a) pods and (b) seeds of beans grown in a Longlands sand with Faure water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ with fertiliser levels of 0, 25, 50, 100 and 150%, as indicated in the legend.....80
- Figure 4.4** Mean mass of seeds (+SE, 3 replicates) of beans grown in a Longlands sand with Faure water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ with fertiliser levels of 0, 25, 50, 100 and 150%, as indicated in the legend.....82
- Figure 4.5** Mean (+ SE) mass of seed of beans grown in the Longlands sand at fertiliser levels of 0, 25, 50, 100 and 150% over the mean Faure water treatment residue application rates (0, 50, 100, 200 and 400 g kg⁻¹). Letters that are different indicate significant differences between treatment means (LSD_{5%} = 0.759).....83
- Figure 4.6** Mean mass of seed (+SE) of beans grown in a Longlands sand at FWTR application rates of 0, 50, 100, 200 and 400 g kg⁻¹ over the mean fertiliser application rates of 0, 25, 50, 100 and 150%) Letters that are different indicate significant differences between treatment means (LSD_{5%} = 0.759).....84

List of Plates

Plate 3.1 Selected images showing the poor growth of some grass species grown in the ash treated with various rates of Rand water treatment residue. (a) *Cenchrus ciliaris* at 200 g kg⁻¹ RWTR, (b) *Cenchrus ciliaris* at 400 g kg⁻¹ RWTR, and (c) *Digitaria eriantha* at 100 g kg⁻¹ RWTR. Images taken after 43 days growth. The white labels in each pot are 70 mm wide.....53

Plate 3.2 Growth of *Eragrostis teff* in (a) the soil material and (b) the spoil material at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ (left to right). Images taken just prior to third harvest. The height of each pot is 19 cm...54

Plate 3.3 Growth of *Digitaria eriantha* in (a) the soil material and (b) the spoil material at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ (left to right). Images taken just prior to third harvest. The height of each pot is 19 cm.....55

Plate 3.4 Growth of *Cenchrus ciliaris* in (a) the soil material and (b) the spoil material at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ (left to right). Images taken just prior to third harvest. The height of each pot is 19 cm.....56

Plate 4.1 Examples of interveinal chlorosis on leaves of dry beans (*Phaseolus vulgaris*) grown in a Longlands sand treated with 400 g kg⁻¹ Faure water treatment residue, 3 weeks after germination.....73

List of Appendices

| | | |
|-------------------|---|-----|
| Appendix 1 | The questionnaire distributed to water treatment authorities to determine raw water treatment and water treatment residue disposal practices in South Africa. The questionnaire was developed before the decision to use the term ‘water treatment residue’, hence the use of the term ‘sludge’..... | 104 |
| Appendix 2 | Method for determining extractable Ca, Mg, K and Na and cation exchange capacity in the water treatment residues and other materials..... | 106 |
| Appendix 3 | Method used for particle size analysis (adapted from Gee and Bauder, 1986)..... | 107 |
| Appendix 4 | List of water treatment facilities that returned partially and completely filled questionnaires. Includes source of raw water and chemical dosing rates (where supplied)..... | 108 |
| Appendix 5 | X-ray fluorescence analysis of the water treatment residues discussed in Chapter 2, the spoil, soil and ash used in Chapter 3, and the Longlands sand used in Chapter 4..... | 110 |
| Appendix 6 | Mean (3 replicates) electrical conductivity (mS m^{-1}) and pH for the first, second and third leachates collected from the soil and spoil treatments at RWTR application rates of 0, 50, 100, 200 and 400 g kg^{-1} . Coefficient of variation (%) values are given for pH and EC for each leachate..... | 111 |
| Appendix 7 | ANOVA tables for (a) <i>Eragrostis teff</i> , (b) <i>Digitaria eriantha</i> and (c) <i>Cenchrus ciliaris</i> grown in the soil material and (d) <i>Eragrostis teff</i> , (e) <i>Digitaria eriantha</i> and (f) <i>Cenchrus ciliaris</i> grown in the spoil material when treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg^{-1} . Raw yield data are available from the author subject to suitable confidentiality agreements..... | 112 |

- Appendix 8** Mean yields (\pm SE, 3 replicates) for the first, second and third harvests for *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil and spoil treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹. Where significant ANOVA F-statistics were obtained, LSD_{5%} comparisons were made¹. LSD_{5%} values and coefficients of variation (CV) are presented for each harvest. Raw yield data are available from the author subject to suitable confidentiality agreements.....113
- Appendix 9** Fertility analyses for *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil and spoil treated with Rand water treatment residue at application rates of 0, 50 100, 200 and 400 g kg⁻¹. The numbers 1, 2 and 3 refer to the first, second and third harvests, respectively. Typical nutrient levels for turf grasses (Bennett, 1993) and *Festuca arundinacea* and *Eragrostis curvula* (Miles, undated) are given.....115
- Appendix 10** Overview of possible causes and mechanisms of grass nutrient uptake and responses when grown in RWTR mixed with spoil or soil (expanded from Section 3.4.3).....116
- Appendix 11** ANOVA tables for (a) aboveground yield (b) root biomass in the RWTR layers and (c) root biomass in the ash layer of *Cynodon dactylon* and *Stenotaphrum secundatum* grown in the 20, 40 and 60 mm layers of Rand water treatment residue over a coal combustion ash with two levels of fertiliser. Raw yield data are available from the author subject to suitable confidentiality agreements119
- Appendix 12** ANOVA tables for (a) number of seeds (b) number of pods and (c) mass of seeds of dry beans (*Phaseolus vulgaris*) grown a Longlands sand treated with Faure water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹ with fertiliser levels of 0, 25, 50, 100 and 150%. Raw yield data are available from the author subject to suitable confidentiality agreements120

Appendix 13 Nutrient concentrations of bean seed grown in a Longlands sand with Faure water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ over fertiliser levels of 0, 25, 50, 100 and 150%.....121

Introduction

Water treatment residue, the by-product from the production of potable water, generally has a sludge like consistency, and in the past has been referred to as 'sludge'. This, however, has led to frequent association with sewage sludges, even though the characteristics of these materials are very different. There have been a number of other terms used to describe this by-product including water sludges, drinking water sludges, and alum-, iron-, polymer-, or lime-sludges, depending on the treatment process. More recently there has been reference to water treatment residuals. This term goes some way in removing some of the association with sewage sludges. In this investigation the material is referred to as water treatment residue (WTR), partly due to some concern over the grammatical correctness of the term 'residual'.

This study formed a component of a larger investigation that considered the effects on physical, chemical and microbial properties of soil after the land disposal WTRs. Moodley (2001) gives an overview of the project history. In brief, Umgeni Water, the main supplier of bulk water in KwaZulu-Natal, South Africa, was seeking an alternative disposal option for an increasing supply of WTR from their largest water purification facility, the Midmar Water Treatment Plant, Howick. At the time (early 1998) the material was being landfilled, at considerable cost to Umgeni Water due to the distance of the treatment facility from the nearest industrial waste disposal site (Durban). To reduce disposal costs, Umgeni Water purchased a nearby farm (Brookdale Farm) for dedicated land disposal. As the farm was being used for agricultural purposes (maize, soyabeans and dairy), an investigation was initiated to determine the impacts on soil properties and plant growth of applying WTR to the land. A field experiment was established, on a Hutton soil form (Soil Classification Working Group, 1991), on the farm for this purpose in October 1998. A second field experiment was established in October 1999, on the University of Natal research farm, Ukulinga, near Pietermaritzburg, on a Westleigh soil form (Soil Classification Working Group, 1991), which allowed for investigations on a different soil type. Initially the investigation consisted of two main studies. The first investigation considered how soil physical properties may be influenced by land application of the WTR from the Midmar Water Treatment Works, while the second investigation considered chemical properties and nutrient uptake by an indicator crop, using the same WTR. Both these investigations considered additional soil types that were tested in laboratory and glasshouse studies.

In June 2000 additional funding from the Water Research Commission (WRC) was received to further the work. This required an expansion of the existing project to a national level, as well as consideration of other effects of land application of the Midmar WTR. To achieve this, two additional projects were created, as well as continued monitoring of the existing field sites to detect long-term changes in soil properties. The first project considered the effect of WTR on the microbial activity when applied to various soils (also using the existing field sites). The other project is presented in this document.

While there would appear to be an increasing body of international literature considering the nature and environmental impacts of WTRs, there is very little information available on the types and characteristics of residues produced in South Africa, and how they are currently disposed of. A review of the available literature is given in Chapter 1, considering the production of drinking water and consequent formation of residues, disposal practices, characteristics of WTRs and how these residues affect soil properties and plant growth.

The objectives of this study were to collect information from South African water treatment authorities and facilities regarding treatment processes, residue production and disposal, as well as the collection of samples of residue from these treatment facilities. The residues were analysed chemically and physically and two were selected for further investigations of their potential for land application to poor quality soils and substrates. In the first investigation, a lime WTR from Vereeniging, South Africa, was applied to topsoil and overburden material from a coal mine and to furnace ash from a coal fired power plant, using a variety of grass species as 'indicator crops', which formed part of the mines' reclamation strategy. The second investigation considered the use of a Fe-polymer residue with a high organic carbon content, from the Western Cape region, for its potential to improve the fertility of a nutrient-poor sandy soil. Common dry beans (*Phaseolus vulgaris*) were used as the test crop, as the likely land use in the region would be food crop production, probably as small scale or subsistence farming. Both were conducted as glasshouse and laboratory investigations. The potential implications of using these WTRs on the selected materials are examined in relation to South Africa in general. The final chapter considers what additional work would be required to ensure environmentally acceptable land application of WTRs.

Chapter 1

Water treatment residue: a review of the literature

1.1 Introduction

Water treatment residues consist primarily of the precipitated hydroxides of the water treatment chemicals along with the material removed from the raw water (sand, silt, clay, humic compounds and dissolved matter) (Elliott *et al.*, 1990b). The ever-increasing demand for clean water has led to an increase in the number and size of water treatment facilities around the world. A consequence of this, however, is an increase in the production of WTRs, which require suitable disposal methods. There are no clear guidelines for the disposal of these residues, but there is a trend towards seeking sustainable methods that are environmentally and socially acceptable. As WTRs are frequently considered as industrial wastes, often associated with or compared to sewage sludges, they are treated as such and have to be disposed of in accordance with local legislation for these types of wastes.

This review considers the formation of the residues, past and current disposal practices, and what effects they may have on the environment. While the literature is not as extensive as for sewage sludges, there does appear to be an increasing interest in the development of alternative disposal practices for WTRs, rather than only landfilling.

1.2 The water treatment process and residue production

The primary objective in the water treatment process is to produce water that is suitable for human consumption. The source of raw water varies and may include rivers, dams, lakes, groundwater and, less frequently, seawater. The source of raw water typically represents the cleanest water available for purification (Elliott *et al.*, 1990b). Of concern, in this discussion, are those sources of water (typically dam, lake or river waters) from which both dissolved and suspended solids need to be removed, using chemical and mechanical procedures (Figure 1.1).

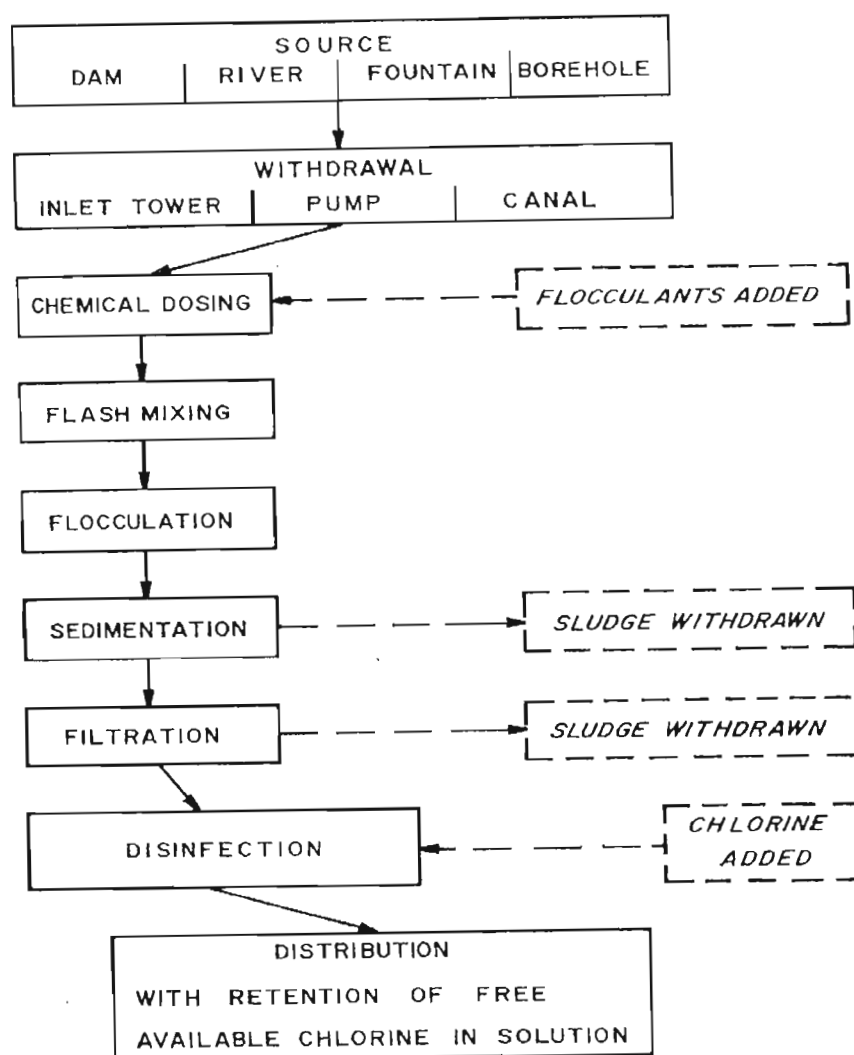


Figure 1.1 A block diagram of conventional or typical water treatment process (CSIR, 1985). The term 'sludge' refers to the residue produced from the treatment process.

Chemicals and additives frequently used to remove dissolved and suspended solids include Al salts ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ or alum), Fe salts (FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$), lime (calcitic, slaked and Ca hydroxides), bentonite, activated carbon or silica, soda ash, organic polymers, and carbon dioxide. Other chemicals may be added for disinfection (usually chlorine gas or ozone) (CSIR, 1985; Hyde and Morris, 2000). Furthermore, additional polymers and mechanical dewatering are often used to thicken residues.

It is not the intention of this discussion to give a comprehensive review of the chemical processes and reasons for use of a particular coagulant, but it should be noted that there are a number of factors that influence the choice of chemical and the procedures that are followed. In brief, the choice of flocculant depends largely on the quality of the raw water. The

flocculants typically increase the density of suspended particles by double-layer compression, the formation of insoluble precipitates or by direct physical entanglement of particles. The dosages used depend largely on the quality of the raw water (turbidity, odour, hardness etc.) (CSIR, 1985). Furthermore, economics play a role in the chemicals used, as does availability and accessibility.

1.3 Past disposal practices and current trends

Proudfit (1968) reports that until about 1946, discharge of water purification wastes directly into the nearest drainage course or body of water was the accepted method of disposal in the United States. However, the formation of an investigative committee by the American Water Works Association (AWWA) changed this practice (Proudfit, 1968). Findings from this committee indicated that until about 1946, 96% of water treatment by-products reached streams untreated. Young (1968) reported a similar situation in the United Kingdom, where discharge of WTR into waterways was becoming unacceptable, and that other alternatives were being considered. Both Proudfit (1968) and Young (1968) discuss the advent of residue dewatering practices that are now in common use at water treatment plants. Residue dewatering reduces the volume of material requiring disposal, making the use of drying lagoons more economically feasible. In an AWWA Research Foundation report (AWWARF, 1969) a number of disposal practices were discussed including lagooning, barging to sea, pipeline to lagoons, sea or sewer, but did not include land disposal. In this report, direct discharge into watercourses was discouraged, although apparently still a frequent occurrence. Albrecht (1972) commented on similar disposal practices for alum WTRs.

In a more recent study of WTR treatment and disposal, Russell (1975) indicated that land application of a lime softening WTR may be an economically and environmentally friendly alternative to direct watercourse discharge or lagooning. It was suggested that this type of WTR be applied to agricultural land using a spreader designed for wastewater disposal, but that tests be conducted to determine optimum application rates. However, the study did not indicate what the optimum disposal rates were or what criteria should be used to evaluate this. In an AWWARF (1981) committee report, the concept of land application was considered further. The application of a lime softening WTR to agricultural land was based on the premise that the WTR could act as a liming agent and be used in place of conventional liming materials. It was also indicated that there appeared to be little negative impact on the quality

of vegetation. Furthermore, it was suggested that WTRs of this nature could be used to reclaim derelict land by acid neutralisation, as in the case of many strip-mines.

Basta (2000), in a review paper, has indicated that currently landfill is the most commonly used disposal option, but due to increased costs, land application is becoming the preferred disposal method. A United States Environmental Protection Agency report (USEPA, 1996) discusses some of the more common land application practices. These include application to agricultural land either as pure WTR or co-application with fertilisers or co-disposal with sewage sludges, silviculture, land reclamation, dedicated land disposal, turf farms, parks and recreational areas and construction sites. A moderate amount of literature has been published to suggest that these and related types of WTR disposal are becoming increasingly popular, when compared to lagooning and landfilling as disposal options. Amongst these are studies relating to land disposal (*inter alia* Bugbee and Frink, 1985; Heil and Barbarick, 1989; Lucas *et al.*, 1994; Ahmed *et al.*, 1997; Moodley, 2001), consideration of WTRs as soil substitutes and alternative growth media (Skene *et al.*, 1995; Gallimore, 1999; Dayton and Basta, 2001), and co-disposal with phosphate rich waste products (broiler litter, biosolids) (Shreve *et al.*, 1995; Peters and Basta, 1996; Ippolito *et al.*, 1999). Attention has also been given to the use of WTRs to remove excess nutrients, in particular P, from agricultural land and nutrient enriched water bodies (Jonasson, 1996; Cox *et al.*, 1997; Haustein *et al.*, 2000). There has also been a study examining the use of alum WTR as a component of broiler litter to reduce NH_4^+ volatilization, a toxic gas in broiler houses (Maurice *et al.*, 1998).

Currently there appear to be no studies on the characteristics of WTRs produced in South Africa, or how these WTRs are disposed of or used agronomically. Some literature exists pertaining to engineering aspects of water treatment facilities in South Africa (Geldenhuis, 1992; Hodgkinson and Rencken, 1992; Polasek, 1997(a and b)). There are also some internal company reports, but these are not in the public domain or available to outside researchers.

1.4 Properties and characteristics of water treatment residues

While available literature regarding WTRs is limited, adequate data are available to give an overview of the nature of these by-products and the effects they may have on soil characteristics and plant growth.

1.4.1 Physical properties

This aspect of WTRs has not been investigated extensively. While the majority of studies focus on the chemical aspects or the uses of WTRs, few studies have specifically examined physical characteristics or their effect on soil physical properties.

Rengasamy *et al.* (1980) applied alum WTR to three soil types (a strongly sodic clay, a leached lateritic sand, and a hard-setting red-brown earth). Water treatment residue was applied at 2 and 20 Mg ha⁻¹. Physical parameters measured included dispersion and slaking, particle size distribution, water retention, aggregate strength and modulus of rupture (MOR). They found that slaking and dispersion decreased with the addition of WTR. An increase in water stable aggregates was also observed with addition of WTR to the soils. Water retention was increased by 18%, 85% and 19% for the clay, the sand and the red-brown earth, respectively, after the addition of 20 Mg ha⁻¹ of WTR as a suspension. The effect of adding a WTR suspension on aggregate strength and MOR was also marked. The increased porosity of these treatments led to weaker aggregates and lower MOR.

Bugbee and Frink (1985) examined the physical effects of WTR when used as an amendment for potting media. They tested an alum WTR as a replacement for (or in equal proportions to) peat, perlite and soil. The general findings were that where alum WTR replaced soil, aeration and water holding capacity were improved. However, differences in bulk density and total pore space were minimal between treatments.

A study by Skene *et al.* (1995) examined the potential of WTR as a plant growth medium. This study examined a polymer WTR and an alum WTR. As part of this study, they examined some physical properties of these two WTRs. They reported that when the WTRs were subjected to a few wetting and drying cycles they broke down to a loose granular structure resembling gravel. These aggregates were, however, not prone to slaking during rapid wetting. This property is known as self-mulching, with the WTRs having a self-mulching value of 96 (out of a theoretical 100), the highest they have ever recorded. The gravel nature means that the WTRs are generally very porous and drain well. The WTRs also exhibited a high water holding capacity, apparently a function of the high clay content.

Ahmed *et al.* (1997) present a comprehensive study of the potential of using an alum WTR as a soil ameliorant. They reported on the water retention characteristics (Figure 1.2) of the alum WTR aggregates and concluded that very little change in water holding capacity occurred between -30 and -1500kPa. This means that there was very little plant available water (PAW). While they did not give a clear explanation for this, it was speculated that the majority of pores within WTR aggregates were $<2\mu\text{m}$ in size. The effect of adding alum WTR to an Urrbrae red-brown earth was also examined. Water treatment residue was added at rates of 0, 200, 400, 800 and 1600 Mg ha^{-1} in a field study. Bulk density was reduced significantly ($p<0.01$), while total porosity and infiltration rate increased significantly ($p<0.01$). Particle density and air-filled porosity showed decreases, but these changes were not significant.

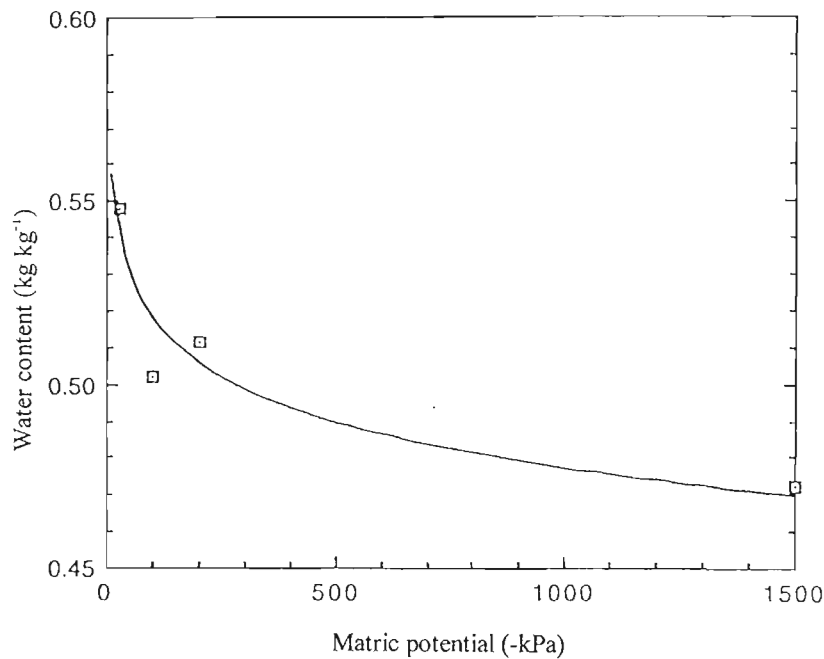


Figure 1.2 A water retention curve of an alum water treatment residue (adapted from Ahmed *et al.*, 1997).

Dayton and Basta (2001) examined 17 WTRs from Oklahoma for plant available water (PAW). They found that the median value of 139 g kg^{-1} was within the typical range for soils (63 to 300 g kg^{-1}). They concluded that while some WTRs may have high water holding capacities, PAW may be quite low. This corroborates the findings of Ahmed *et al.* (1997).

A very comprehensive study examining the physical properties of WTR was conducted by Moodley (2001). Although only a single polymer WTR was used, in depth investigations were conducted on the physical properties of the both WTR and WTR-amended soils. Two field experiments and laboratory investigations were designed to study the influence of WTR, at rates of 0, 80, 320 and 1280 Mg ha⁻¹, on the water retention, hydraulic conductivity, evaporation, aeration, aggregation and soil strength of a variety of soil types. Moodley (2001) found that soil bulk density decreased with increasing rate of WTR addition (regardless of soil type used). An increase in porosity was noted, with consequent increases in water retention at saturation. Little change was recorded for PAW. Saturated hydraulic conductivity showed a marked increase with higher rates of applied WTR, and this was attributed to the increased porosity and the stable nature of the WTR aggregates. This is in agreement with the evidence presented by Skene *et al.* (1995). Air permeability was increased, but little change in aggregate stability was reported for the soils amended with WTR. However, a cautionary note was made, stating that while it appears that the WTR degrades slowly, especially when protected from extremes in weather conditions (such as when incorporated in soil), there may be negative impacts if the WTR were to degrade to its constituent particles. As the WTR is formed by the coagulation of fine material, the possibility exists that over time the bonds holding the particles as discrete aggregates will degrade, and large amounts of silt and clay could be released into the environment. This may lead to detrimental impacts on drainage and aeration, and may also impact on soil chemical properties.

While it generally seems that WTRs have few adverse impacts on soil physical properties, it is necessary to heed the warning of Moodley (2001) to ensure that apparent improvements are not temporary. Unfortunately, most attention has been given to chemical properties (which frequently are immediately measurable), whereas the physical limitations may only be manifested after chemical and physical degradation of the material. Further studies to examine the rates and degree of WTR breakdown would assist in predicting long-term impacts.

1.4.2 Chemical properties

Most studies give, at the very least, a basic overview of the chemical properties of the WTR used in any particular study. While this provides a large amount of data on the basic chemical characteristics, it also makes comparisons difficult due to varying methods of analysis. Basta

(2000) presents an outline of the chemical characteristics of a range of WTRs taken from different sources (Table 1.1).

Table 1.1 Typical elemental composition and selected chemical properties of water treatment residues (adapted from Basta, 2000)

| Major elements | g kg ⁻¹ * |
|-----------------------------------|-----------------------|
| N | 0.495 (0.256) |
| P | 0.226 (0.248) |
| K | 1.7 (0.04 - 5) |
| Ca | 2.7 (0.3 - 5) |
| Mg | 0.45 (0.24 - 0.8) |
| Trace elements | mg kg ⁻¹ * |
| As | 14.7 |
| Cd | 1.0 (<0.1 - 2) |
| Cr | 187 (40 - 513) |
| Cu | 234 (135 - 485) |
| Pb | 79.9 (100) |
| Hg | 1.5 (2.5) |
| Mo | 9.1 (12.9) |
| Ni | 102 (26 - 218) |
| Se | 3.8 (1.5) |
| Zn | 557 (195 - 865) |
| Other | Concentration* |
| Al (g kg ⁻¹) | 21.2 (2.8 - 30) |
| Fe (g kg ⁻¹) | 3.2 (1.2 - 6.6) |
| Si (g kg ⁻¹) | 20 |
| Organic carbon (%) | 3.1 (0.85 - 6.5) |
| pH | 7.0 (5.1 - 8.0) |
| Calcium carbonate equivalence (%) | 15 (10 - 20) |

* Values in parentheses indicate ranges or medians.

Elliott and Dempsey (1991) suggest that, although generally the nature of a WTR is dependant on the treatment process design and performance, most WTRs contain primarily a precipitated hydroxide or carbonate of the coagulant, other treatment additives and the material removed from the raw water (silt, clay, algae, bacteria, colour etc.). However, they do indicate that WTRs have considerably fewer potentially adverse effects on the environment (with the exception of grossly contaminated raw water) than sewage sludges.

Schmitt and Hall (1974) examined a sediment basin residue from the Oak-Ridge Water Treatment Plant in Tennessee by spark source mass-spectrographic analysis for 72 elements, including rare earth elements. They found Fe, Si, Al, K, Ca and Ti to be the most abundant and in similar ratios to those reported for the Earth's crust. The presence of some rare earth elements was attributed to contamination by fly ash from a nearby coal powered steam plant. This was confirmed by photomicrograph images taken of the WTR.

Dayton and Basta (2001) analysed 17 WTRs for a number of chemical parameters to determine their potential as a soil substitute (Table 1.2). They found that the WTRs showed potential to act as soil substitutes as generally nutrients were within typical soil ranges. Where deficiencies existed, it was suggested that moderate amounts of fertiliser could alleviate the problem.

Table 1.2 Some chemical characteristics of 17 water treatment residues and typical soil levels (adapted from Dayton and Basta, 2001)

| Constituent | WTR ¹ | Soil ² |
|---|--------------------|----------------------------|
| pH | 5.3 - 7.8 (7.1) | 5.0 - 8.0 |
| EC (dS m ⁻¹) | 0.22 - 1.1 (0.5) | <4.0 |
| Cation exchange capacity (cmol kg ⁻¹) | 13.6 - 56.5 (30.0) | 3.5 - 35.6 |
| Total N (g kg ⁻¹) | 1.3 - 18.4 (7.0) | 0.2 - 5.0 |
| Organic C (g kg ⁻¹) | 17 - 149 (63) | <30 |
| Soluble - P (µg L ⁻¹) | 34 - 576 (98) | 50 - 200 |
| Olsen - P (mg kg ⁻¹) | 4 - 49 (13.1) | >12 |
| Mehlich 3 - P (mg kg ⁻¹) | 1.6 - 54.4 (6.8) | 32.5 |
| NH ₄ - N (mg kg ⁻¹) | 22 - 140 (51) | 50 - 200 (Total organic N) |
| NO ₃ - N (mg kg ⁻¹) | 3.5 - 123 (17) | |
| K (mg kg ⁻¹) | 19 - 278 (109) | 125 |
| SO ₄ (mg kg ⁻¹) | 12.5 - 453 (138) | 14 |
| Mg (mg kg ⁻¹) | 8 - 1231 (117) | 50 |
| Fe (mg kg ⁻¹) | 8 - 231 (60.4) | 4.5 |
| Zn (mg kg ⁻¹) | 0.12 - 70 (3.0) | 0.8 |
| Ca (g kg ⁻¹) | 0.18 - 21 (2.6) | >0.38 |

1 The range and median (in parentheses).

2 Typical soil values obtained from a variety of sources.

Some studies have examined specific aspects of the chemical make-up of WTRs, in particular metal content and fractionation. Elliott *et al.* (1990b) examined the composition and

distribution of Cd, Cu, Cr, Ni, Pb and Zn in eight alum and Fe WTRs. A five-step chemical fractionation process was used to determine exchangeable, dilute acid extractable, Fe-Mn bound, organically bound, and residual metal concentrations. Total metal concentrations in these WTRs varied widely, but were all below the permissible maximum levels for land application. Chromium and Ni levels were higher in the Fe WTRs, and this was attributed to contaminants in the coagulant. This was supported by Elliott and Dempsey (1991) who reported that, for instance, FeCl_3 derived from pickle liquor from the steel industry had Ni and Cr contaminants that would lead to elevated Ni and Cr in those particular WTRs. Copper, Cr, Ni, Pb and Zn were predominantly bound within the oxide and silicate components, whereas Cd was found to be largely acid extractable or organically bound. They concluded that if these WTRs were applied to acid soils the potential for Cd mobilisation existed. Elliott and Taylor (2000) analysed 32 Pennsylvania WTRs for Mo content. The mean Mo concentration was 3.2 mg kg^{-1} , which is below the land application limit of 18.0 mg kg^{-1} in Pennsylvania. This value was, however, higher than the mean reported for soils, but was not considered problematic. They also found that the Cu:Mo ratio was sufficiently high to prevent molybdenosis (Cu deficiency induced by Mo) in grazing livestock. They suggest that where samples had high Mo concentrations these were linked to the type and source of coagulant, and may reflect high geological concentrations in the watershed concerned.

1.4.3 Phosphorus studies

A number of studies have considered the potential of WTR to remove excess nutrients from contaminated land, water and other waste products. Water treatment residues were found to be beneficial in removing excess N and P from land that had received excess nutrients from poultry litter, manure or fertiliser (Dayton, 1995; Peters and Basta, 1996; Gallimore, 1999; Gallimore *et al.*, 1999; Haustein *et al.*, 2000; Hyde and Morris, 2000; Dayton *et al.*, 2001; Callahan *et al.*, 2002; Elliott *et al.*, 2002).

Some studies have examined the transformation and mechanisms of P uptake in WTR-amended media. Jonasson (1996) conducted a P fractionation study of WTR treated with additional P. It appeared from this study that a large proportion of the added P was chemisorbed by amorphous and crystalline Al and Fe or bound as Ca-P complexes. Cox *et al.* (1997) conducted a fractionation experiment on alum WTR-treated soil (and fertilised with P) to determine the forms and availability of P in the mixtures. They found that 'loosely bound'

or plant available fractions decreased in the mixtures as WTR application rates increased. They also found that Fe, Al and Ca bound fractions increased with increasing WTR application rates. This indicated that P was adsorbed and complexed with these components, making it unavailable for plant uptake. Butkus *et al.* (1998) examined P uptake by metal hydroxides and oxides typically associated with WTRs. They modelled P uptake by hydrous ferric oxide using a diffuse double layer model. From this they found that the amount adsorbed by the hydrous oxide could not account for all P sorbed by WTRs and concluded that a large proportion of the P may also be bound by cationic polymers typically added during WTR thickening. This appears contrary to the general belief that the metal oxides are solely responsible for P adsorption in WTRs.

1.5 Effects on plant growth

A large proportion of the studies have examined the effects of WTRs on plant growth when incorporated into growing media and soil (Table 1.3).

Rengasamy *et al.* (1980) found that maize (*Zea mays*) grown in WTR-amended soil gave the highest yield at WTR application rates of 2 Mg ha⁻¹, with the 20 Mg ha⁻¹ treatment giving a yield intermediate between the control and the 2 Mg ha⁻¹ treatment.

Bugbee and Frink (1985) tested the growth of lettuce (*Lactuca sativa*) and marigolds (*Tagetes* cv. Lemon-drop) in WTR-amended potting materials. They found that lettuce showed P deficiencies when grown in WTR-amended material. The marigolds also gave reduced yields at higher rates of WTR. A concurrent study examined the impact of liquid WTR applied to forested land. While the pH of the soil increased by 0.5 to 1.0 pH unit, no effect was measured on tree growth or nutrient uptake. They concluded that the WTR they tested was not toxic to plants, but may lead to P deficiencies at high application rates under glasshouse conditions.

Elliott and Singer (1988) tested the growth of tomato (*Lycopersicon esculentum*) in an acid silt loam soil treated with a Fe WTR at rates of 0 to 100 g kg⁻¹. They found that the WTR increased soil pH from 5.3 in the control to pH 8.0 in the highest WTR-amended treatment. This was attributed to the high pH and moderate to high calcium carbonate equivalence

(CCE) of the WTR (9.3 and 53.0%, respectively). A reduction in uptake of Cd, Zn, Cu and Ni by the tomato shoots was observed, this being attributed to the high pH.

Table 1.3 Summary of water treatment residue studies that examined the effects of water treatment residues on plant growth

| Author | Type of study | Indicator crop | Type of WTR | Application rate |
|--------------------------------|--------------------|--------------------------------|----------------------------------|------------------------------------|
| Rengasamy <i>et al.</i> (1980) | greenhouse | maize | alum | 2 and 20 Mg ha ⁻¹ |
| Bugbee and Frink (1985) | greenhouse | lettuce and marigolds | alum | 0 - 66% |
| | forest application | sugar maple | alum | 17.5 Mg ha ⁻¹ |
| Grabarek and Krug (1987) | forest application | sugar maple | alum | 15.5 Mg ha ⁻¹ |
| Elliott and Singer (1988) | greenhouse | tomato | iron | 20 - 100 g kg ⁻¹ |
| Heil and Barbarick (1989) | greenhouse | sorghum-sudangrass | alum, iron, polymer | 5 - 25 g kg ⁻¹ |
| Geertsema <i>et al.</i> (1994) | forest application | pine | alum | 0, 6.5 and 9.3 Mg ha ⁻¹ |
| Lucas <i>et al.</i> (1994) | greenhouse | fescue | alum | 0, 1, 2 and 4% |
| Skene <i>et al.</i> (1995) | greenhouse | broadbeans | alum, polymer | 2, 4 and 10% |
| Ahmed <i>et al.</i> (1997) | greenhouse | lawnglass | alum | 0 - 1600 Mg ha ⁻¹ |
| | field experiment | lawnglass | alum | 0 - 1600 Mg ha ⁻¹ |
| Ippolito <i>et al.</i> (1999) | greenhouse | blue grama, western wheatgrass | alum- co- applied with biosolids | 0 - 250 g kg ⁻¹ |
| Basta <i>et al.</i> (2000) | greenhouse | bermudagrass | alum | 100% |
| Codling <i>et al.</i> (2002) | greenhouse | wheat | alum | 0 - 50 g kg ⁻¹ |
| Ippolito <i>et al.</i> (2002) | greenhouse | blue grama, western wheatgrass | Alum, co- applied with biosolids | 0 - 10 g kg ⁻¹ |

Heil and Barbarick (1989) tested the growth of sorghum-sudangrass (*Sorghum bicolor* L. Moench 'NB280S' – *S. sudanese* (Piper) Stapf) in alum and Fe WTR-amended soils. They found that low application rates of either alum or Fe WTR (5 and 10 g kg⁻¹) gave the highest yields, without causing P deficiencies. They also found that Fe deficiencies were corrected when low rates of Fe WTR and higher rates of alum WTR were used on a calcareous soil. Trace metal concentrations were all within acceptable ranges.

Lucas *et al.* (1994) found that an alum WTR reduced tall fescue (*Festuca arundinacea*) growth in a greenhouse study. Although they found WTR additions led to P deficiencies, these were overcome by doubling the recommended P fertilisation rate. They also reported that Mn and Cu concentrations were increased in plant tissue at the higher WTR rates, but neither these nor the resulting reduced yield were a cause for concern. It was noted that, while pot experiments may indicate how the WTR may affect plant growth, these results are not always directly translatable to field conditions.

Skene *et al.* (1995) compared the growth and elemental composition of the foliage of broad beans (*Phaseolus vulgaris*) grown in a soil treated with either an alum or a polymer WTR applied at rates of 20, 40 and 100 g kg⁻¹. They concluded that these WTRs may have potential as growth media, but would require fertilisation for optimal plant growth. They found that the polymer WTR supplied some macro-nutrients and did not immobilise P as much as the alum WTR. Basta *et al.* (2000) examined P uptake by bermudagrass (*Cynodon dactylon*) grown in three different WTR-amended soils. They found that an addition of 200 mg P kg⁻¹ did not increase P availability in the WTRs, but it did increase plant concentrations. They concluded that the WTRs exhibit similar behaviour to allophanic soils that require large P additions to improve the growth of crops.

Ahmed *et al.* (1997) conducted laboratory, glasshouse and field studies and found that the alum WTR used resulted in no detrimental impacts on soil properties. They also report on a number of favourable characteristics. These include increased N availability, neutral to alkaline pH, and reasonable calcium carbonate equivalence. They found that the yield of 'lawngrass' generally increased with WTR application up to rates of 1600 Mg ha⁻¹ in both pot and field experiments. They did note, however, that in the pot experiment, a rate of 800 Mg ha⁻¹ and in the field experiment, a rate of 1600 Mg ha⁻¹, inhibited seed germination. This was attributed to the coarse nature of the WTR, but they suggest that the self-mulching nature of the material would cause rapid breakdown into finer particles. This would possibly improve seed contact with the soil and improve germination. This is in line with the comments of Skene *et al.* (1995) and Moodley (2001). Ahmed *et al.* (1997) also found that in the pot experiment, P concentrations in plant tissue decreased with increasing application rates of WTR, but this was not evident in the field. They concluded that while in the short-term WTR additions could lead to P deficiencies, it does not appear to present any long-term problems in the field. They also report on concerns about Al toxicity, but found that background soil

concentrations were above those of the WTR examined. Elliott and Dempsey (1991) suggest that, as soil Al concentrations are typically high, the factors controlling Al solubility (such as pH) will determine potential toxicity. As many WTRs are reported to increase pH in the soil (due to some liming potential), the potential for Al toxicity is low, and has not been reported in any WTR studies in the literature covered in this review.

Grabarek and Krug (1987) examined the effect on the nutrient uptake of sugar maple forest stands when an alum WTR was surface applied. Concern was expressed over Al toxicity, metal leaching and P adsorption, but their findings indicated that Al toxicity and metal leaching would not be problematic. They reported that the WTR had a strong P binding capacity, but this was seen to be lower than the binding capacity of soils in the area studied and would not cause long-term P deficiencies in the forest trees. In a similar study, Geertsema *et al.* (1994) examined the effect of an alum WTR applied to pine plantation research plots. They found that it had no effect on soil, groundwater or growth of pine trees 30 months after application, although it was noted that in the short-term (eight months after WTR application) N levels in the groundwater were elevated over the control treatment. They indicate that while short-term concerns regarding P deficiencies are reported, it is unlikely to be problematic in the longer term, especially at the field scale. In the South African context, the generally high P sorbing capacity of WTRs may be problematic due to the generally low P status of local soils. However, as indicated by Geertsema *et al.* (1994), these concerns may be confined to glasshouse investigations, as frequently they are not evident on the field scale.

1.6 Codisposal with biosolids

Ippolito *et al.* (1999 and 2002) tested the growth of bluegrama (*Bouteloua gracilis*) and western wheatgrass (*Agropyron smithii*) in mixtures of WTR and biosolids at varying rates mixed into soil. Ippolito *et al.* (1999) found that increasing WTR application rate, co-applied with a constant amount of biosolid, increased bluegrama dry matter yield, while decreasing shoot P and Al concentrations. This was possibly a dilution effect. The western wheatgrass yield was not affected by co-application, but Al concentrations decreased.

Ippolito *et al.* (2002) found that increasing WTR application co-applied with biosolids decreased P concentrations and increased Al concentrations in bluegrama. Similar results were found for western wheatgrass. Both studies conclude that WTR has the ability to

strongly adsorb P, and caution against excessively high application rates when co-applied with biosolids, as a large fraction of the available biosolids P would become unavailable for plant uptake.

1.7 Discussion and conclusions

Although in general WTRs are associated with reduced P availability, there appear to be few other negative impacts. Results from studies are not always consistent, but some trends are apparent. Most WTRs have a lime component, and thus have a liming potential. This may be beneficial in increasing the pH of acid soils. Most WTRs seem to supply a moderate amount of N, Ca, Mg and K, and may contain adequate to high concentrations of micro-nutrients. Frequently where metal concentrations have been noted as elevated, they have still been within typical soil ranges and have not caused aberrations in plant growth. Some authors have cautioned against applying WTRs to acid soils in the event that some of these metals may be mobilised and lead to toxicity for plants. There is also frequent concern over Al toxicity, usually associated with alum WTRs. Generally these concerns have been discredited due to naturally high soil Al concentrations and the alkaline nature of many WTRs (Ahmed *et al.*, 1997).

Many studies have indicated that addition of WTRs to soils may lead to P deficiencies of treated soils, or reduce the availability of added fertiliser P, but this appears to be restricted to greenhouse studies. Although only a few field studies have been conducted, they have not indicated any substantial problems with P deficiency, especially over the long-term (30 months). This has led to the suggestion that the WTRs may act as slow release fertilisers, initially absorbing P and then releasing it again as the WTR degrades (Geertsema *et al.*, 1994). The P sorbing capacity of some WTRs has been seen as a potential benefit under conditions of excessive P. Frequent over-fertilisation, excessive use of P enriched manures and long-term P applications can lead to enriched P run-off and leaching. Due to the P sorbing capacity of WTRs, reported by the majority of authors, they may be beneficially used to reduce these levels. Furthermore, as suggested earlier, they may then also act as P stores and become slow release P fertilisers. However, these suggestions are speculative and would depend on the WTRs ability to release bound P, and this is possibly related to the rate of WTR breakdown and the existing P status of the soil.

There is some evidence that suggests that WTR may reduce PAW, although no studies have found that plant growth has been reduced due to inadequate water availability. This is probably due to the high water holding capacity of the WTRs, and the conditions under which the experiments were conducted. As these studies are generally conducted under controlled environments, little chance exists that plants grown in WTR-treated material would be exposed to wilting point conditions. This would mean that the actual effect on plant growth has not been determined, and it is rather a theoretical or indicator value determined in a laboratory. Improved aeration and water infiltration are generally reported, though. If these WTRs are applied to heavy textured soils, the improved infiltration and aeration may be considered positive effects.

It is obvious that the nature of WTRs is variable, their make-up being related to the quality of raw water and treatment process. This makes it difficult to predict the effect of WTRs on soil properties and plant growth. A common aspect though is the P sorbing potential of most WTRs. Future studies could possibly focus on desorption and degradation mechanisms. This would greatly improve the understanding of WTRs and would possibly allow for better predictions on long-term effects of applying WTRs to land. The paucity of literature relating to South African conditions does not allow predictions to be made of possible outcomes of applying South African WTRs to local soils. It is likely that raw water sources and treatment processes will vary, as will the characteristics of suitable land for application. Consideration would have to be given to both the nature of the WTRs and soil, before a suitable land application strategy is applied.

Chapter 2

Characterisation of South Africa's water treatment residues

2.1 Introduction

Although studies exist that focus on water treatment residues (WTRs), little attention has been given to those produced in South Africa. As this particular study formed a component of a larger investigation examining the effects of land disposal of WTR on soil physical and chemical properties (Introduction), it was necessary to collect and describe WTRs produced in SA. This was deemed important considering the range of water sources in SA and the different treatment processes used to purify raw water.

The primary objectives of this study were:

- to distribute a questionnaire to obtain information regarding water treatment processes and current disposal practices of water treatment facilities in SA;
- to collect WTR samples from water treatment facilities and plants for chemical and physical characterisation; and
- to select two of these WTRs for a glasshouse study to investigate their suitability for disposal on selected materials.

2.2 Materials and methods

2.2.1 Questionnaire

As the first step in collecting information from the water treatment facilities, a list was compiled of the potable water producers in SA. This was achieved by collating lists obtained from Umgeni Water, Department of Water Affairs and Forestry, Water Research Commission and other sources.

A questionnaire was developed that requested information on the name and location of the treatment facility (or multiple facilities in the case of more than one treatment plant); the source of the raw water; volume of WTR produced seasonally; WTR solids content; coagulants and flocculants used and dosing concentrations; WTR thickening procedures and

current disposal practices. Other questions included enquiries about work that may have been conducted on any particular WTR and the amount of interest in the current study by these companies.

The questionnaire (Appendix 1) was based on the assumption that the information obtained would reflect the chemicals and dosing practices currently used. It should be noted that some treatment facilities change their treatment processes depending on the quality of the raw water and availability of treatment chemicals. However, it does give an indication of the range of treatment processes used to produce potable water in SA. The treatment facilities were then contacted and arrangements made to send the questionnaire to the relevant persons for completion. The questionnaire was also posted on the project website (www.wrc.org.za/interest/sludgeweb/index.htm).

In addition to the questionnaire, a sample of air dry WTR was requested from each treatment plant for use in the laboratory characterisation. Five WTRs were collected or received for laboratory studies. While the request for residues was poorly met, three of the WTRs were from the largest water suppliers in South Africa i.e., Rand Water, Cape Metropolitan Council – Faure Water Treatment Plant (WTP) (Faure 1), and Umgeni Water – Midmar Water Treatment Works. The other WTRs were from Amatola Water (East London) and Midvaal Water Company (Stilfontein). A second WTR was received from the Faure WTP (Faure 2) to represent a residue produced when a dramatic change in raw water quality led to a change in the water treatment process. Not all analyses were carried out on this second sample from Faure.

2.2.2 Chemical and physical analyses

The air dry WTRs were milled and passed through a 2 mm sieve. pH was measured in distilled water and 1M KCl using a Radiometer PHM210 pH meter with a standard glass electrode. A soil:solution ratio of 1:2.5 was used (10 g WTR:25 mL solution), and left to stand for about 45 minutes with occasional stirring using a glass rod. Electrical conductivity (EC) was measured at 25°C using a Radiometer CDM83 electrical conductivity meter in a 1:5 WTR:water solution (United States Salinity Laboratory Staff, 1954). Extractable cations and cation exchange capacity were measured by saturating with Sr^{2+} and subsequent replacement

with NH_4^+ (Hughes and Girdlestone, 1994); a description of the method is presented in Appendix 2.

Nitrogen was determined on <0.5mm samples by combustion using a LECO Nitrogen Analyser (Discipline of Animal Science, University of Natal, Pietermaritzburg). Nitrate and ammonia were extracted with 2M KCl (Maynard and Kalra, 1993) and solution concentrations determined colorimetrically using a TRAACS 2000 continuous flow auto analyser. Plant available phosphorus was estimated by extracting with AMBIC (ammonium bicarbonate) solution and P was determined colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990) on a Varian Cary 1E UV-Visible spectrophotometer (UV-Vis). Exchangeable acidity and exchangeable Al were measured according to Sims (1996), with Al being measured by atomic absorption spectrophotometry (AAS, Varian SpectraAA-200). Calcium carbonate equivalence (CCE) was measured according to Jackson (1958). Organic carbon (OC) was digested by potassium dichromate oxidation and determined titrimetrically (Walkley, 1947). Total C and S were analysed by combustion using a LECO CNS 2000 auto analyser (Soil Fertility and Analytical Services Laboratory, KZN Department of Agriculture and Environmental Affairs, Cedara).

Particle size distribution was determined by an adaptation of the pipette method (Gee and Bauder, 1986; Appendix 3). Particle density was determined according to the method of Blake and Hartge (1986). Gravimetric water content was determined at -33kPa and -1500kPa using pressure plate apparatus. Plant available water (PAW) was considered to be the difference in water content between -33 and -1500kPa (Dayton and Basta, 2001).

X-ray diffraction analysis on random powders was carried out on a Philips PW1050 diffractometer using monochromated $\text{Co K}\alpha$ radiation from 3° to 75° 2θ with a scanning step of 0.02° at 1° per minute counting interval. The diffraction data were captured by a Sietronics 122D automated micro-processor attached to the X-ray diffractometer. The samples were then qualitatively analysed to determine major mineralogical components.

Total elemental concentrations were measured by X-ray fluorescence spectrometry (XRF, Geology Section, University of Natal, Durban). DTPA extractable (plant available) Cd, Cu, Co, Cr, Mn, Fe, Ni, Pb and Zn were determined by the method of Liang and Karamanos (1993). The toxicity characterisation leaching procedure (TCLP) (USEPA, 1992) was used to

determine potential toxic effects of metal leaching. A five-step fractionation procedure was used to determine exchangeable (1M MgCl_2), dilute acid extractable (1M NaOAc at pH 5), Fe/Mn bound (0.175M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 0.1M $\text{H}_2\text{C}_2\text{O}_4$), organically bound (0.1M $\text{Na}_4\text{P}_2\text{O}_7$) and residual fractions (acid digest, HF, HNO_3 and HClO_4) of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (Elliott *et al.*, 1990b). Elemental solution concentrations were determined by atomic absorption spectrophotometry.

Phosphorus adsorption isotherms were determined for the WTRs. An adaptation of the method presented by Basta *et al.* (2000) was used. Twenty-five mL of a range of P solutions (0, 2, 4, 8, 16 and 32 mg P L^{-1}) were added in a 0.01M CaCl_2 matrix to 1 g of material. The WTR and P solution mixtures were shaken on a reciprocating shaker for 18 h, allowed to settle for a few minutes and the supernatant filtered and analysed for P colorimetrically (The Non-Affiliated Soil Analysis Work Committee, 1990).

2.3 Results and discussion

2.3.1 Questionnaire

Responses to questionnaires varied and were disappointing in some instances. Questionnaires were returned by 37 water treatment plants, which represented 11 water treatment authorities (of a possible 21). One water treatment authority (Albany Coast Water) indicated that they operated a desalinisation plant producing saline brine that was returned to the ocean and is therefore not included in this study. Appendix 4 gives the complete list of authorities (and treatment plants) that returned questionnaires and some of the responses to the questions. Some questionnaires were incompletely filled out, possibly due to either poor record keeping or poor understanding of the questions asked. Due to this, only the data relating to raw water treatment are reported here (chemicals and dosages used). Where treatment facilities did not give dosing concentrations, they were omitted from the calculations. In most instances, the questionnaires that were returned gave a range of chemical dosing that reflected seasonal changes in raw water quality. A median value was determined from these ranges and used in the summary statistics (Table 2.1).

Table 2.1 Summary data of the types and quantities of various water treatment chemicals used by the treatment facilities that returned adequately answered questionnaires

| | Chemical or additive ¹ | | | | | | | | |
|---------------------------------|-----------------------------------|-----|------|------|-------------------|------|-------|------|-------|
| | Lime | Ben | AlSO | FeSO | FeCl ₃ | LCP | ActSi | NaAl | Other |
| n ² | 33 | 6 | 8 | 2 | 6 | 30 | 3 | 2 | 4 |
| n ³ | 28 | 6 | 8 | 2 | 5 | 23 | 2 | 2 | 3 |
| Mean (mg L ⁻¹) | 16.3 | 2.2 | 20.7 | 8.5 | 6.7 | 7.5 | 4.3 | 2.8 | 14.4 |
| SE | 18.7 | 0.8 | 22.5 | 3.6 | 6.5 | 11.6 | 2.5 | 0.4 | 8.5 |
| Median (mg L ⁻¹) | 8.6 | 2.0 | 9.0 | 8.5 | 4.3 | 3.8 | 4.3 | 2.8 | 16.0 |
| Range min (mg L ⁻¹) | 2.3 | 1.5 | 1.6 | 5.9 | 0.8 | 0.1 | 2.5 | 2.5 | 5.3 |
| Range max (mg L ⁻¹) | 80.0 ⁴ | 3.3 | 65.0 | 11.0 | 16.5 | 57.0 | 6.1 | 3.1 | 22.0 |

¹ Lime - lime, Ben – bentonite, AlSO - Al₂(SO₄)₃.14H₂O, FeSO - Fe₂(SO₄)₃, FeCl₃ - FeCl₃, LCP – long-chain- organic-polymer, ActSi - activated silica, NaAl - sodium aluminate, Other - activated charcoal and CO₂.

² Total number of plants that indicated use of a particular chemical, but not all indicating dosages.

³ Number of plants that indicated the use of a particular chemical and gave dosages. Summary statistics are based on these data.

⁴ Rand Water indicated the use of 60 to 80 mg L⁻¹ CaO, but have been included under conventional lime for convenience.

Lime (or liming agents) were the most commonly used treatment chemicals, followed by the use of organic polymers. Lime is used as a conditioning agent to improve the efficacy of the coagulants and flocculants (itself acting as a flocculant under some conditions) and this may account for its common usage. Organic polymers have proven to be efficient and are relatively cost effective in treating raw water, as well as being used as thickening and dewatering agents. Bentonite is used by some treatment facilities where raw water turbidity is very low because this reduces the efficacy of the coagulants and flocculant (Mr. Farhad Ali, Manager, Midmar Water Treatment Works, *pers. comm.* 2002). The use of Al and Fe salts was limited and they were frequently used in conjunction with polymers. Of these salts, Al₂(SO₄)₃.14H₂O was the most commonly used followed by FeCl₃. The use of Fe₂(SO₄)₃ was only reported by two treatment plants. Other chemicals used included carbon dioxide and activated charcoal. Carbon dioxide has been used in place of liming agents and the use of activated charcoal is usually associated with raw water that has odour and colour problems. This was the situation at the Faure Water Treatment Plant (Firgrove, Western Cape), where dissolved organics and algae cause colour and odour problems in the raw water (Mr. Dawid Smit, Manager, Faure Water Treatment Plant, *pers. comm.* 2003).

2.3.2 Chemical characteristics

Table 2.2 gives the basic chemical properties of the WTRs.

Table 2.2 Some chemical properties of the water treatment residues from five of South Africa’s water treatment facilities

| Property | | Rand | Midmar | Midvaal | Amatola | Faure 1 | Faure 2 |
|--|------------------|--------|--------|---------|---------|---------|---------|
| pH | KCl | 8.66 | 7.78 | 7.66 | 6.94 | 6.19 | 7.23 |
| | H ₂ O | 9.16 | 8.00 | 8.36 | 7.66 | 6.56 | 7.84 |
| Electrical conductivity (mS m ⁻¹) | | 35.10 | 71.50 | 31.27 | 25.33 | 16.40 | 40.50 |
| Total C (g kg ⁻¹) | | 82.20 | 48.80 | 25.60 | 23.80 | 118.90 | nd |
| Organic carbon (%) | | 1.23 | 2.77 | 1.60 | 1.96 | 3.34 | 10.27 |
| Exchangeable acidity (cmol _c kg ⁻¹) | | 0 | 0.20 | 0.10 | 0.10 | 0.10 | nd |
| Exchangeable aluminium (cmol _c kg ⁻¹) | | 0.07 | 0.06 | 0.06 | 0.07 | 0.05 | nd |
| Calcium carbonate equivalence (%) | | 109.06 | 5.92 | 4.48 | 4.09 | 6.94 | nd |

nd not determined.

The pH of the WTRs ranged from 6.19 to 8.66 in KCl and from 6.56 to 9.16 in water. In most instances, the WTRs were alkaline, with only the Faure 1 WTR having a marginally acidic pH. These WTRs are similar to the typical pH range of 5.10 to 8.00 reported by Basta (2000). Electrical conductivity ranged from 16.4 to 71.5 mS m⁻¹, suggesting low to moderate water solubility of salts in the WTRs. These ECs should not present a problem for land disposal, as they are low. Dayton and Basta (2001) similarly report a range of 22.0 to 110.0 mS m⁻¹ for 17 Oklahoma WTRs. Total C in the materials was generally high. The Faure 1 WTR had the highest C concentration, but this was expected, as the residue was a product of the removal of dissolved organics using activated charcoal and lime. It is likely that the Faure 2 had a higher total C content, but this was not determined. The other residues probably reflected the amount of lime (presence of carbonates) and organic polymer added during water treatment and the amount of organic material removed from the raw water. Organic carbon content ranged from 1.2 to 10.3%. The Faure 2 WTR had the highest OC content. Basta (2000) reports values from 0.8 to 6.5%, whilst Dayton and Basta (2001) report values from 1.7 to 14.9%. Elliott *et al.* (1990a) report a mean total OC content of 3% for WTRs from seven Pennsylvania water treatment facilities. Exchangeable acidity ranged from 0.0 to 0.2 cmol_c kg⁻¹ and exchangeable Al from 0.05 to 0.07 cmol_c kg⁻¹. These values suggest very low acid producing potential for these WTRs, possibly a function of the lime components in the residues and their neutral to

alkaline pHs. Calcium carbonate equivalence generally showed low liming potential for the WTRs (all <7%), with the exception of Rand WTR that had a CCE of 109%, due to the high dosing with CaO. The CCE of WTRs examined by Elliott *et al.* (1990a) ranged from 10 to 20%.

2.3.3 Physical characteristics

Table 2.3 gives some of the physical characteristics of the WTRs studied.

Table 2.3 Some physical properties of the water treatment residues from five of South Africa’s water treatment facilities

| Property | Rand | Midmar | Midvaal | Amatola | Faure 1 | Faure 2 |
|---|-----------------------------|--------|-----------|-----------------|---------|-----------|
| Texture ¹ | clay | sand | clay loam | sandy clay loam | sand | silt loam |
| Particle size distribution (%) | Sand (0.053 – 2 mm) | 1.2 | 91.6 | 37.5 | 67.5 | 91.0 |
| | Coarse silt (0.02-0.053 mm) | 1.6 | 2.4 | 2.0 | 1.1 | 1.3 |
| | Fine silt (0.002-0.02 mm) | 34.3 | 2.5 | 31.4 | 2.1 | 4.3 |
| | Clay (<0.002mm) | 62.9 | 3.5 | 29.1 | 29.3 | 3.4 |
| Particle density (g cm ⁻³) | 2.43 | 2.23 | 2.09 | 2.02 | 2.02 | nd |
| Plant available water (g kg ⁻¹) | 18.17 | 53.81 | 40.46 | 8.66 | 29.64 | 197.72 |

1 Soil Classification Working Group (1991).
nd not determined.

The particle size distribution of the WTRs was variable. Samples that were easily dispersed tended to have high amounts of fine silt and clay (Rand, Midvaal and Faure 2), while the remaining WTRs, that were less easily dispersed, had higher amounts of sand (Faure 1, Amatola and Midmar). There was also a marked change in the particle size distribution of the Faure WTRs, due to the change in raw water quality and treatment processes. It might be expected that generally the residues would exhibit high clay and silt fractions. However, the residues are formed by the coagulation of fine particles into larger stable aggregates, and so frequently exhibit a coarse texture. Skene *et al.* (1995), Ahmed *et al.* (1997) and Moodley (2001) report similar characteristics of WTRs. It is possible that as the WTR aggregates degrade, the finer particles would be released, potentially leading to negative impacts on soil physical properties (Moodley, 2001). The particle density ranged from 2.02 to 2.43 g cm⁻³. Plant available water ranged considerably from 8.66 to 197.72 g kg⁻¹. Generally all values were low except for the Faure 2 WTR, which was considerably higher than the Faure 1 WTR.

Dayton and Basta (2001) similarly report a wide range of values of PAW from 26 to 416 g kg⁻¹.

2.3.4 Nutrient concentrations

Nutrient concentrations were variable (Table 2.4), depending on the source of the residue. Total S was generally quite low, with the Faure 1 showing an elevated concentration, probably mostly due to the addition of Fe₂(SO₄)₃ in the treatment process. Nitrate-N ranged from 9.7 to 94.2 mg kg⁻¹ and NH₄-N from 26.33 to 358.4 mg kg⁻¹. Total N concentrations ranged from 200 to 5200 mg kg⁻¹. This indicates that a considerable proportion of the N is bound in less soluble (or less available) forms in the WTRs, except in the Rand WTR, where NO₃-N and NH₄-N accounted for about 60% of the total nitrogen, even though the total concentration was low. Although Dayton and Basta (2001) report a much higher range in total N from 1 300 to 18 400 mg kg⁻¹, the concentrations of NO₃-N (22 to 140 mg kg⁻¹) and NH₄-N (3.5 to 123.0 mg kg⁻¹) were similarly low. Ammonium bicarbonate extractable P was generally very low, except for the Midvaal and Faure 2 WTR. The CEC of the WTRs ranged from 15.9 to 41.8 cmol_c kg⁻¹ and, with the exception of the Rand WTR, all were above 25 cmol_c kg⁻¹.

Table 2.4 Nutrient concentrations of the water treatment residues from five of South Africa’s water treatment facilities

| Property | Rand | Midmar | Midvaal | Amatola | Faure 1 | Faure 2 |
|--|-------|--------|---------|---------|---------|---------|
| Total S (mg kg ⁻¹) | 10 | 210 | 130 | 320 | 1 200 | nd |
| Total N (mg kg ⁻¹) | 200 | 1 000 | 2 800 | 2 600 | 5 200 | 4 800 |
| NO ₃ – N (mg kg ⁻¹) | 94.23 | 16.80 | 12.76 | 31.80 | 9.65 | 11.53 |
| NH ₄ – N (mg kg ⁻¹) | 26.33 | 170.15 | 358.38 | 62.40 | 108.48 | 32.10 |
| AMBIC P (mg kg ⁻¹) | 4.70 | 4.46 | 31.51 | 0.74 | 6.33 | 21.50 |
| Extractable cations (cmol _c kg ⁻¹) | Ca | 4.54 | 31.01 | 38.28 | 28.49 | 37.31 |
| | Mg | 15.75 | 9.13 | 14.33 | 8.76 | 13.42 |
| | Na | 1.37 | 0.52 | 0.56 | 0.88 | 0.66 |
| | K | 0.38 | 0.51 | 0.78 | 0.39 | 0.30 |
| Cation exchange capacity (cmol _c kg ⁻¹) | 15.85 | 26.59 | 41.81 | 25.38 | 33.47 | 35.79 |

nd not determined.

The Rand WTR had a Ca:Mg ratio of about 1:3, whilst the remaining WTRs were 2:1 or 3:1. This indicates that a Ca:Mg imbalance could occur in soils treated with the Rand WTR. Although the Rand WTR had very high concentrations of total Ca (Appendix 5), it is clear that this Ca is in an unavailable form. Generally extractable Ca and Mg appear to be at adequate plant available concentrations, but K may be too low for satisfactory plant growth.

2.3.5 Other analyses

X-ray diffraction analysis revealed small amounts of quartz in all samples. While it may be that sand particles are removed from the raw water, the most likely source is the introduction of sand grains to the WTR during backwashing of sand filters used during water treatment. Except for the Faure WTRs, all other WTRs had detectable calcite, most notably the Rand WTR. The obvious source is the use of lime in the water treatment process, and although Rand Water uses CaO, calcite is formed, a result of the use of CO₂ during water treatment. The apparent lack of calcite in the Faure 1 sample may be due to the slightly acidic nature of this WTR. All the WTRs showed the presence of clays (which was expected), but these were not characterized. The organic nature of the Faure WTRs and the generally poorly crystalline nature of the other WTRs made determination of mineralogical properties by XRD particularly difficult. Rengasamy *et al.* (1980) also found that, apart from small amounts of quartz in their alum residue, the XRD pattern consisted largely of disordered materials, probably amorphous hydrous oxides of Al, Fe and Mn, as well as organic fractions.

These results of total elemental analysis (Appendix 5) can be considered to represent the worst case potential for toxicity problems. This would be pertinent if acidic conditions caused dissolution of precipitated elements and mineral particles. As indicated by Schmitt and Hall (1974), who examined a sediment basin residue for 72 elements, Si, Ca, Mg, K, Fe and Ti were generally the most abundant elements in the WTRs. As mentioned earlier, a notable point is the very high total Ca and Mg contents of the Rand WTR when compared to the other WTRs. The Rand WTR also had a relatively low total Al. Similarly, the Faure 1 WTR had a low Al content. This is not surprising considering that this latter residue is a product of the removal of dissolved organics (rather than turbidity removal). Total Cr and Ni were highest in the Midvaal WTR, perhaps a result of contamination from the FeCl₃ coagulant (Elliott and Dempsey, 1991).

Plant available metals (DTPA extractable) and TCLP extractable metals (Table 2.5) are possibly better indicators of potential metal mobility, availability and toxicity to plants.

Table 2.5 DTPA and TCLP extractable metals (mg kg^{-1}) of the water treatment residues

| Element | Rand | | Midmar | | Amatola | | Midvaal | | Faure 1 | | Faure 2 | |
|---------|-------|------|--------|------|---------|-------|---------|-------|---------|------|---------|------|
| | DTPA | TCLP | DTPA | TCLP | DTPA | TCLP | DTPA | TCLP | DTPA | TCLP | DTPA | TCLP |
| Cd | 0.66 | bd | 0.42 | bd | 0.45 | bd | 0.50 | bd | bd | bd | 0.30 | nd |
| Co | 0.42 | bd | 0.63 | bd | 0.70 | bd | 1.06 | bd | 1.82 | bd | 2.59 | nd |
| Cr | 1.16 | bd | 1.18 | bd | 1.45 | bd | 1.86 | bd | bd | bd | bd | nd |
| Cu | 1.76 | bd | 5.78 | bd | 1.39 | bd | 7.16 | bd | 0.41 | bd | 0.29 | nd |
| Fe | 48.70 | bd | 87.70 | bd | 63.30 | bd | 246 | 5.50 | 65.00 | 7.90 | 42.70 | nd |
| Mn | 38.80 | 310 | 88.90 | 235 | 13.23 | 44.80 | 22.10 | 539 | 725 | 849 | 420 | nd |
| Ni | 0.56 | bd | 1.34 | bd | 0.61 | bd | 3.39 | bd | bd | bd | bd | nd |
| Pb | 0.20 | bd | 1.07 | bd | 2.67 | bd | 1.43 | bd | 0.79 | bd | 1.64 | nd |
| Zn | 1.48 | bd | 3.01 | bd | 2.04 | bd | 8.64 | 23.70 | 10.27 | 2.51 | 10.89 | nd |

bd below detection.

nd not determined.

Generally, DTPA extractable metal concentrations were low, with Fe and Mn concentrations being elevated in most of the WTRs. The Faure 1 WTR had exceptionally high Mn values. This was attributed to contaminants in the $\text{Fe}_2(\text{SO}_4)_3$ used to treat the raw water. A sample of the liquid $\text{Fe}_2(\text{SO}_4)_3$, used by the Faure WTP, was analysed for Mn and found to contain 723 mg L^{-1} Mn. The Faure WTRs also had somewhat elevated concentrations of Zn, possibly also from the coagulant used. Nickel concentrations in the Midvaal WTR were slightly elevated, possibly due to contamination from the Fe-salt used for water purification. The TCLP extraction gave high concentrations of Mn for all WTRs, while the remaining elements occurred at low concentrations or were below the detection limits. This suggests that these WTRs would not present metal toxicity problems if disposed of to land, possibly with the exception of Mn. This would be particularly true if acid or reducing conditions persisted, releasing unavailable forms of Mn (Adriano, 1986). The alkaline nature of most of the WTRs would aid in immobilising the metals.

In the five-step fractionation extraction (Table 2.6), little was removed as exchangeable, with the Fe concentration of the Midvaal and Faure 1 being notable, probably due to the use of Fe-salts in their treatment processes. Only small amounts of Mn were exchangeable, with the Rand WTR being below detection.

Table 2.6 Five step fractionation of water treatment residues from five of South Africa’s water treatment facilities. Results from Elliott *et al.* (1990b) are given for comparative purposes

| Rand | | | | | | Midmar | | | | | |
|---------|-------------------|------------------|-------------|---------------|----------|--|-------------------|-----------|-------------|---------------|----------|
| | MgCl ₂ | Weak Acid | Fe/Mn bound | Organic bound | Residual | | MgCl ₂ | Weak Acid | Fe/Mn bound | Organic bound | Residual |
| Cd | bd | 2.9 ¹ | 0.4 | 8.20 | 24.0 | Cd | bd | bd | bd | bd | 30.0 |
| Co | bd | 5.2 | bd | bd | 47.0 | Co | bd | 0.3 | bd | bd | 80.0 |
| Cr | bd | bd | bd | 2.60 | 339.0 | Cr | bd | bd | bd | 21.4 | 254.0 |
| Cu | 0.1 | 7.8 | 9.0 | 8.80 | 32.0 | Cu | bd | 4.5 | 15.2 | 0.6 | 58.0 |
| Fe | bd | 62.6 | 4 908.8 | 2 004.4 | 24 743.0 | Fe | bd | 244.5 | 14 373.5 | 4 962.4 | 5 6450.0 |
| Mn | bd | 941.8 | 1 541.4 | 141.8 | 1 057.0 | Mn | 23.3 | 1 026.7 | 6 869.6 | 1 668.4 | 528.0 |
| Ni | 3.6 | 13.3 | bd | bd | 38.0 | Ni | 1.17 | bd | bd | bd | 62.0 |
| Pb | bd | 84.8 | 4.0 | bd | 340.0 | Pb | bd | 26.4 | bd | bd | 460.0 |
| Zn | bd | 8.9 | 0.9 | bd | 87.6 | Zn | bd | 3.6 | bd | bd | 129.2 |
| Amatola | | | | | | Midvaal | | | | | |
| | MgCl ₂ | Weak Acid | Fe/Mn bound | Organic bound | Residual | | MgCl ₂ | Weak Acid | Fe/Mn bound | Organic bound | Residual |
| Cd | 0.3 | bd | 0.2 | bd | 41.0 | Cd | 0.2 | 0.3 | bd | bd | 57.0 |
| Co | bd | 1.3 | bd | bd | 121.0 | Co | bd | 1.9 | bd | bd | 114.0 |
| Cr | bd | bd | bd | 26.4 | 417.0 | Cr | bd | bd | 20.0 | 47.4 | 352.0 |
| Cu | bd | 0.3 | 8.4 | bd | 41.0 | Cu | bd | 3.3 | 21.8 | 3.6 | 67.0 |
| Fe | bd | 47.5 | 4 522.2 | 2 386.8 | 58 373.0 | Fe | 245.9 | 1 062.2 | 23 998.2 | 5 889.6 | 58 378.0 |
| Mn | 4.5 | 36.3 | 96.0 | bd | 248.0 | Mn | 7.1 | 426.7 | 854.2 | 222.8 | 275.0 |
| Ni | 4.5 | 1.7 | bd | bd | 63.0 | Ni | bd | 16.2 | 37.6 | 4.6 | 84.0 |
| Pb | bd | 18.4 | bd | bd | 620.0 | Pb | bd | 12.0 | bd | bd | 740.0 |
| Zn | bd | 1.3 | bd | bd | 150.5 | Zn | bd | 14.2 | 27.5 | 6.3 | 186.5 |
| Faure 1 | | | | | | Elliott <i>et al.</i> (1990b) ² | | | | | |
| | MgCl ₂ | Weak Acid | Fe/Mn bound | Organic bound | Residual | | MgCl ₂ | Weak Acid | Fe/Mn bound | Organic bound | Residual |
| Cd | 0.1 | 0.3 | 1.6 | bd | 58.0 | Cd | 5.8 | 19.0 | bd | 38.0 | 38.0 |
| Co | bd | 1.8 | 10.0 | 5.40 | 138.0 | Co | nd | nd | nd | nd | nd |
| Cr | bd | bd | 16.0 | 47.4 | 225.0 | Cr | 1.0 | 2.4 | 38 | 10.0 | 49.0 |
| Cu | bd | 0.2 | 7.4 | 2.6 | 57.0 | Cu | 1.0 | 5.8 | 32 | 6.3 | 55.0 |
| Fe | 737.0 | 1 111.4 | 91241.8 | 2 111.6 | 289850.0 | Fe | nd | nd | nd | nd | nd |
| Mn | 5.0 | 897.1 | 1 847.0 | 991.4 | 3 235.0 | Mn | nd | nd | nd | nd | nd |
| Ni | 3.7 | 6.6 | 20.6 | bd | 73.0 | Ni | 0.6 | 12.0 | 31.8 | 4.5 | 51.0 |
| Pb | bd | 11.2 | bd | bd | 830.0 | Pb | 4.2 | 2.6 | 8.4 | 13.0 | 72.0 |
| Zn | bd | 63.3 | 134.2 | 44.3 | 362.8 | Zn | 0.5 | 17.0 | 34 | 6.0 | 42.0 |

bd below detection. nd not determined. 1 Concentrations are expressed as mg kg⁻¹.
2 mean values reported by Elliott *et al.* (1990b) using the same procedure on 7 WTRs.

As expected, dilute acid extraction removed a greater concentration of metals, with Fe and Mn tending to show the greatest increase in concentration. Also notable was the increase in Zn concentration of the Faure 1 WTR and the Pb concentration of the Rand WTR. This indicates that these elements may become mobile under acid conditions. Gibson and Farmer (1986, cited by Elliott *et al.*, 1990b) indicate that the sum of the exchangeable and dilute acid extractable fractions represent the maximum availability of the metals to plants. On this basis, Elliott *et al.* (1990b) found Cd to be the likely cause of concern in the WTRs they studied, accounting for some 25% of the total Cd concentration. In the WTRs examined here, the Cd fractions accounted for very small proportions (0 to 8%) of the total Cd concentration. Nickel, however, was more readily removed by these extractants for all the WTRs except the Midmar WTR, and Mn represented about a quarter of the total content for the Rand and Midvaal WTRs. Lead in these two fractions represented a large proportion of the total for the Rand WTR (19.8%). It would appear that under acid conditions, the Rand WTR is likely to release moderate amounts of these metals. This may be due to these cations being bound as carbonate compounds that readily undergo dissolution (releasing the metals) under acid conditions.

The chromate extractable (Fe/Mn oxide bound) fractions tended to show high Fe and Mn concentrations, with Zn increasing in concentration for the Faure 1 WTR. For all the WTRs studied Fe concentrations were highest in the chromate extractable fractions (apart from residual concentrations) accounting for between 7 and 27% of the total Fe content. Manganese accounted for a high proportion of the Fe/Mn oxide bound fraction (2% to 68% of the total Mn concentration). The organically bound fraction again showed moderate levels of Mn and Fe. Concentrations of Cr were also notable in the Midmar, Amatola, Midvaal and Faure 1 WTRs. The residual fraction showed sharp increases in all metal concentrations for all WTRs. These metals are considered unavailable, as they are bound in mineral lattices, are not readily released, and as for the XRF data, represent the worst case.

2.3.6 Phosphorus adsorption

The P adsorption isotherms for the WTRs are shown in Figure 2.1. To give an indication of how the WTR adsorption isotherms may compare to soils, a Hutton and a Westleigh topsoil (Soil Classification Working Group, 1991) were included in the study. These were selected as they have previously been used as test soils for the land application of the Midmar WTR (Moodley, 2001). The P requirement value of 0.2 mg L^{-1} (Fox and Kamprath, 1970) is

commonly used as the benchmark to determine P sorption potential, but is considered by some authors as being excessively high (Dayton, 1995). A number of lower values have been proposed that are generally soil and crop specific. For the purposes of this investigation the value of 0.05 mg L⁻¹ reported by Zupancic (1996) will also be used. This value was derived for bermudagrass, being an estimate from other similar values for grain crops. In addition, a hypothetical value of 1 mg L⁻¹ was also selected for comparative purposes. The amounts of P sorbed to achieve these residual values (taken from Figure 2.1) are given in Table 2.7. The Faure 1 WTR sorbed the most P to achieve a residual concentration of 0.05 mg L⁻¹, while the Midmar WTR sorbed slightly less, but was still moderately high. The Rand WTR sorbed considerably less, and the Amatola and Midvaal WTRs sorbed very little P. However, all the WTRs were higher than both the Hutton and Westleigh topsoils. To achieve 0.2 mg L⁻¹ residual P in solution there were sharp increases in P sorption for all WTRs and soils.

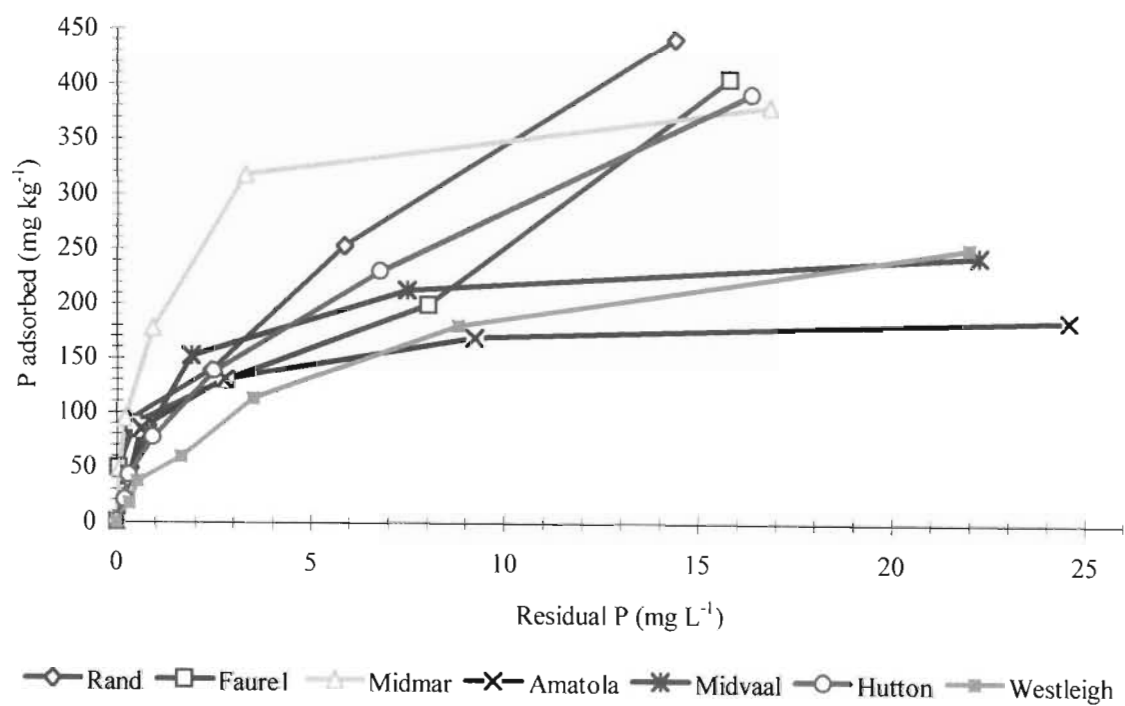


Figure 2.1 Phosphorus adsorption isotherms for the Rand, Midmar, Faure 1, Amatola and Midvaal water treatment residues. Two additional soils (Hutton and Westleigh) are included for comparative purposes.

Table 2.7 The amount of P sorbed by the Rand, Faure 1, Midmar, Amatola and Midvaal water treatment residues and a Hutton and Westleigh topsoils to achieve residual P concentrations of 0.05, 0.20 and 1.00 mg L⁻¹

| Sample | Amount of P sorbed (mg kg ⁻¹) to achieve the residual P values (mg L ⁻¹) indicated | | |
|-----------|--|-------------------|-------------------|
| | 0.05 ¹ | 0.20 ² | 1.00 ³ |
| Rand | 25 | 68 | 104 |
| Faure | 50 | 64 | 96 |
| Midmar | 38 | 88 | 180 |
| Amatola | 5 | 24 | 90 |
| Midvaal | 5 | 24 | 90 |
| Hutton | 5 | 19 | 75 |
| Westleigh | 3 | 10 | 38 |

1 Zupancic (1996).
2 Fox and Kamprath (1970).
3 Hypothetical value.

The most notable increases were for the Amatola and Midvaal WTRs that showed almost five-fold increases in P sorption, although the Midmar WTR had the highest P sorption at this concentration. The sorption capacities of the WTRs to achieve 1 mg L⁻¹ solution P were similar for the Rand, Faure 1, Amatola and Midvaal, while the Midmar WTR sorbed about double that of the other residues. The Hutton and Westleigh topsoils sorbed less than the WTRs. However, if one considers the trends shown in Figure 2.1, it is clear that the Rand and Faure 1 WTR have not achieved maximum sorption, while the Midmar, Amatola and Midvaal WTR appear to be tending toward some sorption maximum. Zupancic (1996) reports P sorption values of 10, 250 and >800 mg kg⁻¹ to achieve a residual P of 0.05 mg L⁻¹ for three alum WTRs and so the values reported here (from 5 to 50 mg kg⁻¹) can be considered to be at the low end of the possible range.

The P sorbing potential of WTRs have been reported and used to test their ability to remove P from soils, manures and water (e.g. Shreve *et al.*, 1995; Jonasson, 1996; Peters and Basta, 1996; Cox *et al.*, 1997; Ippolito *et al.*, 1999; Haustein *et al.*, 2000). These authors have generally attributed the P sorbing capacity to the presence of amorphous and crystalline oxides and hydroxides of either Al and Fe, or Ca compounds. A number of mechanisms may be responsible for P sorption. Jonasson (1996), using a P fractionation process, found that fertiliser P added to an alum WTR appeared to be chemisorbed by amorphous and crystalline Fe and Al as well as forming stable Ca-P compounds. The organic fraction was considered to be of little importance due to the low organic matter content of the WTR. Dayton *et al.* (2001), however, attribute adsorption to Al and Fe oxides and hydroxides, rather than

precipitation reactions, as the primary mechanism for P sorption by the WTRs they studied. They indicated that the formation of Ca-P minerals (other than monetite and brushite) would be too slow for the 15 hr batch equilibration they used. Furthermore, they did not observe concurrent losses of Ca and P from solution that would be necessary for the precipitation of these two minerals. Butkus *et al.* (1998) modeled P adsorption by Fe oxide compounds. They concluded it was likely that, while metal oxides are responsible for P adsorption, cationic organic polymers may bind with P via a complexation reaction.

In a separate experiment to determine maximum sorption (including possible precipitation reactions), P was added to the WTRs over a range of 250 to 6 000 mg L⁻¹. Data from this experiment (not shown) indicate that for all the WTRs there are a number of 'steps', until some maximum was reached. As a hypothetical exercise, for demonstrative purposes, a P residual concentration of 3 000 mg L⁻¹ was selected and P sorption determined from the sorption curves. At this concentration the amount of P sorbed was 20 000, 12 000, 8 000, 4 000, and 2 000 mg kg⁻¹ for the Rand, Faure 1, Midmar, Midvaal and Amatola WTRs, respectively. While these values have little meaning in practical situations, it does indicate the high sorbing potential of these residues, suggesting complex interactions with lime, hydrous oxides, organics and clay components of the WTR, leading to multi-layer adsorption and precipitation reactions.

2.4 General discussion and conclusions

Although some of the WTRs studied had low nutrient concentrations, in particular N and P, they may be useful to improve conditions for plant growth in degraded or nutrient-poor soils. The alkaline nature of most of the WTRs (in particular the Rand WTR) would enable them to increase the pH of acid soils. Fertiliser additions may help overcome some of the nutrient deficiencies, possibly with the exception of P. The moderately high P sorbing capacity of these WTRs indicates that large amounts of added P could be removed, but this study has not considered desorption of P from these residues. Desorption and plant growth studies may better show how these residues might affect P availability. A number of studies have reported on the P sorption capacity of WTRs and how they may reduce P uptake by plants grown in glasshouse investigations in either pure WTR or mixtures of soil or potting media and WTR (*inter alia* Elliott and Singer, 1988; Heil and Barbarick, 1989; Skene *et al.*, 1995; Ahmed *et al.*, 1997; Basta *et al.*, 2000; Codling *et al.*, 2002). However, field experiments have shown

that plant uptake is apparently not affected by additions of WTR (Grabarek and Krug, 1987; Geertsema *et al.*, 1994).

In some instances, the high amounts of Mn may lead to toxicity problems (in particular the Faure and Midmar WTRs), especially if used under acid or reducing conditions. It is unlikely that any of the other metals would be problematic. Furthermore, consideration needs to be given to land application rates as well as existing background soil concentrations and characteristics and the intended purpose of the land treated with the WTR (Elliott *et al.*, 1990a). These factors may influence the rate and frequency of application.

A number of studies have reported on improved soil physical properties as a result of WTR additions (Rengasamy *et al.*, 1980; Skene *et al.*, 1995; Ahmed *et al.*, 1997; Moodley, 2001). While not intensively investigated here, some WTRs had high water holding capacity. This may improve water retention of some soils, while improving infiltration of heavy textured soils, if the WTRs are applied to land. However, Moodley (2001) has indicated that if the WTR applied to a soil were to decompose to its constituent fractions (clay and silt in most instances) then clogging of soil pores may lead to reduced infiltration and water retention in affected soils. In an ongoing investigation using the field trials reported on by Moodley (2001), data suggest that, after five years, the physical properties of a Hutton soil treated with WTR at application rates as high as 1280 Mg ha⁻¹ are returning, after having shown increased water retention, to similar conditions as the control treatments (personal observation, see project website: <http://www.wrc.org.za/interest/sludgeweb/index.htm>).

As part of the present study, two WTRs were selected for further investigation of their potential for land application. As a larger study is currently in progress using the Midmar WTR (Moodley, 2001; Buyeye, unpublished data) it was decided that WTRs with different characteristics to the Midmar WTR should be selected and ideally should represent the other two major water suppliers in South Africa, namely the Cape Metropolitan Council and Rand Water. Rand Water supplies the greater Johannesburg region, while the Faure WTP is the Cape Metropolitan Council's largest plant supplying Khayelitsha (and Cape Town at times) in the Western Cape.

The Rand Water WTR was chosen for the following reasons:

- the very different chemical nature of the material (when compared to other WTRs);
- the availability of material from Rand Water's Panfontein disposal ponds; and
- pre-existing communications between Rand Water and a nearby coal mine to use the residue on the mine as part of the mine's reclamation strategy.

The choice of the Faure 1 WTR was based on similar criteria to the Rand WTR i.e.:

- the high Fe and organic carbon content of the residue (obviously different from the Rand WTR);
- the large volume of residue produced and its availability; and
- the potential of the residue to be used on nutrient-poor sands (common to the local region) to improve fertility.

The Rand WTR was used to test the growth of selected grass species on mixtures of Rand WTR and material from the nearby mine (Chapter 3). The Faure 1 WTR was applied to a nutrient-poor sand to test whether the growth of a crop could be improved (Chapter 4).

Chapter 3

Land application of Rand Water's water treatment residue to selected mine material and coal combustion ash: laboratory and glasshouse investigations

3.1 Introduction

The use of industrial by-products to improve the conditions of mine wastes for plant growth and to simultaneously act as a potential disposal option for the by-product have been reported extensively in the literature. Sopper (1992) reviews a number of studies that consider the use of sewage sludge as an ameliorant on mine dumps to improve soil properties and plant growth. Other materials used on mine tailings have included fly ash (Taylor and Schuman, 1988; Welden *et al.*, 1999; Bhumbra *et al.*, 2000; Seoane and Leiros, 2001); sawdust (Roberts *et al.*, 1988); and manures and papermill sludges (Haering *et al.*, 2000). Revegetation of coal combustion ash dumps has been reported by Mulhern *et al.* (1989), Carlson and Adriano (1991), and van Rensburg *et al.* (1998). There are no studies that examine the use of WTRs on mined land, although Dayton and Basta (2001) and Zupancic (1996) consider the use of WTR as a soil substitute, and the potential of WTR to aid in mined land reclamation. However, they did not specifically test the effects of applying WTR to mined land, thus making it difficult to predict how either material would be affected by the other.

As outlined in Section 2.4, the Rand Water WTR (RWTR) was selected for investigations into its use on a coal mine (New Vaal Colliery) near Vereeniging, South Africa. Potential uses of the RWTR included, amongst others, as fill material in voids, a liming material, neutralisation of acid hotspots and to improve plant growth. As the particular interest of the wider project (Introduction) was land application of the WTRs and the effects on soil properties and plant growth, it was decided that laboratory and pot experiments would be used to investigate the latter aspect. The mine management suggested materials to be used in the investigations, and these included the sandy soil material removed from the land prior to mining (3 to 6 m in depth), the overburden material removed from above the coal seams consisting of shale interspersed with calcareous nodules and coal fragments, and a coal combustion residue (fly ash) from a nearby power plant (Lethabo Power Station).

The primary objectives of the study were:

- to characterise the spoil, soil and ash;
- to examine the effect of RWTR on the properties of the spoil, soil and ash;
- to measure the yield response of three grass species grown in mixtures of RWTR and the selected materials; and
- to determine nutrient uptake by the grass species tested.

It is important to note that this was a preliminary investigation into the land disposal or application of RWTR at this mine. Land disposal offers a potentially viable option of discarding of one waste type onto another or using properties of a soil to assimilate the waste. In this instance the disposal of RWTR onto the mine may present Rand Water with a suitable disposal option, reducing the need to lagoon and store large quantities of waste WTR. The benefit to the mine would only be realised if use of the RWTR on their materials proved successful and assisted reclamation efforts.

3.2 Materials and methods

3.2.1 Material collection and preparation

The spoil and soil were collected from storage piles at New Vaal Colliery in January 2002. Ash (few days old) from Lethabo Power Station, and the RWTR (few weeks old, dry material) from Rand Water's disposal site (Panfontein) were collected on the same day. The material was transported to the University of Natal, Pietermaritzburg and air-dried before further handling. The ash, soil and RWTR were all mechanically milled and passed through a 2 mm sieve. The ash and soil material tended to be naturally fine, passing easily through a 2 mm sieve. The spoil material was collected as large coarse fragments, and needed to be milled to a suitable size fraction for the pot experiment. The size chosen (crushed to pass through a 8.5 mm sieve) was considered to best represent a compromise between field conditions and a suitable seedbed for plant establishment. It was suggested that the spoil material weathered to a gravel texture, over a few months, when exposed to environmental conditions (Mr. Pieter Smit, mine environmental officer, *pers. comm.* 2002).

3.2.2 Laboratory materials and methods

All laboratory analyses were conducted on <2 mm material. Where required the materials were mixed at the same rates used in the pot experiment i.e., 50, 100, 200 and 400 g kg⁻¹ RWTR mixed with either ash, soil or spoil (Section 3.2.3). For water retention studies, materials of the same size fraction as in the pot experiment were used.

3.2.2.1 Chemical analyses

The methods used for chemical analyses follow those presented in Section 2.2.2. In addition, saturated pastes were made (United States Salinity Laboratory Staff, 1954) and extracted by suction through Buchner funnels connected to a vacuum pump. Extracts were analysed for Ca, Mg, Na and K by atomic absorption spectrophotometry (Varian SpectraAA-200), electrical conductivity (EC), nitrate (colorimetric analysis using a TRAACS 2000 Auto Analyser) and phosphate (colorimetric, The Non-Affiliated Soil Analysis Work Committee, 1990) on a Varian Cary 1E UV-Visible spectrophotometer. The pH and EC of mixtures of ash, spoil or soil with RWTR were also determined in a 1:5 material:water extract.

3.2.2.2 Physical analyses

Particle size distribution was determined by an adaptation of the pipette method (Gee and Bauder, 1986; Appendix 3). Percent aggregation was measured by the double pipette method (United States Salinity Laboratory Staff, 1954).

3.2.2.3 Water retention studies

As it was not possible to obtain field cores of RWTR and waste mixtures, water retention was measured using repacked soil cores to simulate the conditions of the pot experiment. Stainless steel core rings (75 mm i.d. x 50 mm tall) were packed with the same mixtures used in the pot experiment. The 50 g kg⁻¹ treatment was omitted due to equipment constraints. Each ring had a fine open mesh cloth placed underneath to prevent loss of material. The volume of the rings was calculated and mixtures were added to give the same bulk density as the mixtures in the pot experiment. The cores were allowed to saturate for 24 h, allowed to drain for about 10 minutes and then weighed. This was taken as the saturated mass of the core. The cores were

then placed on a tension table at -1 kPa matric potential. After 48 h equilibration time, the cores were re-weighed and the tension increased to -2 kPa. This process was repeated for -3, -4, -5, -7.5 and -10 kPa matric potentials. The cores were then placed on ceramic pressure plates in pressure pot apparatus and subjected to 30 and 100 kPa pressure (to give equivalent matric potentials of -30 kPa and -100 kPa) for about seven days or until equilibrium was reached. Gravimetric water loss was then converted into an equivalent volumetric water content using the equation:

$$\theta_v = \theta_m \times \rho_b \times \rho_w^{-1}$$

where, θ_v is the volumetric water content ($\text{m}^3 \text{m}^{-3}$), θ_m is the mass water content (kg kg^{-1}), ρ_b is the bulk density of the mixture (kg m^{-3}) and ρ_w is the density of water (kg m^{-3}).

3.2.3 Study 1 - Pot experiment

3.2.3.1 Establishment of the pot experiment

Each pot (200 mm i.d.) had a fine glass-wool membrane placed over the drainage-holes and was lined with a polypropylene bag, which had a few holes punched in the base. Pure ash, soil and spoil were then placed in a pot, lightly tapped a few times and the mass of each material determined. A small space was left at the top of each pot to allow for watering. These masses were then used as the basis for all subsequent calculations, and all pots were filled with mixtures of RWTR and waste to the respective masses of the pure waste material. The rates chosen were 50, 100, 200 and 400 g kg^{-1} , as well as unamended treatments of pure waste material (control pots). Part of the objective of the study was to determine upper limits for land application of RWTR, and this range was selected to extend from a moderately low to a very high application rate. Furthermore previous, unpublished work had examined similar rates and shown some success on material from the mine.

Basal fertiliser was applied to each treatment. Current mine practice is to apply 1 Mg ha^{-1} of 2:3:2 (22) (N:P:K) and 1 Mg ha^{-1} of single superphosphate per hectare. A fertility analysis indicated that the ash had adequate available P, thus none was added to these treatments. The ash received 0.1973 g N and 0.1973 g K per pot as KNO_3 and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The soil and

spoil treatments received 0.1948 g N, 0.187 g K and 0.618 g P per pot as $\text{NH}_4\text{H}_2\text{PO}_4$ and KH_2PO_4 . This approximated the fertiliser additions used by the mine.

The three grass species chosen for the experiment, based on current mine practice, were *Digitaria eriantha* Steud., *Cenchrus ciliaris* L. and *Eragrostis teff* (Zucc.). *Eragrostis teff* is a fast growing annual, whilst *Cenchrus ciliaris* and *D. eriantha* are slower establishing, but more persistent perennial species. The grasses were planted from seed and the pots covered in clear polypropylene sheets until germination. Tap water was used to maintain the pots at or near field capacity. The EC of the tap water ranged from 9.02 to 10.12 mS m^{-1} and pH ranged from 6.8 to 7.7. Plants were thinned to three plants per pot at 20 to 30 mm height. Where germination and initial growth was poor, seedlings (germinated in petri dishes) were planted to ensure the correct number of plants per pot. This was necessary for a number of the ash treatments. The pots were watered every 2 to 3 days to avoid water stress. The frequency of watering increased as plants grew larger and evapotranspiration increased.

The experiment was arranged in a randomised complete block design (Rayner, 1967) with a single treatment factor (RWTR application rate). Pots were arranged in three blocks (replicates) according to the random design generated by the statistical package Genstat V (Release 4.1, Lawes Agricultural Trust, Rothamsted Experimental Station). Each pot was placed on a collecting tray, to prevent loss of sediment and water. The experiment started in March 2002. The mean glasshouse temperature range was from 14 to 28°C (min=10°C, max=31°C) for the duration of the trial.

3.2.3.2 Grass harvest

It quickly became apparent that growth in the ash treatments was very poor, and most plants died within the first few weeks. This aspect of the pot experiment was therefore terminated once it was apparent that the selected plant species would not germinate or develop much beyond the seedling stage. Consequently no harvests or leaching trials were conducted on these treatments. A second study was then established using the ash material and RWTR (Study 2, Section 3.6).

The remaining treatments were first harvested 45 days after establishment (DAE). The plants were harvested at approximately 10 mm above soil level, and the material placed in paper

bags and dried at 65°C for two days in a forced-draft oven. Dry mass yield was determined for each pot. The pots were then refertilised with the previously described fertiliser applications. Additional fertiliser was added at 80 DAE to correct apparent N and P deficiencies in some treatments. In addition a mixture simulating 1 Mg ha⁻¹ of 2:3:1 N:P:K fertiliser was added as (NH₄)₂HPO₄ and KH₂PO₄. Fertiliser was blanket applied across all treatments to ensure equal conditions in all treatments. As *E. teff* is an annual it was reseeded after each harvest. The experiment was harvested again at 115 DAE. The pots were refertilised with 2 Mg ha⁻¹ of the 2:3:1 fertiliser. *Digitaria eriantha* and *C. ciliaris* were finally harvested at 150 DAE, while the *E. teff* treatments were allowed to continue for an additional three weeks due to slower growth. The harvesting times chosen were based largely on the overall performance of the treatments, which led to some variation in growth periods.

Statistical analyses of yield data for each grass species were carried out by one-way ANOVA and where significant F-statistics were found, LSD comparisons were made, at the 5% level of significance, using the software package Genstat V (Release 4.1, Lawes Agricultural Trust, Rothamsted Experimental Station). Raw yield data are available from the author subject to suitable confidentiality agreements.

Plant material from each harvest was sent for analysis of P, K, Na, Ca, Mg, Cu, Mn, Zn, Fe and B (where sample size permitted) to the Soil Fertility and Analytical Services Laboratory (KZN Department of Agriculture and Environmental Affairs, Cedara). Due to some treatments having inadequate sample, the replicates were bulked for chemical analysis. This unfortunately negates statistical analysis. No sample of the first harvest was available for *D. eriantha* grown in the soil treated with 400 g kg⁻¹ RWTR due to poor growth. The remaining plant material was analysed for total nitrogen by combustion using a LECO Auto Analyser (Discipline of Animal Science, University of Natal).

3.2.3.3 Leaching experiment

After each harvest, and prior to fertiliser additions, excess water was added to each pot to permit the collection of approximately 100 mL of leachate. Any excess leachate was returned to the surface of the pot. The leachate was analysed for pH and EC. Apart from these leaching events the pots remained unleached.

3.3 Results and discussion

As the characteristics of the RWTR were discussed in Chapter 2, only new data will be presented and discussed here.

3.3.1 Chemical properties

3.3.1.1 General

Table 3.1 gives some selected chemical characteristics of the pure materials.

Table 3.1 Some chemical characteristics of the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery

| Property | | Ash | Spoil | Soil |
|--|------------------|-------|-------|------|
| pH | KCl | 9.50 | 7.48 | 4.88 |
| | H ₂ O | 9.63 | 7.63 | 6.14 |
| Electrical conductivity (mS m ⁻¹) | | 32.50 | 38.20 | 4.21 |
| Organic carbon (%) | | bd | 7.87 | bd |
| Exchangeable acidity (cmol _c kg ⁻¹) | | bd | 3.26 | 0.38 |
| Exchangeable aluminium (cmol _c kg ⁻¹) | | 7.14 | bd | 0.08 |

bd below detection.

The soil material was acidic, while the spoil and ash had an alkaline pH. The ash was the most alkaline. Adriano *et al.* (1980) report pH values of ashes ranging from 5.5 to 12.0, while van Rensburg *et al.* (1998) reported a pH of 9.5 (in water) for a fine coal ash dump in South Africa. Adriano *et al.* (1980) attribute the pH of the ash to the concentrations of S, Ca and Mg in the coal, where high S contents tend to give acidic ash, and high Ca and Mg an alkaline ash. The marginal alkalinity of the spoil was attributed to the presence of calcareous material (Mr. Pieter Smit, mine environmental officer, *pers. comm.* 2002). It was indicated, however, that the mine had nett acid drainage, due to acid hotspots within the spoil deposits. The material collected was considered to be representative of the general spoil conditions. The EC of the soil was the lowest and the spoil the highest. The ash was marginally lower than the spoil. The EC data suggest that salt leaching would not be a problem. Exchangeable acidity was highest in the spoil, but negligible in the ash and soil, while exchangeable Al was high in the ash and negligible in the spoil and soil. The high exchangeable Al content of the ash may be due to the very high pH, the value representing soluble Al rather than exchangeable Al.

The spoil was the only waste that had a notable concentration of organic carbon (OC). This was attributed to the presence of coal fragments in this material. It was not expected that the ash would contain any OC, as this is lost during combustion (Adriano *et al.*, 1980). The soil material was a mixture of the topsoil and sub-surface horizons originally over the parent rock that is now the spoil material. The soil material was very uniform in nature and extended down a few metres (Mr. Pieter Smit, mine environmental officer, *pers. comm.* 2002). It is likely that the sample collected for this study originated mostly from the lower horizons where OC content would be low.

3.3.1.2 Nutrient concentrations

The nutrient concentrations of the pure materials are given in Table 3.2.

Table 3.2 Some nutrient concentrations of the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery

| Property | | Ash | Spoil | Soil |
|--|----|------|-------|-------|
| Total nitrogen (mg kg ⁻¹) | | bd | 700 | bd |
| NO ₃ – N (mg kg ⁻¹) | | 9.23 | 9.15 | 9.00 |
| NH ₄ – N (mg kg ⁻¹) | | 2.33 | 4.16 | bd |
| AMBIC extractable P (mg kg ⁻¹) | | 151 | 4.32 | bd |
| Extractable cations (cmol _c kg ⁻¹) | Ca | 7.76 | 8.71 | 5.03 |
| | Mg | 1.52 | 3.25 | 4.66 |
| | Na | 2.18 | 1.49 | 1.66 |
| | K | 0.28 | 0.14 | 0.24 |
| Cation exchange capacity (cmol _c kg ⁻¹) | | 5.64 | 12.91 | 12.77 |

bd below detection.

Total N was below the detection limit for the ash and soil, and at a low concentration in the spoil. Low concentrations of NO₃-N and NH₄-N were also found. Extractable P concentrations were low in the soil and spoil, but exceptionally high in the ash. Similar results were found by the original fertility analysis and were supported by XRF data that showed very high total P concentration in the ash (Appendix 5). Pathan *et al.* (2003) reported similar findings on a variety of coal combustion ashes. Extractable Ca was moderate in all the materials. The soil and spoil also showed moderate concentrations of extractable Mg, while the ash was considerably lower. All the materials showed slightly elevated Na concentrations,

while extractable K was low. The CEC of the materials was generally low, the soil and spoil being similar. The ash was very low, even though moderate levels of extractable cations were found. It is possible that the method used to estimate extractable cation concentrations also caused dissolution of some of the bound cations, overestimating these values, in particular Ca.

3.3.1.3 Saturated paste

Saturated paste data (Table 3.3) reflect the trends shown for EC (Table 3.1) and extractable cations (Table 3.2), although concentrations were considerably lower.

Table 3.3 Saturated paste analysis of untreated ash, spoil, soil and the Rand water treatment residue

| Property | | Ash | Spoil | Soil | RWTR |
|--|--------------------|-------|-------|------|-------|
| Saturation % | | 55.1 | 45.3 | 52.3 | 62.0 |
| EC (mS m ⁻¹) | | 238.0 | 328.0 | 36.5 | 146.0 |
| Cations (cmol _c L ⁻¹) | Ca | 1.49 | 0.62 | 0.31 | 1.06 |
| | Mg | 0.15 | 1.48 | 0.08 | 2.82 |
| | Na | 1.46 | 1.20 | 0.11 | 0.07 |
| | K | 0.06 | 0.04 | 0.01 | 0.06 |
| SAR ¹ | | 1.61 | 1.17 | 0.25 | 0.05 |
| Anions (cmol _c L ⁻¹) | NO ₃ -N | 0.06 | 0.01 | 0.01 | 0.98 |

bd below detection.

nd not determined.

1 sodium adsorption ratio = ([Na]/((Ca+Mg)/2)^{0.5})) (from Levy, 2000).

The 1:5 water extracts tended to suggest that salinity would not be problematic, but the EC of the saturated paste extracts indicate potential salinity problems for the ash and spoil. The United States Salinity Laboratory Staff (1954) indicate that soils with an EC of >400 mS m⁻¹, for the saturated paste extract, may reflect soil salinity problems. Further weathering of the ash and spoil material may lead to an increase in EC, that may become problematic to plant growth. It is, however, unlikely under field conditions where adequate leaching would remove excess salts from the rooting zone. The solubility of the base cations tended to be low. The ash had the highest concentrations of Ca and Na, and the spoil showed the highest concentrations of Mg and Na. The Na concentration in the saturated paste extract of the spoil is nearly as high as that reported for extractable Na, indicating that most of the Na is in a readily soluble form. The sodium adsorption ratios (SAR) indicate that sodicity should not be

a problem, though the SAR of the ash and spoil were considerably higher than that of the soil. Concentrations of phosphate were below detection and concentrations of NO₃-N were negligible in the saturated paste extracts, for all materials. The RWTR was also included in this investigation and the Ca and Mg concentrations were moderately high, while Na and K concentrations were low. The phosphate concentration was below detection and NO₃-N concentration was slightly elevated.

3.3.1.4 Elemental concentrations

X-ray fluorescence data (Appendix 5) indicate that the materials consisted mainly of Si and Al, with the ash showing slightly lower concentrations of Si and increased concentrations of Al, when compared to the other materials. Other concentrations of elements were low, except for a high S concentration in the spoil. This suggests that the spoil may have acid-producing potential, especially if this element is in pyritic form (Carrucio *et al.*, 1988).

Plant available metals (DTPA extractable) were generally low (Table 3.4), with elevated Cr concentrations in the ash when compared to the other materials. Iron concentrations were highest in the spoil and ash, but lower in the soil. The soil had notably a higher concentration of Mn than the either the spoil or ash. It is, however, unlikely that the concentrations of plant available metals would lead to toxicity problems.

Table 3.4 Plant available metals (DTPA extractable) for the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery

| | Cd | Co | Cr | Cu | Fe | Mn | Ni | Zn | Pb |
|-------|------------------------|------|------|------|-------|-------|------|------|------|
| | (mg kg ⁻¹) | | | | | | | | |
| Ash | 0.48 | 0.38 | 4.12 | 0.60 | 24.56 | 1.39 | 0.63 | 1.12 | bd |
| Spoil | 0.84 | 1.01 | 0.75 | 2.37 | 26.28 | 7.71 | 1.02 | 4.01 | 1.40 |
| Soil | 0.53 | 0.45 | 0.40 | 0.30 | 6.30 | 25.37 | 0.44 | 0.50 | bd |

bd below detection.

3.3.1.5 pH and electrical conductivity

The pH and EC of the ash decreased with increasing RWTR additions (Table 3.5). The EC decreased notably up to 100 g kg⁻¹ of RWTR added, but remained relatively constant thereafter up to the maximum RWTR addition.

Table 3.5 pH and electrical conductivity (mS m⁻¹) of the ash, spoil and soil treated with 0, 50, 100, 200 and 400 g kg⁻¹ of Rand water treatment residue

| RWTR rate (g kg ⁻¹) | Ash | | Spoil | | Soil | |
|------------------------------------|------|------|-------|------|------|------|
| | pH | EC | pH | EC | pH | EC |
| 0 | 9.63 | 32.5 | 7.63 | 38.2 | 6.14 | 4.2 |
| 50 | 9.54 | 27.9 | 7.73 | 33.1 | 7.48 | 14.3 |
| 100 | 9.48 | 24.7 | 7.78 | 29.8 | 7.66 | 14.4 |
| 200 | 9.41 | 24.0 | 7.88 | 28.7 | 7.83 | 14.1 |
| 400 | 9.30 | 24.5 | 8.01 | 26.8 | 8.00 | 14.3 |

The spoil showed an increase in pH and a decrease in EC with increasing RWTR additions. The soil also showed an increase in pH with increasing RWTR additions. It should be noted though that the initial increase with 50 g kg⁻¹ RWTR added was dramatic, but then smaller increases in pH occurred up to the maximum RWTR application rate. This was possibly due to a low buffering capacity of the soil. These results suggest that addition of RWTR, even at low rates, leads to a high pH that may induce deficiencies, especially of trace nutrients. These results may not reflect long-term changes, however. Under field conditions the effects of leaching, weathering, fertilisation and plants would influence EC and changes in pH. For instance, the high S content of the spoil may lead to acidification, which in turn would increase weathering rates and increase EC and possibly lower pH.

3.3.1.6 Phosphorus adsorption

Phosphorus adsorption curves (Figure 3.1) showed that the ash had an exceptionally high P sorption capacity. To achieve residual P values of 0.05, 0.20 and 1.00 mg L⁻¹ the ash sorbed 12.5, 38.0 and 174.0 mg kg⁻¹ P, respectively. Gray and Schwab (1993) found that bottom ash and fly ash showed high P fixing capacities in a laboratory study. They attributed the P sorption to precipitation reactions rather than adsorption reactions due to the presence of soluble Ca oxides, Ca hydroxides and Ca silicates, and high pH. This had the effect of lowering solution P very rapidly, the consequence of which is that added P would not be available for plant growth. It is probable that a similar mechanism is operative for the ash used in this study. The high sorbing capacities of the ash may cause severe P deficiencies, especially if mixed with the RWTR.

The spoil and soil showed moderately low P sorbing capacities, the soil showing a slightly

higher P sorbing capacity at low P concentrations. The low sorbing capacity of the spoil may be attributed to the heterogeneous nature of the material, and it is likely that once the spoil has undergone some decomposition the P sorption capacity would increase. Pulford and Duncan (1975) examined P adsorption by coal spoil and concluded that amorphous Fe oxides (formed from pyrite oxidation) were largely responsible for the P sorption, although the presence of Al and Ca compounds were not discounted. They also indicate that, as the material weathers, it is likely that P sorption would increase (as more pyrite and other reactive surfaces are exposed) and that sulphate may compete with phosphate for reactive sites. The spoil sorbed 1.6, 6.5 and 20.0 mg kg⁻¹ P and the soil sorbed 2.5, 10.5 and 30.0 mg kg⁻¹ P to achieve residual P concentrations of 0.05, 0.20 and 1.00 mg L⁻¹, respectively.

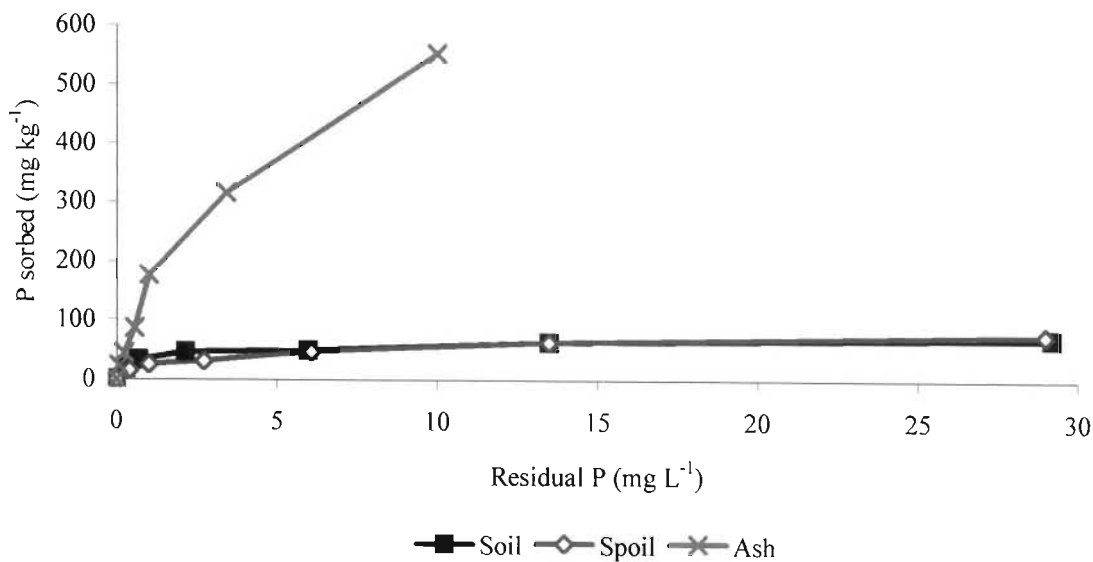


Figure 3.1 Phosphorus adsorption isotherms for the ash, spoil and soil.

3.3.2 Physical properties

Both the soil and spoil had high amounts of sand, and the ash was largely sand and silt with very little clay (Table 3.6).

Table 3.6 Some physical properties of the ash, spoil and soil from Lethabo Power Station and New Vaal Colliery

| Property | | Ash | Spoil | Soil |
|---|-------------------------------|--------------|---------------|-----------------------|
| Texture ¹ | | silt loam | sandy loam | sandy clay loam |
| | Sand (0.053 – 2 mm) | 38.8 | 75.5 | 71.9 |
| Particle size distribution (%) | Coarse silt (0.02 - 0.053 mm) | 16.1 | 3.1 | 4.1 |
| | Fine silt (0.002 - 0.02 mm) | 39.7 | 10.2 | 3.1 |
| | Clay (<0.002mm) | 5.4 | 11.2 | 20.9 |
| Aggregation (%) | | 56.39 | 59.02 | 65.52 |

¹ Soil Classification Working Group (1991).

The particle size distribution of the spoil was expected considering the material was collected as large coarse fragments. Furthermore, as the spoil was only milled to less than 8.5 mm, a large proportion of the material used in the pot experiment was larger than 2.0 mm. Dry sieving showed that 31.13% of material was >4.75mm, 31.93% was between 2.00 and 4.75 mm and 36.94% was <2.00mm. The soil and ash were naturally less coarse. All the materials exhibited a high degree of aggregation, ranging from 56.39 to 65.52%. The RWTR was also included in this investigation and found to be very well aggregated (85.19%).

3.3.3 Water retention studies

The water retention curves for the waste and RWTR mixtures (Figure 3.2) indicate that in all cases increasing RWTR addition increased volumetric water content at all matric potentials. It is likely that the lower bulk density of the RWTR led to the increase in water retention. The increase in water retention of the ash due to the addition of RWTR was less noticeable than in the soil and spoil. The effect of RWTR on the ash was only marked at -100 kPa matric potential for the 400 g kg⁻¹ RWTR treatment, where water content increased from 0.12 m³ m⁻³ in the pure ash to 0.27 m³ m⁻³. It is possible that the similarities in texture and bulk density of the ash and RWTR led to an apparently reduced effect of the RWTR on the retention characteristics of the ash in the wetter range. The effect of RWTR on the spoil was more evident. The low saturation value of the pure spoil material was probably due to the coarse nature of the material. The presence of large pores allowed water to drain freely from the core under gravity leading to an apparently low saturation value. This suggests that for this material the 10 minute drainage period prior to measurement of saturation mass was too long and so underestimated saturation mass. It does, however, imply that this water would not be

available for plant use as it would drain from the rooting zone very readily.

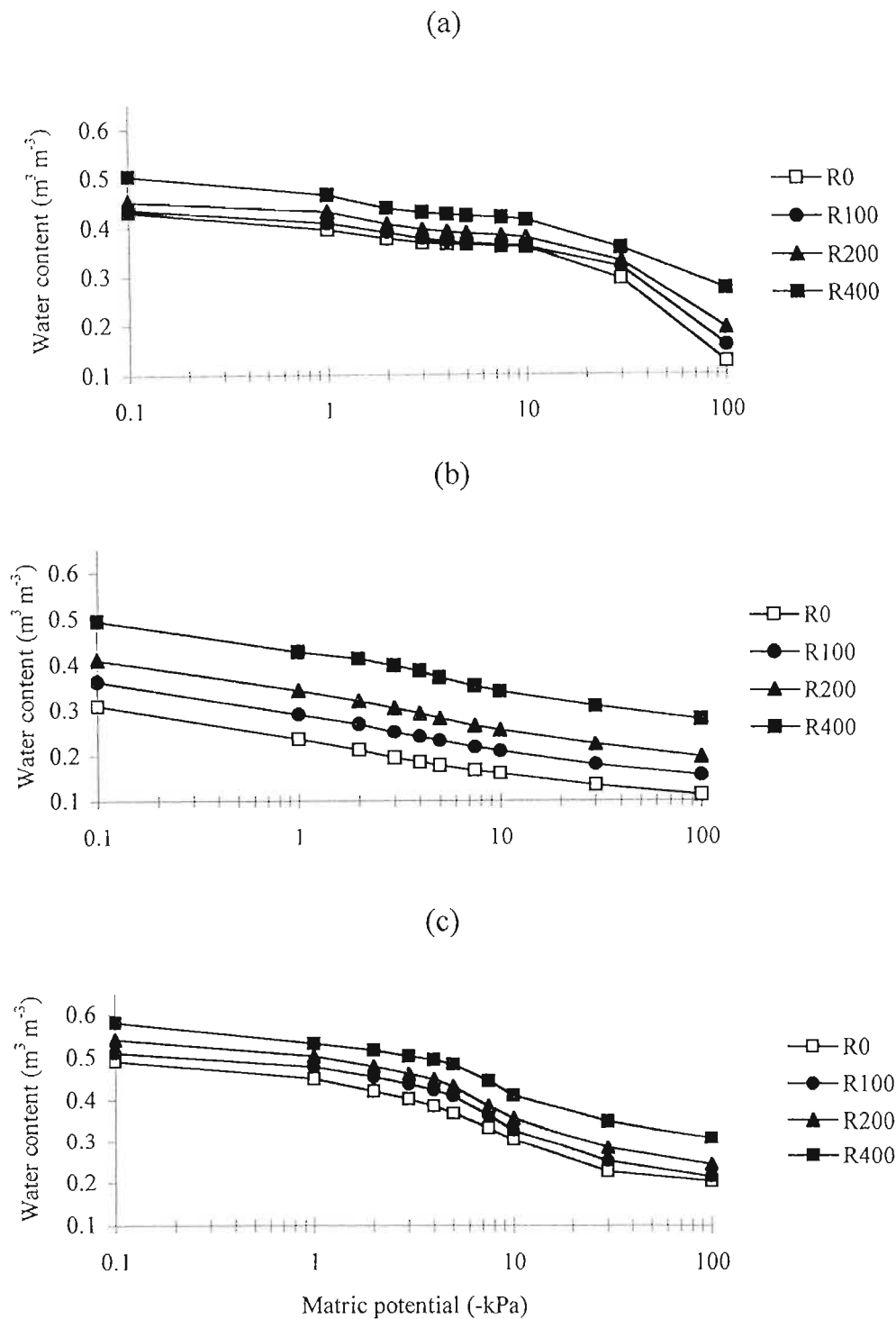


Figure 3.2 Water retention curves for (a) ash, (b) spoil, and (c) soil treated with 0, 100, 200 and 400 g kg^{-1} Rand water treatment residue (R0, R100, R200 and R400, respectively).

Stewart and Daniels (1992) examined a number of coal refuse properties, including water

retention. They too found reduced water holding capacities of the coal refuse when compared to a natural soil. In addition the coarser coal materials had lower water retention capacities than the finer materials, suggesting that water cannot be held in the pores by hydrostatic tension. They also attributed the reduced water holding capacity to the occurrence of hydrophobic carbonaceous material (coal fragments) in the refuse. The sharp increase in water holding capacity of the spoil with RWTR additions, shows that the RWTR dramatically increases water holding capacity. The soil showed a similar trend to that of the ash. The presence of fine sand and a moderate amount of clay led to moderately high saturation water contents. The addition of RWTR did not increase the saturation water contents dramatically, but a marked increase was noticeable at -30 and -100 kPa. This indicates that RWTR will improve water retention in the drier range, which would be advantageous for soil moisture conservation.

It is clear that additions of RWTR to the waste materials increase their water holding capacity. This is particularly evident in the spoil material, where the greatest benefit could be measured. It should be noted that for the spoil and soil in particular, plant available water (PAW) may not be increased by RWTR additions. It is clear that generally the retention curves run parallel. Although wilting point was not measured here, the data suggest that, if the measured trends continue, PAW will be constant regardless of improvements in water holding capacity at individual matric potentials.

3.4 Pot experiment

3.4.1 Leaching experiment

Mean EC and pH of the leachates are given in Appendix 6. Generally the EC and pH increased with increasing rates of RWTR, although, not consistently, and fertiliser additions may also have had an influence. There was also a noticeable increase in EC and pH at each subsequent leaching event for all RWTR treatments. In general the control treatments showed a decrease in pH after each leaching event. This decrease in pH could be attributed to the addition of acidifying fertiliser (NH_4^+), as well as the effect of nutrient uptake by roots, releasing H^+ ions (Tisdale *et al.*, 1993). The pattern measured for EC in the control treatments was more variable. The soil treatments with *E. teff* and *C. ciliaris* and the spoil treatment with *E. teff* tended to show an increase in EC for each subsequent leaching event, while the EC of

other treatments tended to decline.

The sharp increase in EC with increasing RWTR additions for all treatments was not considered representative of what may happen on a field scale. The EC frequently exceeded the 400 mS m^{-1} level set by the United States Salinity Laboratory Staff (1954) for saturated paste extracts as the general acceptable tolerance for plants. Under these conditions, it may have been expected that the grasses, especially in the spoil medium, should not have grown as well as was found. The most likely cause for the extreme EC was that the pots were only leached on three occasions with a relatively small quantity of water (when compared to the water holding capacity of the material in the pot). Under these conditions it is probable that salts would collect at the base of the pot during normal watering (no leaching). During a leaching event the leachate collected would mainly represent the soil solution at the base of the pot, which would have a high content of accumulated salts. This effect was then exacerbated as more salts were allowed to collect prior to the following leaching event. In a leaching experiment conducted by Stewart *et al.* (1997), it was found that coal refuse leached in columns had an initial EC of about 200 mS m^{-1} , which is in agreement with the values reported here. They found that EC increased dramatically, peaking at between $1\,400$ and $1\,800 \text{ mS m}^{-1}$. This was attributed to pyrite oxidation and salt dissolution with varying leaching regimes (including a drought cycle in this period). Nonetheless, it indicates the potential for high EC generation in such material. Stewart *et al.* (1997) then report that the EC gradually decreased to similar levels reported for the initial conditions. This supports the notion that under field conditions, with continual removal of oxidation and weathering products, the EC may decrease to acceptable levels. However, Geldenhuys and Bell (1998) found that on a coal mine in South Africa, the EC of water drained from a backfilled mined area ranged from 350 to 570 mS m^{-1} , which was 10 to 15 fold greater than a water supply upstream from the mine. This shows that elevated EC can be problematic, even under field conditions, although the EC measured in that study was of water that had leached the mine spoil material, removing excess salts from this area. While the removal of excess salts from the backfilled area may seem favourable, these salts may present concerns for surface and groundwater contamination downstream from the mine site.

Decomposition of the RWTR may also have partly attributed to the increase in pH with increasing RWTR additions. The low buffering capacity of the soil led to the high pH of the leachate from the RWTR-treated pots. While the spoil had some acid-generating potential, the

presence of calcareous material in the spoil and the strong neutralising potential of the RWTR would have counteracted any acid production. Under field conditions it is unlikely that EC and pH would reach the levels reported here due to regular leaching events (rainfall, irrigation) removing accumulated salts from surface horizons.

3.4.2 Yield

As mentioned earlier (Section 3.2.3.2) the growth of the grasses in the ash material was very poor (Plate 3.1), this aspect of the study was terminated, and consequently no meaningful data were obtained from the ash-based experiments.

There were significant differences in yield for *E. teff*, *D. eriantha* and *C. ciliaris* when grown in the soil material, but the differences were non-significant when grown in the spoil material (Table 3.7 and Appendix 7). A high degree of variability among the replicates of some treatments was evident. This was reflected in the high standard error values and coefficients of variation (CV) for some of the treatments (Table 3.7). A number of trends are evident though and the discussion will focus on these, considering variability and the causes where necessary.

Table 3.7 Summary ANOVA statistics for mean total yield for *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil and spoil material treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹

| Grass | Waste | F-ratio | d.f. ¹ | Probability | CV ² (%) |
|--------------------|-------|---------|-------------------|-------------|---------------------|
| <i>E. teff</i> | Soil | 26.61 | 4,8 | <0.001 | 8.7 |
| <i>D. eriantha</i> | Soil | 17.72 | 4,8 | <0.001 | 17.2 |
| <i>C. ciliaris</i> | Soil | 8.62 | 4,8 | 0.005 | 4.1 |
| <i>E. teff</i> | Spoil | 0.85 | 4,8 | 0.534 | 19.4 |
| <i>D. eriantha</i> | Spoil | 1.94 | 4,8 | 0.197 | 8.1 |
| <i>C. ciliaris</i> | Spoil | 1.07 | 4,8 | 0.430 | 11.5 |

1 d.f. degrees of freedom.
2 CV coefficient of variation.

Plates 3.2, 3.3 and 3.4 show images of the treatments prior to the third harvest. Figures 3.3 and 3.4 show the mean total yields for the soil and spoil treatments, respectively. Appendix 8 gives the results for each individual harvest.



Plate 3.1 Selected images showing the poor growth of some grass species grown in the ash treated with various rates of Rand water treatment residue. (a) *Cenchrus ciliaris* at 200 g kg⁻¹ RWTR, (b) *Cenchrus ciliaris* at 400 g kg⁻¹ RWTR, and (c) *Digitaria eriantha* at 100 g kg⁻¹ RWTR. Images taken after 43 days growth. The white labels in each pot are 70 mm wide.

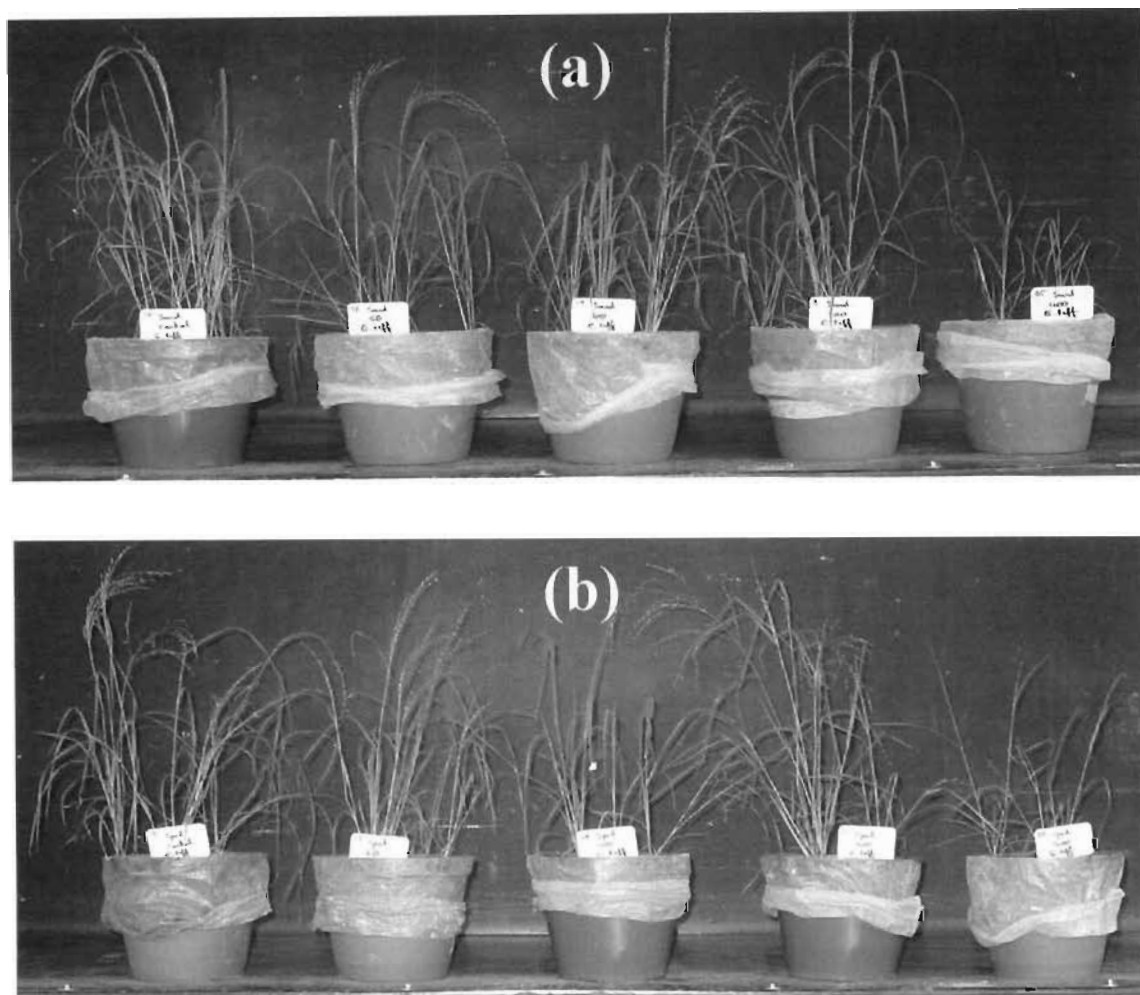


Plate 3.2 Growth of *Eragrostis teff* in (a) the soil material and (b) the spoil material at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ (left to right). Images taken just prior to third harvest. The height of each pot is 19 cm.

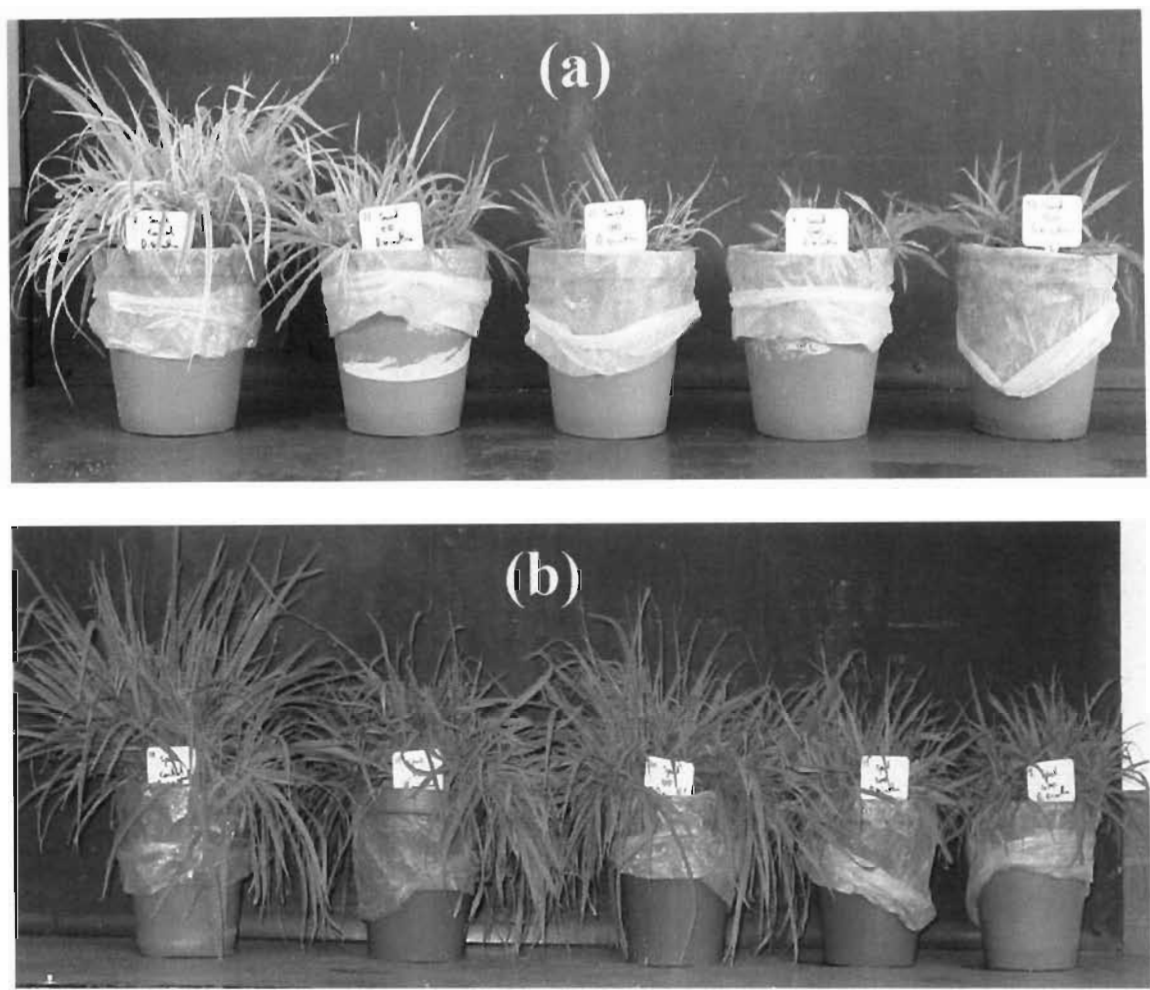


Plate 3.3 Growth of *Digitaria eriantha* in (a) the soil material and (b) the spoil material at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ (left to right). Images taken just prior to third harvest. The height of each pot is 19 cm.

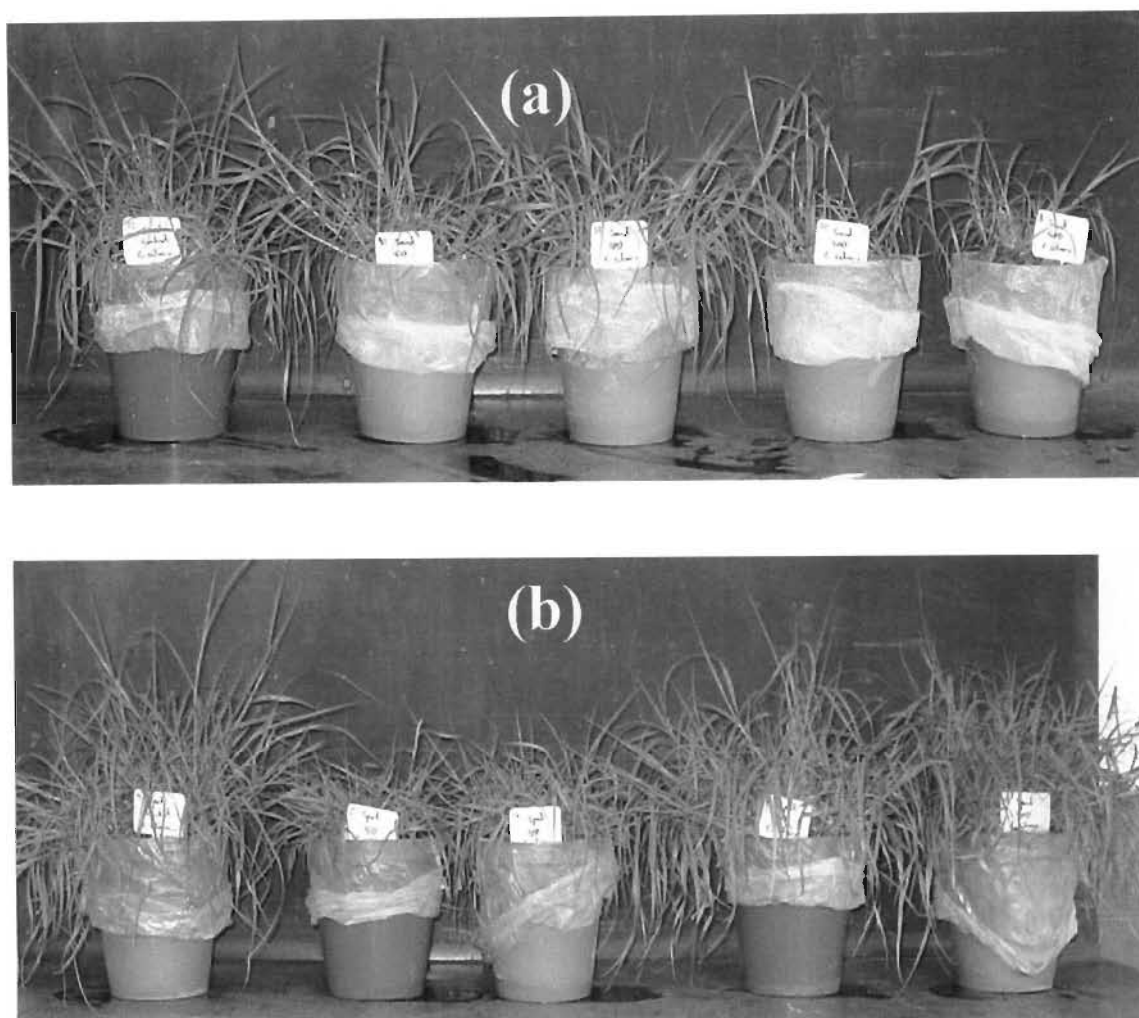


Plate 3.4 Growth of *Cenchrus ciliaris* in (a) the soil material and (b) the spoil material at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ (left to right). Images taken just prior to third harvest. The height of each pot is 19 cm.

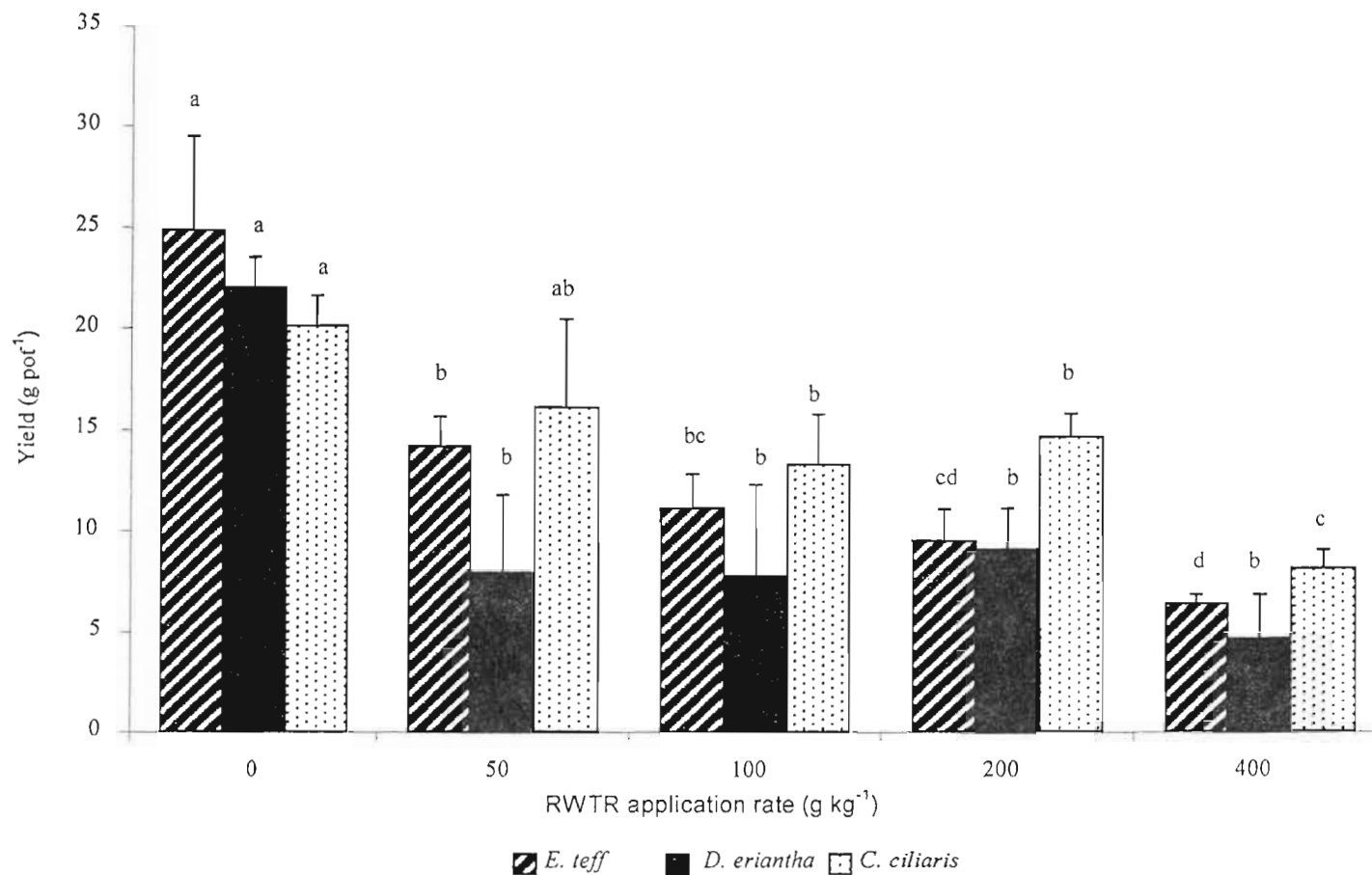


Figure 3.3 Mean total yields (+SE, 3 replicates) for harvests of *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil material treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹. Letters that are different indicate significant differences between treatment means within a grass species (LSD_{5%}: *E.teff* 4.5, *D.eriantha* 5.2, *C.ciliaris* 4.9).

3.4.2.1 Soil/RWTR mixtures

Eragrostis teff decreased in total yield with increasing additions of RWTR, with the control treatment performing significantly better than the RWTR-amended treatments. The highest yields were recorded for the first harvest, with the 0, 50 and 100 g kg⁻¹ treatments performing similarly. The control treatment performed significantly better than the 200 and 400 g kg⁻¹ RWTR treatments. The second harvest showed a slight increase in yield for the control treatment, but a sharp decrease for the RWTR-treated pots. The yield of the control treatment for the third harvest decreased substantially, while the remaining treatments (except the 100 and 200 g kg⁻¹ treatment) also decreased from the second cut. In the third harvest there were no significant differences between the 0, 50, 100 and 200 g kg⁻¹ RWTR treatments. The 400 g kg⁻¹ RWTR treatment performed very poorly.

This dramatic decline in performance of the RWTR treatments resulted in the overall poor performance seen for total yield. It should also be noted that at the first cut the coefficient of variation (CV) was moderately low, but increased sharply with each subsequent harvest, indicating an increase in the variability of the replicates. The CV for the mean total yield suggest that overall variability was low, however. This general decline in performance for each subsequent harvest is partly attributable to the increase in EC seen in the leachate data, but may also be due to certain trace nutrients becoming deficient due to the high pH of some treatments, even though no deficiencies were evident. Although these results suggest that RWTR additions have a negative impact on the growth of *E. teff* in the soil, the results from the first harvest indicate that it will grow well up to RWTR additions of 200 g kg⁻¹.

Furthermore, *E. teff* is planted as an annual, nurse crop. The principle of using such a crop is to establish rapid cover on the soil surface to afford protection against erosion and, ultimately, to provide a source of organic matter when the plants die (Jones *et al.*, 1975; Wood and Buchanan, 2000). This is considered to aid the establishment of more persistent, but slower growing vegetation (perennial species). As *E. teff* is planted as a nurse crop, it is unlikely that a second crop would be seeded in the field, although a second crop is unlikely to perform as poorly as indicated by the second and third harvests of the pot experiment.

Digitaria eriantha showed a decrease in total yield with increasing RWTR additions. The control treatment had a significantly higher yield than the other treatments. Initially the

growth was poor for all treatments, except the control, but improved markedly by the second harvest, decreasing slightly at the third cut. In all instances the control treatment performed significantly better than the RWTR treatments. The decrease in yield with increasing RWTR additions may be because *D. eriantha* is a perennial species. It requires more time to establish, but once established is likely to be more tolerant of changes in growing conditions. The general decrease in yield for the third harvest (compared to the second harvest) was possibly due to an increase in pH to over 8.0 for most treatments and may also be attributable to the relatively short growing period from the previous harvest (35 days compared to 70 days for the second cut). These data suggest that once *D. eriantha* is established it may grow moderately well in the soil with RWTR application rates of up to 200 g kg^{-1} . However, it performed consistently better with no RWTR additions and may not be a suitable species to use under these conditions.

Cenchrus ciliaris decreased in mean total yield. The yield of the control and 50 g kg^{-1} RWTR treatments did not differ significantly from one another, while the yield of the 400 g kg^{-1} RWTR treatment was significantly lower than all other treatments. The decrease in yield with increasing RWTR additions was evident at all harvests. The 400 g kg^{-1} RWTR treatment performed the worst at the first harvest, but did not perform significantly differently from the other treatments at harvests two and three. However, it did perform the poorest in both instances. Although the best yields were generally recorded for the control treatments, good performance was seen at most rates of RWTR, except for the highest application. As with the other two species tested, addition of rates up to 200 g kg^{-1} are likely to give acceptable yields. It should be noted that although the 200 g kg^{-1} RWTR treatment for both harvests two and three had high yields, these are associated with very high standard errors.

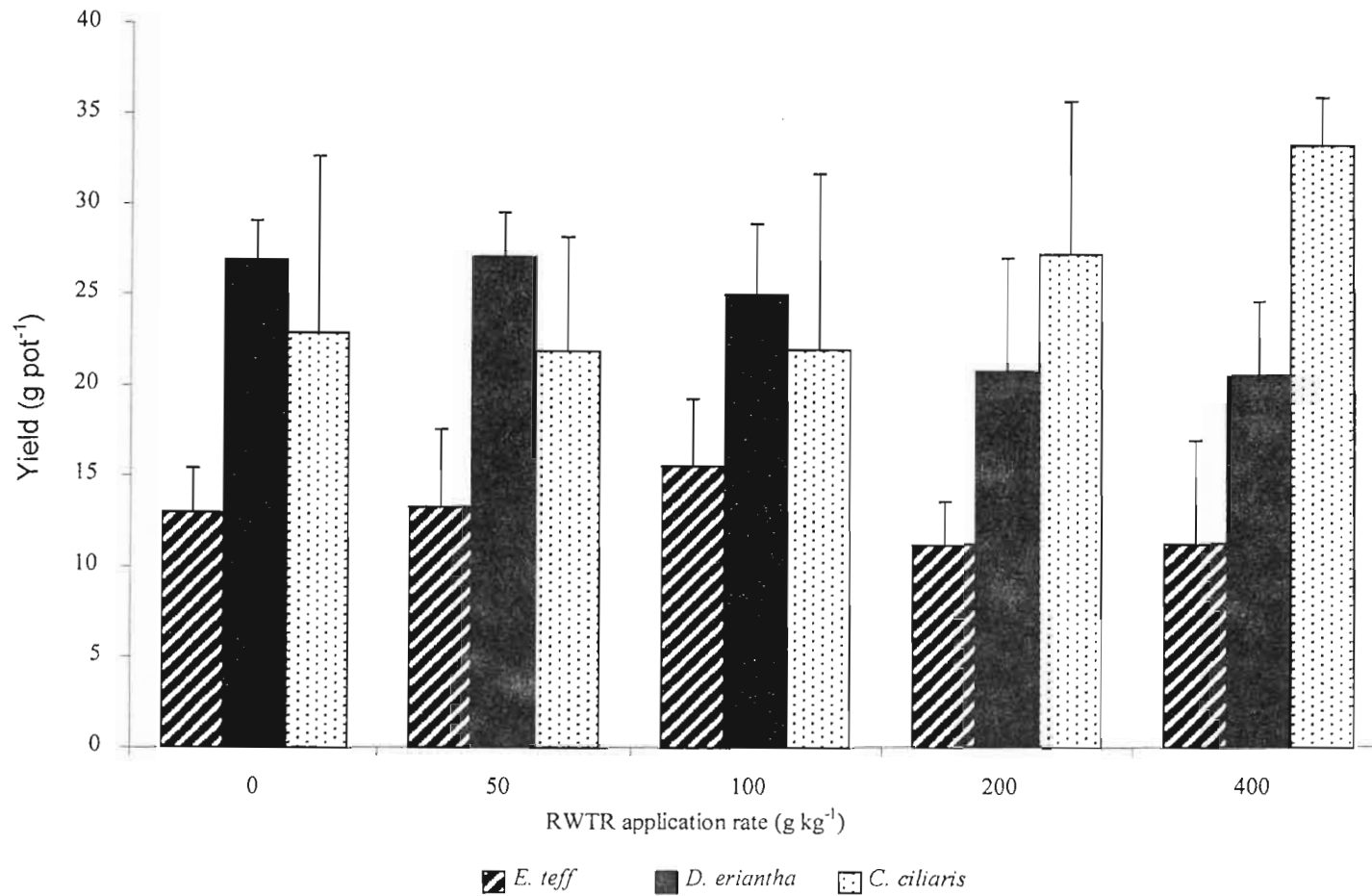


Figure 3.4 Mean total yields (+SE, 3 replicates) for harvests of *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the spoil material treated with Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹.

3.4.2.2 Spoil/RWTR mixtures

Eragrostis teff increased in total yield up to the 100 g kg⁻¹ RWTR application rate and then decreased with higher rates, although the differences were not significant. Yield increased as RWTR application rate increased for the first harvest. The second harvest showed increases in yield from the first harvest for each treatment. The 100 g kg⁻¹ RWTR treatment yielded the highest. The 200 and 400 g kg⁻¹ treatments performed the poorest. The third harvest showed a sharp decrease in yield for all treatments. This decline in yield may be due to the EC increasing to a level where the growth of the seedlings was impaired. As was the case for *E. teff* in the soil, the poor yield from the last harvest skewed the total yield values. This again creates an impression that the RWTR is not a suitable ameliorant at high rates. However, the yields from the first and second harvests suggest that the growth may be satisfactory if one takes into account the typical use of this species as a nurse crop. Under these conditions, medium to high application RWTR rates may be practical. The poor yields of the first harvest, from the control treatment and low RWTR treatments, may have been due to the seedlings not being able to establish easily in the coarse material. The addition of 200 and 400 g kg⁻¹ of RWTR may have improved root contact with the soil, due to the addition of finer material, and consequently led to the improved yields of those treatments. Decomposition of the coarse material in the control and low RWTR treatments to a finer grade material may have improved the physical environment, improving root contact by the second harvest, hence the improved yield.

Digitaria eriantha showed a decrease in total yield with increasing RWTR rate, but the differences between treatments were not significant. The yield from the first harvest was very poor for all treatments, but increased markedly for subsequent harvests. The yield of the second harvest did not show much difference between treatments, but by the third harvest substantial improvements in yield were seen for the control, 50 and 100 g kg⁻¹ treatments. The general increase in yield was probably due to the plants adapting to the growing conditions. The decrease in yield for the 200 and 400 g kg⁻¹ RWTR application rates is possibly due to the high EC and pH as indicated by the leachate data.

Cenchrus ciliaris was the only species that increased in mean total yield as RWTR application rate increased, although the differences between treatments were not significant. The 400 g kg⁻¹ treatment performed well. There was a decline in yield for the 400 g kg⁻¹ treatment by the

third harvest, while, generally, the other treatments showed marginal increases. The 400 g kg⁻¹ treatment still had the highest yield, although it was not significantly better than the other treatments.

3.4.3 Effect of pH and electrical conductivity on yield

Initially the poor growth of some treatments was attributed to high EC and pH. However, when yield was plotted against leachate EC or pH, the data showed a high degree of variability and no strong relationships were found, even when the data was transformed (results not shown). It is possible that elevated EC and pH may have influenced yield, but it is questionable considering the favourable performance of some treatments. Generally grass yield declined with increasing RWTR application rates, and this appeared to be associated with an increase in leachate EC and pH. The exception was *C. ciliaris* grown in the spoil treatment, which appeared to show a tolerance of both saline and alkaline conditions. This reinforces the notion that the high EC and pH in the leachate were a result of salt accumulation at the base of the pot, and thus they did not have as direct an influence on plant growth as expected. Where growth of the grass was vigorous it is possible that root development was limited to the upper, less saline, portions of the pots. The poor performance of *E. teff* especially for the last harvest may be due to elevated EC and pH, where growing conditions were unsuitable for seedling establishment and growth. While it is unlikely that the leachate data give a realistic representation of the entire soil solution EC and pH, these data do suggest that the EC and pH were probably also elevated in the upper portions of the pot. This was, however, not examined.

3.4.4 Plant analyses

Appendix 9 gives the results of the grass analysis of each harvest and include typical nutrient concentrations for turf grasses (Bennett, 1993) and *Eragrostis curvula* (Schröd.) and *Festuca arundinacea* (Shreb.) (Miles, undated) for comparative purposes. For the sake of brevity the nutrient uptake will be discussed in brief here, but a more comprehensive overview of possible causes and mechanisms for the patterns of uptake observed are given in Appendix 10.

There were no apparent trends for Ca uptake, with values generally being lower than those

reported by Bennett (1993), but similar to those reported by Miles (undated). Magnesium concentrations increased with increasing RWTR additions in all grasses and wastes, but this was not unexpected considering the high amounts of available Mg in the RWTR. *Digitaria eriantha* did, however, tend to have higher Mg concentrations than the other two species. The concentrations found here exceed those reported by Bennett (1993) and Miles (undated), perhaps indicating luxury uptake by the plants. Potassium concentrations tended to be high and within typical ranges for grasses, although the pattern of uptake was variable. Uptake of Na showed marginal increases with increasing RWTR additions, but as levels were very low this was not of concern. Phosphorus concentrations showed a decrease in tissue concentration for a number of treatments as RWTR increased, but concentrations remained adequate for plant growth. As P was added to the pots during the experiment, it was unlikely that P deficiencies would occur, even though the RWTR has a potentially high P sorbing capacity (Section 2.3.6). Nitrogen uptake did not show any consistent pattern of uptake, but the second and third harvests did show higher N tissue concentrations. This was probably due to further N applications prior to these harvests. The N concentrations reported for the first harvest were below the sufficiency ranges reported by Bennett (1993) and Miles (undated), but were adequate for the last two harvests.

Trace nutrient uptake was variable. Zinc and Mn uptake tended to increase, while Fe and Cu uptake tended to decrease with increasing RWTR additions. Manganese concentrations frequently exceeded typical ranges for grasses, as given by Pendias and Pendias (1984) who report that world-wide background concentrations for grasses range from 17 to 334 mg kg⁻¹ and that, typically, symptoms of toxicity will only be seen at concentrations over 500 mg kg⁻¹. The increase in Fe concentrations was attributed to moderate amounts of available Fe in the RWTR, and in the spoil. While Fe deficiency is typical of calcareous or over-limed media (Mortvedt, 2000), this was not apparent. The Fe concentrations reported here are within or above the typical ranges reported for grasses. Boron uptake was variable, with the concentrations in the soil treatments being below the typical grass ranges. The spoil treatments, however, were considerably higher, this being attributed to high B concentrations in the spoil, although this was not measured.

The concentrations reported here indicate that nutrients were present in sufficient concentrations to support the growth of the plants, although poor growth was observed for a number of treatments. It is possible that other trace nutrients, not measured here, were either

at toxic or deficient concentrations. The high pH of many of the treatments may have led to some other trace nutrients becoming unavailable to plants, or weathering of the material may have released some trace elements at toxic concentrations. However, no symptoms of toxicity or deficiency were visually apparent that would have suggested a possible cause of the poor plant growth.

3.5 General discussion and conclusions

The high variability in the yield data for almost all treatments makes it difficult to predict how RWTR would affect the growth of these grass species on the materials when used under field conditions. The use of mean yield allowed clarification, but many of the differences were not significant. If one uses mean yield data as a guide for applying RWTR to these materials, then the application of RWTR to the soil should be avoided or used at a minimum application rate, possibly lower than tested here. However, the RWTR can be applied at maximum applications on the spoil material, without apparently causing a significant loss in production of the grasses tested, even though leachate EC and pH seemed excessively high.

If one considers only the trends seen (without statistical support) then it would appear that *C. ciliaris* was the only species to benefit from RWTR additions when grown in the spoil material. This, however, may not be a true reflection of what may occur under field conditions. As the other treatments showed decreases in total yield with increasing RWTR additions, it may indicate that very high applications of RWTR ($>200 \text{ g kg}^{-1}$) to these materials would not be suitable for these species. As was noted, however, the variability between replicates was high in some instances which could have skewed the data and led to the decreases seen in total yield. It was also shown that, for a number of the apparently poor performing treatments, the individual harvests indicated that these grasses had a potential to perform better than suggested by the mean total yield data.

It is likely that the high EC and pH of some treatments reduced yield. These high EC and pH values are partly attributable to the design of the experiment. The pots were leached only on three occasions, which led to the accumulation of salts and increased EC. This could then lead to osmotic imbalances, making it more difficult for plants to take up nutrients and water. This may have led to the newly germinated *E. teff* seedlings not being able to perform as well as when the EC was lower at the earlier harvests. The yield of the perennial grasses tended to

improve as they became established, indicating an increased tolerance to the high EC and pH of some treatments. The poorer overall performance of the grasses in the soil material may also be partly explained by poor physical properties for plant growth. As both the RWTR and the soil had moderately high amounts of fine particles, compaction may have created physical barriers to root penetration and, in conjunction with the high pH, have reduced the plants' ability to obtain adequate nutrients for strong growth.

3.6 Study 2: The use of RWTR as a growth medium over a coal combustion ash

3.6.1 Introduction

As the growth of *E. teff*, *D. eriantha* and *C. ciliaris* in mixtures of RWTR and ash was very poor or unsuccessful, it was proposed by representatives from the power plant that the RWTR could be used as a growth medium over the ash material. It had been suggested that the ash dumps be capped with a suitable cover material and vegetation established to reduce wind and water erosion. Furthermore, the possibility existed that the ash would be reprocessed in the future to extract certain elements found at elevated concentrations, therefore the surface cover and vegetative layer should be able to be easily removed, and the ash below remain relatively free of other contaminants (such as root material, fertilisers etc.).

A pot experiment was designed to test the potential of the RWTR as a growth medium over the ash material, using two creeping grass species. The objectives of the study were:

- to determine biomass production of grasses growing in RWTR layers over the ash;
- to determine the optimum RWTR layer thickness; and
- to determine if grass performance was improved with fertiliser application.

3.6.2 Materials and methods

The same ash and RWTR were used as described in the previous pot experiment (Section 3.2.3), but the RWTR was spread over the ash material (rather than incorporated). The size fraction of the RWTR used was slightly larger than previously (<3.5mm). Three levels of RWTR (thickness) were selected i.e., 20, 40 and 60 mm. A fertilised and unfertilised treatment were tested. The fertiliser treatment consisted of 1 Mg ha⁻¹ of the 2:3:2 fertiliser

used in the previous experiment. This was mixed into the RWTR before being applied over the ash. The two grass species chosen, *Stenotaphrum secundatum* (Walt.) O. Ktze. (coastal buffalo) and *Cynodon dactylon* (L.) Pers. cv. Seagreen (bermudagrass), were selected for their tolerance of alkaline conditions and their creeping growth form (Gallimore, 1999; Prof. A.L.P. Cairns and Mr. J. Klug, *pers. comms.* 2002). They were planted as seedlings (purchased from a local nursery). The watering of the pot experiment was the same as described for the previous experiment. The pots (150 mm i.d.) were arranged in a randomised complete block design (Rayner, 1967) with three replicates (36 pots in total), generated by the statistical package Genstat V (Release 4.1, Lawes Agricultural Trust, Rothamsted Experimental Station).

After 6 weeks the above ground biomass was harvested. Root material was collected from the RWTR and ash layers, by washing and sieving. The vegetative materials were placed in paper bags, dried at 65°C and then weighed to determine dry yield. Statistical comparisons were by two-way ANOVA. If the F-statistic was significant then LSD comparisons of means, at the 5% level of significance, were made (Genstat V, Release 4.1, Lawes Agricultural Trust, Rothamsted Experimental Station). Raw yield data are available from the author subject to suitable confidentiality agreements.

3.6.3 Results and discussion

The thicker RWTR layers improved growth of both species (Table 3.8), with a highly significant overall fertiliser by grass interaction ($F_{1,22}=15.98$; $p<0.001$) (Appendix 11), with *C. dactylon* performing significantly better than the other treatments (Table 3.8). Initially the *C. dactylon* plants showed signs of leaf tip burn (especially in the 20 mm RWTR layers), but this disappeared as they grew larger. The cause of the symptoms were not identified, but could be B toxicity (Bennett, 1993) as this is frequently associated with coal combustion ash (Carlson and Adriano, 1993). *Cynodon dactylon* grown in the unfertilised RWTR performed similarly to *S. secundatum* grown in either fertilised or unfertilised layers. *Stenotaphrum secundatum* showed signs of P deficiency, though the severity appeared less in the fertilised treatments. This may be expected considering the high pH and P sorption capacity of the RWTR. It would appear that *C. dactylon* was more tolerant of low P availability than *S. secundatum*. It is apparent that the fertiliser treatments improved the yield of both grass species, as did using a thicker RWTR layer.

Table 3.8 Mean (\pm SE, n=3) above ground dry yield (g pot⁻¹) for *Cynodon dactylon* and *Stenotaphrum secundatum* grown in three different Rand water treatment residue layers over a coal combustion ash, for both the fertilised (Fert) and unfertilised treatments (Unfert). LSD_{5%} comparisons for mean yield over the different Rand water treatment residue layers are also given

| | | RWTR thickness (mm) | | | Mean yield across RWTR thicknesses ¹ |
|----------------------|--------|---------------------|------------|------------|---|
| | | 20 | 40 | 60 | |
| <i>C. dactylon</i> | Fert | 5.87 | 9.05 | 11.08 | 8.67a |
| | | ± 2.72 | ± 0.88 | ± 2.73 | |
| | Unfert | 3.07 | 4.41 | 6.29 | 4.59b |
| | | ± 0.27 | ± 1.07 | ± 0.68 | |
| <i>S. secundatum</i> | Fert | 3.01 | 4.48 | 6.92 | 4.80b |
| | | ± 0.43 | ± 2.21 | ± 3.05 | |
| | Unfert | 3.80 | 4.43 | 5.99 | 4.74b |
| | | ± 1.35 | ± 0.62 | ± 0.44 | |

¹ Letters that are different indicate significant differences (LSD_{5%} = 1.47).

Basta *et al.* (2000) tested the growth of *C. dactylon* in three alum WTRs with different P fertiliser rates. They found that grass grown in two of the WTRs gave moderate yields that were similar to a comparative soil treatment. Addition of fertiliser P did not significantly improve yield in any of the WTRs tested. Gallimore (1999), in a similar investigation using alum WTRs, found that growth of *C. dactylon* could be supported, and that no addition of P was necessary for satisfactory growth. Even though both of these studies found that addition of P did not improve growth, both report that plant P concentrations were below recommended plant tissue concentrations for optimal growth, even in fertilised treatments. This supports the current findings that *C. dactylon* may be tolerant of low P availability.

Root biomass (Table 3.9) of *C. dactylon* in the unfertilised RWTR layers did not show a clear pattern, with the 40 mm RWTR layer performing best. In the fertilised treatments the 40 and 60 mm layers showed similar performance, with both being better than the 20 mm RWTR layer. *Stenotaphrum secundatum* root biomass in the RWTR layers showed increases with increasing layer thickness, regardless of fertiliser treatment. The ANOVA (Appendix 11) showed that there was a significant grass species by RWTR layer thickness interaction ($F_{2,22}=5.26$; $p=0.014$) and that *S. secundatum* performed significantly better than the other treatments (Table 3.10).

Table 3.9 Mean (\pm SE, n=3) root dry yield (g pot⁻¹) for *Cynodon dactylon* and *Stenotaphrum secundatum* grown in the three different Rand water treatment residue layers for both the fertilised (Fert) and unfertilised (Unfert) treatments

| | | RWTR thickness (mm) | | |
|----------------------|--------|---------------------|------------|------------|
| | | 20 | 40 | 60 |
| <i>C. dactylon</i> | Fert | 1.88 | 2.43 | 2.66 |
| | | ± 0.54 | ± 0.34 | ± 0.63 |
| | Unfert | 1.43 | 2.74 | 1.60 |
| | | ± 0.15 | ± 0.75 | ± 0.32 |
| <i>S. secundatum</i> | Fert | 1.17 | 2.05 | 3.69 |
| | | ± 0.64 | ± 0.73 | ± 1.14 |
| | Unfert | 1.69 | 2.57 | 3.03 |
| | | ± 0.71 | ± 0.55 | ± 0.44 |

Table 3.10 Mean root dry yield (g pot⁻¹) for *Cynodon dactylon* and *Stenotaphrum secundatum* grown in the three different layers of Rand Water’s water treatment residue over a coal combustion ash

| | RWTR thickness (mm) | | |
|------------------------|---------------------|-------|--------|
| | 20 | 40 | 60 |
| <i>C. dactylon</i> | 1.66c ¹ | 2.58b | 2.13bc |
| <i>S. stenotaphrum</i> | 1.43c | 2.31b | 3.36a |

1 Letters that are different indicate significant differences between treatment means (LSD_{5%} = 0.771).

The root biomass in the ash layers (results not shown) showed no pattern and, as expected, was considerably lower than the root biomass in the RWTR layers. There were no significant overall treatment effects or interactions found (Appendix 11). The root biomass in the ash layers of the treatments where little or no root material was initially established (i.e., 40 and 60 mm RWTR layers) was exceptionally low and in some cases no roots were found. The 20 mm RWTR treatments had some root material, but this was as a result of planting in the ash layer. These roots all appeared stunted, with little or no signs of growth. It was clear that the roots did not perform well and would not grow into this layer. van Rensburg *et al.* (1998) tested the growth of a number of grass species (including *C. dactylon*) on a fine coal-ash dump in South Africa, using various ameliorative treatments. They reported that yield was low in the control treatments, due to the poor physical properties of the ash. The physical characteristics of the ash may also have created a physical barrier to root penetration, and hence the low yield observed in the present study. Furthermore the high exchangeable

(soluble) Al concentration of the ash (Table 3.1) may have stunted root growth.

Stenotaphrum secundatum produced a large number of stolons, regardless of treatment. While the performance of this grass was poorer than that of *C. dactylon*, its vigorous creeping habit could be beneficial. The purpose of the grass is to help stabilise the capping material (RWTR) and the rapid spread of the grass would increase the rate at which this may occur. If at each node the plant roots successfully, it will then start producing stolons and spread. Even if the parent plant then dies or shows reduced performance, the ramets (daughter plants) may contribute to creating a vegetative mat over the RWTR. It is possible that under these conditions P uptake by the plants may improve because of a more widespread rooting system. In the pot experiment the roots were confined to a small volume, which needed to supply vigorous stoloniferous growth, and possibly led to the P deficiencies observed. *Cynodon dactylon* also showed prolific stoloniferous growth and, as it appeared more tolerant of the growing conditions, may create a more sustainable cover. This, in addition to a rhizomatous habit (van Rensburg *et al.* 1998; Gallimore, 1999), would offer increased protection against wind and water erosion to the RWTR layers, in turn protecting the ash below.

3.6.4 Conclusions

Initial indications are that the RWTR may act as a suitable growth medium over the ash material, and that a thicker layer may be more beneficial. It was apparent that additional fertiliser improved the performance of *C. dactylon* significantly, while marginally, but not significantly, improving the performance of *S. secundatum*. This was probably due to partial alleviation of the low P availability in the RWTR layer. *Cynodon dactylon* appeared to be more tolerant of the alkaline conditions, while *S. secundatum* showed P deficiency symptoms. Both species produced a large number of stolons and it is likely that under field conditions they would spread quickly and offer reasonable cover. Even though *S. secundatum* did not perform as well as *C. dactylon*, it is likely to aid in stabilising the RWTR cap. *Cynodon dactylon* would give better cover and would also further stabilise the material as it produces underground rhizomes in addition to the surface stolons. It is also very tolerant of a wide range of growing conditions.

Chapter 4

The use of a water treatment residue from the Faure Water Treatment Plant to improve the fertility of a sandy soil

4.1 Introduction

Currently the Faure Water Treatment Plant (Cape Metropolitan Council, Cape Town) produces between 4 000 Mg (summer) and 11 000 Mg (winter) wet WTR, which is currently landfilled. The cost of disposal of this material is considerable and a more economically viable (as well as environmentally friendly) alternative needs to be found. It is also likely that WTR production will increase substantially in the future as there are plans to double the capacity of the treatment plant (Mr. Dawid Smit, Manager, FWTP, *pers. comm.* 2003).

A number of studies report on the nutrient supplying potential of some WTRs. After some consideration, it was decided that the Faure 1 WTR (FWTR) might be beneficially applied to the areas of highly leached sands that are common in the region of the treatment facility. Furthermore, results from earlier work (Section 2.3.2) showed that this WTR was only marginally acid (but did have a lime component), with moderate amounts of organic carbon and a high total C content (Table 2.2). These data also indicate that the FWTR has potential to supply Ca and Mg and a number of trace nutrients (including Fe, S and Zn), and has a moderate amount of total N. The only concerns were a high Mn concentration and the high P sorbing capacity of the FWTR. However, a potential benefit of the latter, if the FWTR were to be applied to a dystrophic sandy soil, may be to reduce P loss through leaching. If the WTR then subsequently decomposes it may release some of this P, essentially acting as a slow release P fertiliser. Geertsema *et al.* (1994) have commented that this may be a likely mechanism of P release from WTR, as only a few studies have shown P deficiencies under field conditions. It does, however, imply that adequate initial P will be added to overcome initially the high P sorption by the WTR.

This study was thus developed with the following objectives:

- to characterise the sandy soil selected for use in this study;
- to test the growth of dry beans in mixtures of FWTR and the nutrient-poor sand;
- to determine a suitable fertiliser application rate for the mixtures; and

- to determine the nutrient and elemental uptake by the seed.

Dry beans were selected as the test crop, as they are a common crop in small-scale agriculture and are easy to cultivate and manage under glasshouse conditions.

4.2 Materials and methods

4.2.1 Material collection and preparation

Water treatment residue was collected and dried at the Faure Water Treatment Plant and delivered to the University of Natal, Pietermaritzburg. The sandy E horizon material from a Longlands (Lo) soil (Soil Classification Working Group, 1991) was collected from the South African Sugar Association Experimental Station, Mt Edgecombe, KwaZulu-Natal in an area that, although previously cultivated, had been under natural grassland for the past 10 years. The Lo sand was placed in 50 kg polypropylene bags and transported to the University of Natal, Pietermaritzburg. The sand was air-dried and milled to pass through a 2 mm sieve. The FWTR was milled to pass through a 2.8 mm sieve; this size being selected to allow both ease of handling and to be a suitable size for use in the pot experiment.

4.2.2 Laboratory investigations

Basic chemical and physical properties, DTPA extractable metals, total elements (XRF) and P sorption were determined on the Lo sand by methods described in Section 2.2.2. The effect of the FWTR on the pH and EC of the Lo sand and the water retention characteristics of both the Lo sand and the FWTR-treated Lo sand were determined by methods described in Section 3.2.2.

4.2.3 Pot experiment

This essentially followed the method given in Section 3.2.3. The FWTR was added to the soil at rates of 0, 50, 100, 200 and 400 g kg⁻¹. These rates were the same as used in the RWTR study (Section 3.2.3). Each pot contained 2.6 kg of material, this being determined by the mass of sand a pot could contain. The Lo sand and FWTR were thoroughly mixed at the required rates, and then the fertiliser solution was added and the materials remixed. Four

levels of fertiliser were used as well as an unfertilised treatment. The fertiliser requirement was based on levels of 90 kg N ha⁻¹, 60 kg P ha⁻¹ and 90 kg K ha⁻¹, which are suggested rates for dry beans grown on a light dystrophic soil (Archer, 1988; Birch *et al.*, 1991). The fertiliser was added as a solution of (NH₄)₂HPO₄, KNO₃ and NH₄NO₃, to give 100% values of 0.225 g N, 0.150 g P and 0.225 g K. Three other levels were used i.e., 25, 50 and 150%, and a control (0% level). The control treatment had an equivalent amount of distilled water added to maintain the water content of the material the same as those to which fertiliser solutions were added. The mixtures were placed in plastic pots (180 mm i.d.) lined with a polypropylene bag, perforated in the base.

The experiment had 25 treatment combinations, replicated three times and was arranged in a randomized complete block design (Rayner, 1967), generated by the statistical package Genstat V (Release 4.1, Lawes Agricultural Trust, Rothamsted Experimental Station). Six dry bean (*Phaseolus vulgaris*, cv. Ghadra) seeds were planted in each pot in late November 2002. The seedlings were thinned after a week to four plants and again a week later to leave the two healthiest plants. The pots were watered as required to avoid water stress using tap water. The EC of the tap water ranged from 8.78 to 9.97 mS m⁻¹ and pH ranged from 6.5 to 7.6. The mean glasshouse temperature ranged from 16 to 38°C (min=14°C, max=41°C). Supports for the plants were provided as they grew to prevent the plants lodging.

From an early stage in the experiment the FWTR treatments showed interveinal chlorosis and necrotic lesions on the cotyledonous leaves and subsequently on all new leaves. These chlorotic areas eventually turned a dark brown to black with these leaves dying in some instances (Plate 4.1). The severity of the symptoms increased with increasing FWTR applications and was seemingly not related to fertiliser application rates. While it was suspected that Mn toxicity was the cause, additional bean plants were grown in three additional pots (six plants per pot) of the 400 g kg⁻¹ FWTR treatment (unfertilised) to be analysed to determine possible causes. Once sufficient plant growth had occurred, all leaves showing the symptoms were harvested and oven dried at 65°C for 48 h. This material was sent to the Soil Fertility and Analytical Services Laboratory, KZN Department of Agriculture and Environmental Affairs, Cedara for fertility (Ca, Mg, K, Na, P, Zn, Cu, Mn, Fe and B) and C, N and S analysis.



Plate 4.1 Examples of interveinal chlorosis on leaves of dry beans (*Phaseolus vulgaris*) grown in a Longlands sand treated with 400 g kg⁻¹ Faure water treatment residue, 3 weeks after germination.

4.2.4 Harvesting

The pods were harvested in mid-February 2003 after all the plants had senesced and the pods had dried on the plants. The pods were placed in paper bags and dried at 65°C in a forced draft oven for 48 h. Once dry, the mass of complete pods was determined for each treatment, as was the number of pods per pot (two plants). The beans were then removed from the pods and the number and mass of beans were recorded for each treatment. Statistical comparisons were by two-way ANOVA. If the F-statistic was significant then LSD comparisons of means, at the 5% level of significance, were made (Genstat V, Release 4.1, Lawes Agricultural Trust, Rothamsted Experimental Station). Raw yield data are available from the author subject to suitable confidentiality agreements. The bean seeds were then sent for analysis of Ca, Mg, K, Na, P, Zn, Cu, Mn and Fe at the Soil Fertility and Analytical Services Laboratory, KZN Department of Agriculture and Environmental Affairs, Cedara.

4.3 Results and discussion

4.3.1 General characteristics

Some chemical and physical properties of the Lo sand are given in Table 4.1.

Table 4.1 Some chemical and physical properties of the Longlands sand from the South African Sugar Association Experimental Station

| Property | | Longlands |
|--|-----------------------------|------------|
| pH | H ₂ O | 4.94 |
| | KCl | 4.64 |
| Electrical conductivity (mS m ⁻¹) | | 2.12 |
| Organic carbon (%) | | 1.99 |
| Exchangeable acidity (cmol _c kg ⁻¹) | | 0.19 |
| Exchangeable aluminium (cmol _c kg ⁻¹) | | 0.09 |
| Texture ¹ | | sandy loam |
| Particle size distribution (%) | Sand (0.053 – 2 mm) | 77.2 |
| | Coarse silt (0.02-0.053 mm) | 4.3 |
| | Fine silt (0.002-0.02 mm) | 6.4 |
| | Clay (<0.002mm) | 12.1 |

¹ Soil Classification Working Group (1991).

The sand was acid, with a low electrical conductivity and a moderately high organic carbon content. Extractable acidity and Al were low. Particle size analysis showed that the material was dominantly sand, with about 12% clay, giving it a sandy loam texture. The nutrient concentrations of the Lo sand are given in Table 4.2. Total N was low, as was NO₃-N and NH₄-N. Available P was higher than expected, either due to previous fertilisation of the area or due to the high amount of organic carbon. Concentrations of all the extractable bases were low, in particular K, as was the cation exchange capacity.

Table 4.2 Some nutrient concentrations of the untreated Longlands sand

| Property | Sand | |
|--|-------|------|
| Total N (mg kg ⁻¹) | 300 | |
| NO ₃ – N (mg kg ⁻¹) | 8.03 | |
| NH ₄ – N (mg kg ⁻¹) | 20.73 | |
| AMBIC P (mg kg ⁻¹) | 10.67 | |
| Exchangeable cations (cmol _c kg ⁻¹) | Ca | 1.60 |
| | Mg | 1.54 |
| | Na | 0.39 |
| | K | 0.01 |
| Cation exchange capacity (cmol _c kg ⁻¹) | 2.72 | |

Plant available metals (Table 4.3) were mostly low, with only Fe being notably elevated, and Pb and Mn slightly elevated. X-ray fluorescence analysis (Appendix 5) showed that the Lo sand was almost entirely Si, which was expected as the soil had a very high sand fraction.

Table 4.3 Plant available metals (DTPA extractable) of the Longlands sand

| | Cd | Co | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|------|---------------------|----|----|------|-------|-------|----|------|------|
| | mg kg ⁻¹ | | | | | | | | |
| Sand | bd | bd | bd | 0.92 | 82.17 | 13.96 | bd | 1.99 | 1.64 |

bd below detection.

As indicated earlier, the FWTR showed potential to supply a large number of the nutrients deficient in the Lo sand. As both the FWTR and Lo sand were moderately P deficient it was apparent that P fertilisation may be needed, particularly in the short term.

4.3.2 Phosphorus adsorption

The P adsorption isotherm of the Lo sand (Figure 4.1) shows that P sorption was quite low. At residual P solution concentrations of 0.05, 0.20 and 1.00 mg L⁻¹, the Lo sand sorbed 0.6, 3.0 and 15.0 mg kg⁻¹ P, respectively. This was considerably lower than the values given for the FWTR (Section 2.3.6). The low sorption capacity suggests that P is unlikely to be fixed, and may be leached from the plant root zone. The addition of FWTR to the Lo sand would increase its P sorption capacity, possibly reducing this loss of P.

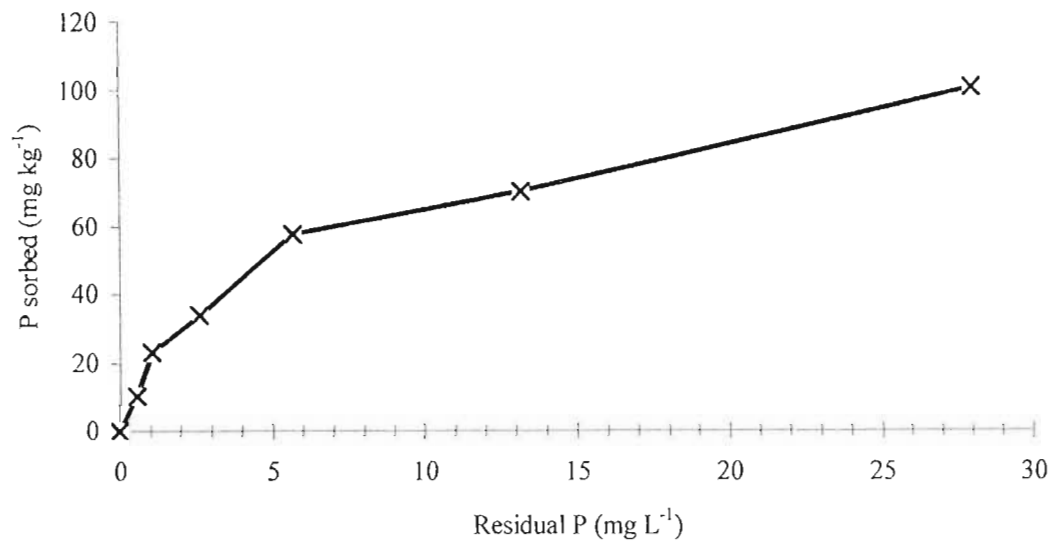


Figure 4.1 Phosphorus adsorption isotherm of the Longlands sand.

4.3.3 pH and electrical conductivity

As expected the addition of FWTR increased both the pH and EC of the Lo sand (Table 4.4). The pH increased by 1.33 units from the control to the 400 g kg⁻¹ application rate, while the EC showed a more than two fold increase over the same range, but was still low, however.

Table 4.4 pH and electrical conductivity (mS m⁻¹) of the Longlands sand treated with 0, 50, 100, 200 and 400 g kg⁻¹ of Faure water treatment residue

| FWTR rate (g kg ⁻¹) | pH | EC |
|------------------------------------|------|------|
| Control | 4.94 | 2.17 |
| 50 | 5.29 | 2.68 |
| 100 | 5.61 | 3.76 |
| 200 | 5.82 | 4.72 |
| 400 | 6.27 | 5.97 |

4.3.4 Water retention characteristics

The effect of increasing FWTR additions to the Lo sand was to increase the volumetric water content at almost all matric potentials (Figure 4.2).

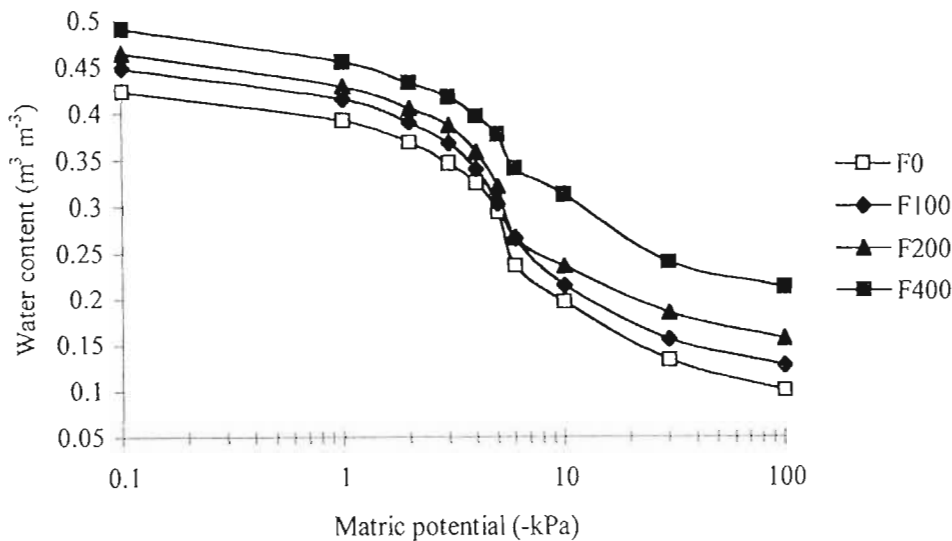


Figure 4.2 Water retention curves for the Longlands sand treated with 0, 100, 200 and 400 g kg⁻¹ Faure water treatment residue (F0, F100, F200 and F400, respectively).

At -5 kPa the FWTR added at 100 and 200 g kg⁻¹ appeared only to increase water content marginally over the pure Lo sand, but the 400 g kg⁻¹ FWTR showed a substantial increase in water content. The difference in water contents was notable at -10, -30 and -100kPa, suggesting that the FWTR increased the number of fine pores, which led to higher water contents at these matric potentials. As was the case for the RWTR mixtures (Section 3.3.3), generally the curves run parallel, suggesting that plant available water would not be greatly affected by FWTR additions to this soil.

4.3.5 Pot experiment

4.3.5.1 Leaf analysis

To enable discussion of the yield of the bean plants it is necessary to consider the findings of the nutritional analysis of the bean plants grown in the unfertilised 400 g kg⁻¹ treatment to

determine causes of the leaf chlorosis symptoms described earlier. Generally the plant nutrients tended to be within the recommended nutrient ranges (Table 4.5).

Table 4.5 Nutrient concentrations of bean leaves grown in a Longlands sand treated with 400 g kg⁻¹ Faure water treatment residue, without fertiliser. Recommended nutrient ranges reported by Bennett (1993) and Bergmann (1992) are given for comparison

| | N | S | Ca | Mg | K | P |
|-----------------|-----------------------------------|-------|-----------|-----------|-----------|-----------|
| | ------(%)----- | | | | | |
| Leaf sample | 3.42 | 0.25 | 1.93 | 0.59 | 1.96 | 0.19 |
| Bennett (1993) | 4.25-5.50 | 0.17 | 0.35-2.00 | 0.25-1.00 | 1.70-3.00 | 0.25-0.60 |
| Bergmann (1992) | 3.00-6.00 | - | 0.50-2.00 | 0.25-0.70 | 2.00-3.00 | 0.25-0.50 |
| | B | Cu | Fe | Mn | Zn | |
| | ------(mg kg ⁻¹)----- | | | | | |
| Leaf sample | 61.0 | 13.7 | 196.0 | 1208.0 | 44.0 | |
| Bennett (1993) | 15-50 | 10-30 | 50-540 | 20-100 | 20-70 | |
| Bergmann (1992) | 25-80 | 7-15 | - | 40-100 | 30-70 | |

Leaf tissue P concentration was below the recommended range, perhaps due to dilution because of the high planting density (6 plants per pot). Symptoms of P deficiency were not observed, and this is perhaps surprising considering the high P sorbing capacity of this WTR and that no fertiliser had been added to the pots. The only element that was considerably over the recommended range was Mn, being some 12 fold higher than the upper limit of 100 mg kg⁻¹ recommended for bean plants. The symptoms seen on these plants matched some of those described by Bergmann (1992) and Bennett (1993), which may be a combination of actual Mn toxicity and induced deficiencies, due to Mn having antagonistic effects on the uptake of other elements (Mg, Ca, Zn, Cu and Fe). This was cause for concern, as these concentrations may indicate that FWTR is not suitable for land application purposes, especially if the land is to be used for crop growth. However, it should be noted that in the case of dry beans, the crop is the seed, and it may be more useful to consider nutrient uptake by the seed as an indicator of potential toxicity problems (Section 4.3.5.3). Skene *et al.* (1995) tested the growth of beans (*P. vulgaris*) in mixtures of sand and either an alum or polymer WTR. Although nutrient uptake by the seed was not examined, they found no toxicity problems caused by trace nutrients in the foliage of the plants. They did indicate, however, that supplementary fertiliser was needed to realize optimal growth of the plants. Elliott and Singer (1988) reported that uptake of Cd, Zn, Cu and Ni was reduced in tomato shoots grown in a FeCl₃ coagulant WTR-amended soil. They also did not report any toxicity problems, but indicated that

supplementary fertiliser would be needed. Lucas *et al.* (1994) tested the growth of tall fescue in an alum WTR-treated soil. They found elevated Mn concentrations in the tall fescue with increasing rates of WTR (0, 10, 20 and 40 g kg⁻¹), which was initially suspected to be the cause for a decrease in yield seen in this experiment. However, in a subsequent experiment to test whether Mn was the cause of the decreased yield, they found that, although Mn exceeded recommended levels, plant growth was seemingly unaffected. While the study by Lucas *et al.* (1994) indicates the potential for Mn toxicity, the WTR application rates used were considerably lower than those used in this investigation. As Mn was the likely cause of the chlorotic symptoms seen in this study, attempts to reduce the Mn toxicity were considered and tested in an observational study (Section 4.3.5.4).

4.3.5.2 Yield

Analysis of variance (Appendix 12) showed that there were no significant fertiliser by FWTR application rate interactions, for either pod or seed number, but that each treatment factor had a significant individual effect on the measured variables (Table 4.6).

Table 4.6 Summary ANOVA statistics for number of pods and number of seeds for each treatment factor and interactions

| Variable | Treatment factor | F-ratio | df | Probability |
|-----------------|-------------------|---------|------|-------------|
| Number of pods | Fertiliser | 35.83 | 4,48 | <0.001 |
| | FWTR | 9.43 | 4,48 | <0.001 |
| | Fertiliser x FWTR | 1.38 | 4,48 | 0.191 |
| Number of seeds | Fertiliser | 44.19 | 4,48 | <0.001 |
| | FWTR | 3.14 | 4,48 | 0.022 |
| | Fertiliser x FWTR | 1.11 | 4,48 | 0.377 |

It was apparent that increasing additions of fertiliser with any particular FWTR rate improved pod (Figure 4.3a) and seed (Figure 4.3b) production. The mean effect of FWTR additions, however, tended to be more variable. The number of pods and seeds tended to increase with increasing rates of FWTR up to 100 g kg⁻¹, but showed marginal decreases with higher rates of FWTR. For both variables, the highest yield was recorded from the 100 g kg⁻¹ FWTR treatment with 150% fertiliser application. Comparisons by LSD_{5%} (Table 4.7) showed that the 150% fertiliser treatment (over mean FWTR application rate) yielded significantly better than the other treatments, while the 50 and 100 g kg⁻¹ FWTR rates (over mean fertiliser rate) performed significantly better than the other treatments. In the case of total number of pods (Table 4.8) the 150% fertiliser treatment (over mean FWTR application rate) yielded

significantly better than the other treatments, while the 100 g kg⁻¹ FWTR rates (over mean fertiliser rate) performed significantly better than the other treatments, with the 50, 200 and 400 g kg⁻¹ FWTR treatments performing similarly.

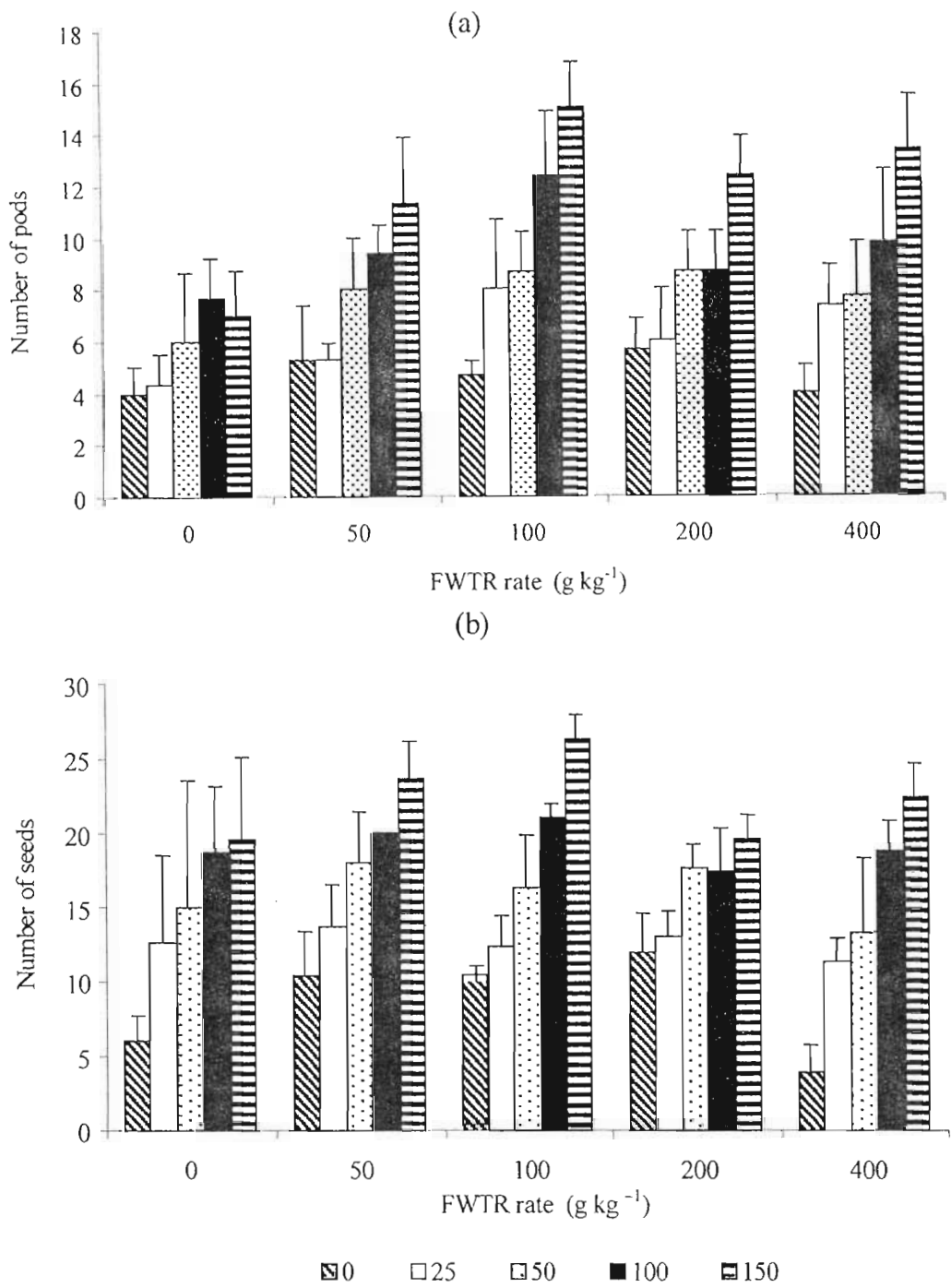


Figure 4.3 Mean (+ SE, 3 replicates) number of (a) pods and (b) seeds of beans grown in a Longlands sand with Faure water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ with fertiliser levels of 0, 25, 50, 100 and 150%, as indicated in the legend.

Table 4.7 $LSD_{5\%}$ comparisons of mean seed mass for each treatment factor for dry beans grown in a Longlands sand treated with 0, 50, 100, 200 and 400 g kg⁻¹ Faure water treatment residue with fertiliser applications of 0, 25, 50, 100 and 150%

| Fertiliser application rate (%) ¹ | | | | |
|--|--------|--------|--------|--------|
| 0 | 25 | 50 | 100 | 150 |
| 8.47e ³ | 12.60d | 16.07c | 19.33b | 22.33a |
| FWTR application rate (g kg ⁻¹) ² | | | | |
| 0 | 50 | 100 | 200 | 400 |
| 14.40c ³ | 17.13a | 17.20a | 15.93b | 14.13c |
| 1 Fertiliser application rate, over mean FWTR application rate. | | | | |
| 2 FWTR application rate, over mean fertiliser application rate. | | | | |
| 3 Letters that are different indicate significant differences between treatment means for each treatment factor ($LSD_{5\%}$: fertiliser = 1.162; FWTR = 1.162). | | | | |

Table 4.8 $LSD_{5\%}$ comparisons of mean number of pods for each treatment factor for dry beans grown in a Longlands sand treated with 0, 50, 100, 200 and 400 g kg⁻¹ Faure water treatment residue with fertiliser applications of 0, 25, 50, 100 and 150%

| Fertiliser application rate (%) ¹ | | | | |
|---|-------|-------|-------|--------|
| 0 | 25 | 50 | 100 | 150 |
| 4.73e ³ | 6.20d | 7.80c | 9.53b | 11.80a |
| FWTR application rate (g kg ⁻¹) ² | | | | |
| 0 | 50 | 100 | 200 | 400 |
| 5.80c ³ | 7.87b | 9.73a | 8.27b | 8.40b |
| 1 Fertiliser application rate, over mean FWTR application rate. | | | | |
| 2 FWTR application rate, over mean fertiliser application rate. | | | | |
| 3 Different letters indicate significant differences between treatment means for each treatment factor ($LSD_{5\%}$: fertiliser = 1.317; FWTR = 1.317). | | | | |

The effect of FWTR on seed mass (Figure 4.4) followed essentially the same trend as described for the seed and pod numbers, although seed mass was highest in the 400 g kg⁻¹ FWTR application rate with 150% fertiliser. As before there were no significant interaction effects, but the individual variables had significant effects overall (Appendix 12, Table 4.9). Individual seed size (results not given) and mass were not affected by any treatment with all treatments yielding seed of similar mass.

Table 4.9 Summary ANOVA statistics for mass of seeds for each treatment factor and treatment interactions

| Variable | Treatment factor | F-ratio | df | Probability |
|---------------|-------------------|---------|------|-------------|
| Mass of seeds | Fertiliser | 52.36 | 4,48 | <0.001 |
| | FWTR | 8.76 | 4,48 | <0.001 |
| | Fertiliser x FWTR | 1.07 | 4,48 | 0.404 |

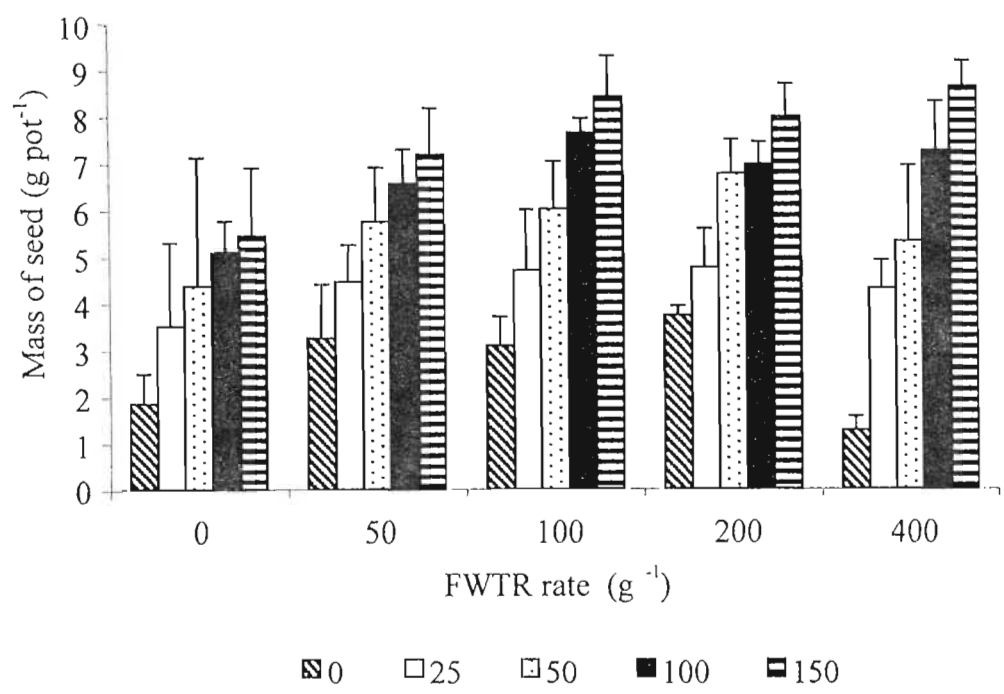


Figure 4.4 Mean (+SE, 3 replicates) mass of seed of beans grown in a Longlands sand with Faure water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ with fertiliser levels of 0, 25, 50, 100 and 150%, as indicated in the legend.

Comparisons by LSD_{5%} (Figure 4.5) showed that the 150% fertiliser treatment (over mean FWTR application rate) performed significantly better than the other treatments. There was an increase in mean seed mass with increasing rates of fertiliser over the FWTR application rates. This suggests that the 100% level was perhaps not the ideal fertiliser application rate under these conditions, with the 150% level performing significantly better. While it was indicated that beans grown in the 400 g kg⁻¹ FWTR without fertiliser appeared to have satisfactory foliar nutrient levels (Section 4.3.5.1), it is clear that additional fertiliser improved the mass of seed significantly.

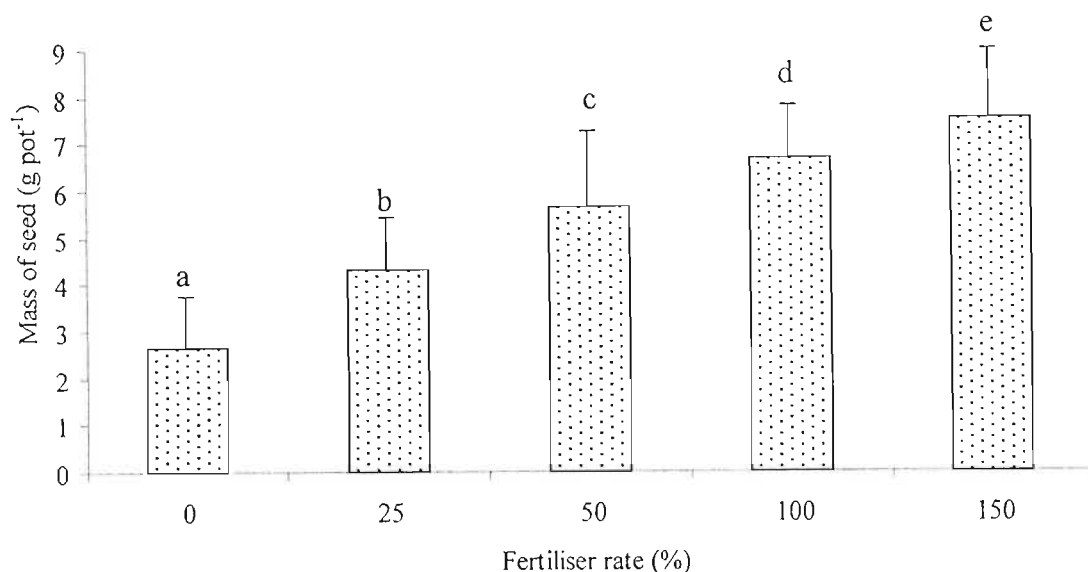


Figure 4.5 Mean (+ SE) mass of seed of beans grown in a Longlands sand at fertiliser levels of 0, 25, 50, 100 and 150% over the mean Faure water treatment residue application rates (0, 50, 100, 200 and 400 g kg⁻¹). Letters that are different indicate significant differences between treatment means (LSD_{5%} = 0.759).

Comparisons by LSD_{5%} of mean seed mass, for FWTR application rates, showed that the control treatment was significantly lower than the other treatments, which were not significantly different from one another (Figure 4.6). Maximum yield was achieved at the 200 g kg⁻¹ FWTR application rate. This suggests that addition of FWTR improves the yield of bean seed in a nutrient-poor sand.

However, from Figure 4.4 it would appear that without fertiliser the 400 g kg⁻¹ FWTR application negatively affects seed production in the bean plant, perhaps as a result of Mn toxicity and associated antagonistic effects, or possibly a P deficiency considering the high P sorption capacity of the FWTR (Section 2.3.6). This effect was less obvious for the fertilised treatments, indicating that addition of N, P and K may help overcome the growth-limiting or growth-inhibiting factor.

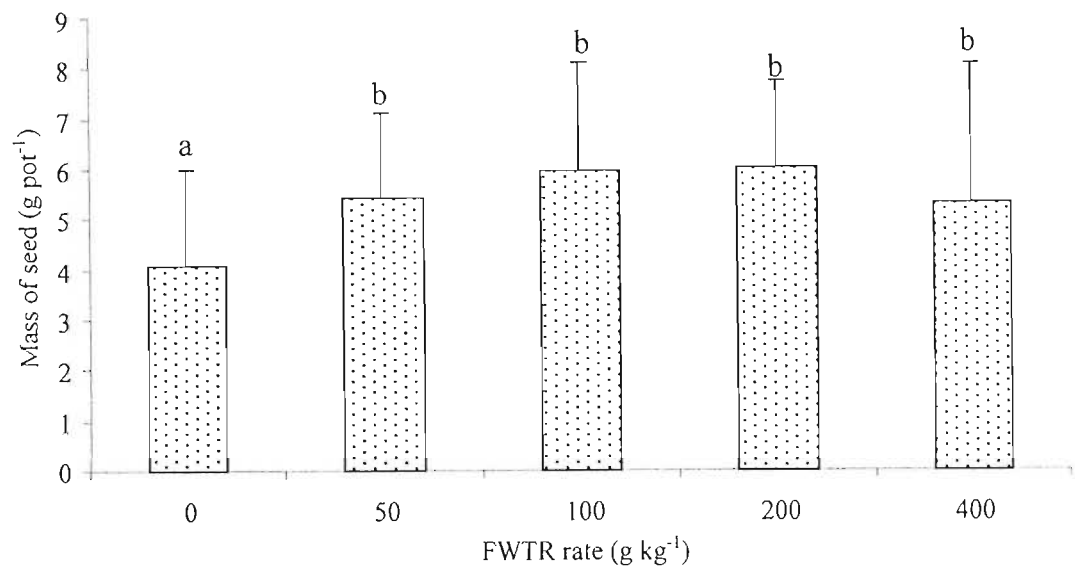


Figure 4.6 Mean mass of seed (+SE) of beans grown in a Longlands sand at Faure water treatment application rates of 0, 50, 100, 200 and 400 g kg⁻¹ over the mean fertiliser application rates of 0, 25, 50, 100 and 150%. Letters that are different indicate significant differences between treatment means (LSD_{5%} = 0.759).

From these data, to achieve maximum yield the recommendation would be to apply the FWTR at 400 g kg⁻¹ with 150% fertiliser. This, however, requires that the highest fertilisation rate be used and implies associated costs. To achieve a similar level of production the FWTR can be applied at 400 g kg⁻¹ with the 100% fertiliser level, even though this treatment produced 1.39 g pot⁻¹ less than the 400 g kg⁻¹ FWTR treatment with 150% fertiliser. The cost of fertiliser may require that the lower fertiliser rate be used, but in any event the yield data suggest that the FWTR can be applied at the maximum rate used here, even though there were indications of Mn toxicity in the foliage. To determine whether this may be detrimental to seed quality one needs to consider nutrient translocation to the seed.

4.3.5.3 Nutrient uptake by bean seed

While no distinguishing patterns of uptake were evident in the bean seeds (Appendix 13) for Ca, Mg and Na, there did appear to be small increases in the amounts of P and K with increasing additions of fertiliser. There appeared to be little effect of FWTR additions on the uptake of Ca, Mg, Na, K, or P, however. The FWTR additions appeared to have more effect on trace nutrient uptake, in particular Mn and Fe. Zinc and Cu concentrations were variable,

with Zn showing slight increases in concentration with increasing fertiliser additions. Manganese and Fe showed increases in concentration with increasing FWTR, but this was not surprising considering the high concentrations of both these elements in the FWTR. The concentrations, however, were always low. Although there was evidence of Mn toxicity in the foliage of the bean plants, the concentration in the seed indicates that they would be suitable for consumption. However, while the seed may be suitable for consumption, they may not be usable for propagation (planting), due to physiological damage to the seed testa sometimes associated with toxic levels of certain elements (Dr. A. Modi, and Prof. P. Greenfield, *pers. comms.* 2003). Furthermore, consideration of fleshy vegetable crops (e.g. tomatoes, lettuce) may also show higher translocation of toxic elements into these portions of the crop, possibly making them unsuitable for consumption. This would require further investigation.

4.3.5.4 Mn toxicity alleviation

As a result of the chlorosis evident in the leaves of the bean plants, beans were grown in the 400 g kg⁻¹ FWTR treatment with a variety of 'ameliorative' treatments applied to try and reduce or alleviate the Mn toxicity. A lime treatment (approximately 2 Mg ha⁻¹) was used to increase the pH, which it was speculated could reduce Mn availability or solubility. Nutrient uptake by grasses, from Study 1 (Section 3.4.4, Appendix 8), suggested that as pH increases Mn availability decreases. The bean plants with this treatment died shortly after the lime additions and it was suspected that the increase in pH over the already suitable level (Table 4.5) led to a reduction in the availability of other essential nutrients and, in conjunction with the Mn toxicity, caused a rapid death of the plants.

As Mn may have severe antagonistic effects on Fe uptake, it was speculated that due to the high Mn availability, the Fe/Mn balance may be causing the symptoms. This was again supported by data from Study 1 (Section 3.4.4, Appendix 8), where decreases in Mn concentration coincided with increases in Fe concentration. To determine whether additional Fe would help alleviate this, a commercially available 13% Fe chelate supplement for potted plants was either mixed with the soil and FWTR mixture at the manufacturer's recommended rates or applied as a foliar spray on germinated seedlings. In the incorporated treatment the bean seeds did not germinate, and in the other treatment the seedlings had a strong negative response to the foliar application of Fe, the leaves withering and dying within hours of application.

A 1:5 FWTR:water extract showed that the FWTR had 6.35 mg kg^{-1} water-soluble Mn and so leaching of the mixture to remove some of this excess Mn could possibly improve bean growth. To test this hypothesis, beans were grown in a 400 g kg^{-1} FWTR treatment that was watered excessively. Water was applied to the treatment so that it would drain from the base of the pot. The pot was then only rewatered once the material appeared dry. This was to lessen the possibility of creating reducing conditions in the pot that would lead to Mn reduction and increased availability. Initial indications were that this treatment had the potential to alleviate the Mn toxicity. While previously the Mn toxicity symptoms had been noticed on the cotyledonous leaves and subsequently on the new leaves, this treatment did not show these symptoms. The new leaves also developed a little more before showing the symptoms. It is considered that under the imposed leaching regime, continual removal of the Mn led to increased solubilisation of Mn, or possibly the creation of micro-sites with reducing conditions that may have caused the release of Mn. This was partly confirmed by an increase in the Mn concentration of the leachate collected from this experiment (results not shown). In addition, the continual leaching of this treatment could have caused a loss of other essential nutrients, which may have exacerbated any symptoms seen. However, this observational investigation does suggest that under field conditions adequate leaching and a suitable fertiliser regime may satisfactorily remedy the problem, but this will require further investigation.

4.4 Conclusions

While there was concern that Mn toxicity would be a problem for seed production, it would appear that this was limited to the higher FWTR application rates with low fertiliser additions. As it would appear that the source of the Mn was the coagulant salt used to treat the raw water, the problem may be entirely overcome by using a 'clean' coagulant. It is likely, however, that such a change would increase the cost of treatment due to the increased cost of purchasing a coagulant with less Mn.

It is suggested that leaching will decrease Mn concentrations adequately to lessen or prevent toxicity, but this would require careful management, to ensure that other mobile nutrients were not lost in excessive quantities, leading to other negative impacts on plant growth.

The effect of the FWTR was only tested on a single crop species in this investigation and further investigation using other crop species would be essential if the material was to be applied to areas where the land is to be used for food crops. The decomposition rate of the FWTR is not known and this would also require further investigation to ascertain whether multiple applications are possible on the same area, and at what frequency these applications could occur.

Chapter 5

General conclusions

Although the response to the questionnaire was poorer than expected, the information collected illustrated that a number of treatment processes are being used in South Africa, and that the range of chemical dosing is wide. The addition of long-chain organic polymers would, from these data, appear to be the most commonly used treatment process, but they were frequently used in conjunction with other coagulants, flocculants and lime. As mentioned, the possibility exists that the treatment chemicals may introduce other potentially toxic elements into the residues. This appeared to be the case for the FWTR, where a high concentration of Mn was evident in the $\text{Fe}_2(\text{SO}_4)_3$ used by the treatment plant. As the size and number of water treatment works increase the volume of WTR produced is likely to increase, and the use of uncontaminated treatment chemicals may assist in achieving 'clean' WTRs, which may be easier to dispose of to land than they might otherwise be. Furthermore, it should be noted that the treatment processes used may change over time, and may even alternate between a number of processes, depending on the quality of the raw water and the availability and cost of selected treatment chemicals from suppliers.

Although only five WTRs were investigated here, it is considered these are representative of many generated through the production of potable water in South Africa and they included samples from the three largest treatment facilities in the country. The sample from the Midmar Water Treatment Plant has been extensively investigated in other studies, while samples from the Faure Water Treatment Plant and Rand Water allowed investigation of residues that were derived from raw water from very different catchments and different treatment processes. The samples investigated showed that these residues vary considerably in elemental and nutrient composition, with implications for the land application of these materials. In general these residues do not have high concentrations of potentially toxic elements, possibly with the exception of Mn in the FWTR. These residues appear to have the potential to supply some macro- and micro-nutrients for plant growth, although the potential for P sorption is high.

The application of the RWTR to the sandy soil material from a coal mine increased the pH and EC substantially, but additions to the spoil increased the pH, while lowering the EC. The

sharp increases in pH may have possibly led to a decreased availability of some micro-nutrients, but this was not evident for the elements examined in this study. Generally, the application of up to 400 g kg⁻¹ (approximately 960 Mg ha⁻¹) of RWTR to the spoil did not significantly reduce grass growth, although some trends were apparent. *Eragrostis teff* performed moderately well in the first two harvests but yield declined dramatically by the third harvest. This was evident for the higher RWTR application rates. This may have been a combination of unfavourable growing conditions for the seedlings, considering that *E. teff* was reseeded for each harvest. *Digitaria eriantha* and *C. ciliaris*, however, showed an improvement in yield from the first harvest, and continued to yield well to the last harvest. *Eragrostis teff*, in the soil, initially performed well in the control and at low RWTR application rates, while the higher RWTR application rates consistently yielded poorly, declining substantially from the first harvest to the last. *Digitaria eriantha* and *C. ciliaris* showed improved yields with each subsequent harvest, but the yields at the higher RWTR application rates were consistently lower than those of the control and lower RWTR applications. These differences were not always significant though. It would appear that applying RWTR at 200 g kg⁻¹ (approximately 480 Mg ha⁻¹) to the soil would give satisfactory results. These application rates are, however, not recommended until adequate field-testing has been conducted. Nutrient uptake by the plants did not indicate any severe deficiencies or toxicities, and the elements measured in this investigation were largely discounted as causes for the observed trends in yield. A number of problems became evident as a result of the investigation being conducted as a pot experiment. Most notable was salt accumulation in the pots, which may have adversely affected plant growth, and that the plants may have become pot bound. This reinforces the notion that these studies should be further investigated on a field scale, using laboratory and glasshouse studies to determine and refine the parameters that should be tested.

The use of RWTR as a cover material over the ash appeared to offer a potential means of protecting the ash from external erosive forces. Yield of *C. dactylon* and *S. secundatum* was highest in the 60 mm RWTR layer with fertiliser added. *Cynodon dactylon* yielded better than *S. secundatum*, apparently being the hardier species. *Stenotaphrum secundatum* showed signs of P deficiency, but still grew moderately well. The use of these rapidly establishing and fast growing stoloniferous species would potentially offer rapid vegetative cover (and stabilisation) of the capping material, and consequently protection of the ash below.

The use of the FWTR on a nutrient-poor soil did not seem to improve bean yield, when applied without fertiliser. The addition of fertiliser greatly enhanced the yield of all treatments, notably the treatments that had FWTR added. The highest yield was achieved in the 400 g kg⁻¹ FWTR treatment with 150% fertiliser. The exact reason for this improvement in yield is not clear, when one considers the negative effect on the yield of bean seed when FWTR was applied at 400 g kg⁻¹ without fertiliser. While symptoms of Mn toxicity were evident, it would seem that the additional fertiliser allowed the plants to yield significantly better than many of the other treatments with lower rates of FWTR. Uptake of toxic elements by the seed did not appear to be a problem, but this may not necessarily be the case for other crop species where the fleshy parts and leaves of the crop are consumed (such as tomato or lettuce). An attempt to leach excess Mn from the soil in the FWTR treated pots appeared to temporarily alleviate or reduce the severity of the Mn toxicity. It is probable that under field conditions, with increased leaching, and greater dilution of the FWTR in the soil, the Mn toxicity would not be so severe. The obvious solution to the problem, however, would be to use other or 'cleaner' treatment chemicals, although this may have additional associated costs. These additional costs would have to be balanced against the high cost of disposal to landfill compared to the application to land in the surrounding areas.

The application of WTRs to land is becoming an increasingly popular method of disposal for these types of waste. In the South African context there would appear to be little work that has considered this approach, with Umgeni Water being the first water utility to initiate such extensive investigations into land application as a disposal option. For this approach to be viable, however, the selected area of disposal should ideally be near the treatment facility and be suitable for land disposal. This requires that a full characterisation of the WTR be conducted, as well as a survey and characterisation of the potential disposal site. The intended use of the land would also require consideration. If the intended use is agricultural production then careful consideration needs to be given to the consequences of the possible introduction of toxic elements into the crops grown. If the WTRs are to be applied to mined land, more careful consideration needs to be given to the possibility of exacerbating any existing environmental and plant inimical conditions. While not the case in this investigation, excessive acidity may lead to rapid breakdown of WTRs, releasing potentially toxic elements and possibly inducing physical problems due to decomposition of the WTRs. Other

considerations of land application are whether the treatment process varies, hence affecting the nature of the WTR produced; suitable application rates of a particular WTR to an area of land, based on current legislated limits or what can be shown to be an environmentally acceptable level; and whether there are plans to increase the size of a treatment plant and consequently the volume of WTR produced.

This investigation has shown that there is excellent potential for land application of WTRs to selected soils and materials, but further investigations are required to improve our understanding of the current findings and to allow for the development of clear guidelines and methods for use by the water purification industry and specifically the evaluation of sites identified for the disposal of WTRs.

Chapter 6

Further research

As these were preliminary investigations, a number of avenues exist for further research. The poorer than expected response to questionnaires and requests for WTR samples did not allow for a complete overview of South Africa's residues. For the development of suitable test methods, guidelines and methods of disposal of WTRs there would need to be a greater input from all water authorities and treatment facilities. This would require that the concerned companies and authorities be adequately informed of the benefits of such work to them in terms of finding suitable alternative disposal options that may be more cost effective, environmentally sound and possibly beneficial to the treated areas. The questionnaire would require further development, possibly with simplification of questions, but also an expansion of the questions asked. The aim would be to collect comprehensive information about each treatment facility's operations, but in such a fashion as to remove possible misinterpretation of the questions.

Obtaining samples of WTR for laboratory investigations proved to be difficult, partly due to the reliance on treatment facilities to collect and send the samples. It may be that with a clearer understanding of the purpose of the overall study a greater number of samples would be received. Where this is not the case, it may require that samples be collected from the treatment sites by the research team. Analysis of WTR samples would follow the methods described in this investigation, but a set of parameters and methods would require definition for use by the industry to determine the potential liability or beneficial impacts that a WTR may have. These methods and criteria would depend on the general nature of the WTRs (e.g. polymer vs. lime vs. alum WTRs) and the possible land application purpose (e.g. agricultural vs. derelict vs. recreation). The methods prescribed may also be related to how the test method correlates to effects on soil properties and plant growth, which would be obtained by glasshouse and field investigations under a variety of conditions.

Further investigations into the breakdown rates, and the implications thereof, of the WTRs would also play a major role in the development of guidelines and models for the disposal of the material to land. Other possible avenues of investigation include consideration of the elemental composition of treatment chemicals and characterisation of the raw water quality.

These investigations would help determine sources of potentially toxic elements in the WTR and would perhaps prompt the production of less toxic WTRs, which may then possibly help reduce disposal costs.

The use of RWTR on materials from a coal mine aimed to determine a maximum RWTR application rate that would not negatively impact on soil properties and plant growth. It would be necessary to refine the application rates chosen, possibly with more attention given to the lower application rates, as generally it was found that 400 g kg^{-1} RWTR was unsuitable. As the RWTR was applied as a relatively fine material ($<2\text{mm}$), it may be feasible to use a larger size fraction. This may slow the rate of chemical reaction, while improving the texture as a capping material. It may, however, have a less favourable impact on the hydraulic properties of the already coarse spoil material. Another aspect, not considered, was suitable fertilisation rates. Blanket fertiliser applications were used here, but variable application rates may be more suitable. Further studies using pot experiments should also consider an increase in material leaching, which would be more likely to simulate field conditions.

The three species of grass tested were representative of the most commonly used species at this mine. However, a number of other species are used in conjunction with these. Consideration could be given to the use of leguminous species and possibly deep rooted plants (trees and shrubs). It may also be worth considering salt tolerant species. If the proposed end use of the mined land is for livestock production, more attention should be given to uptake of elements not measured here. This is to ensure that deficiencies and toxicities do not occur that may negatively impact on livestock production and possibly human nutrition.

Also not investigated here, were the effects of RWTR additions on microbial populations and behaviour. Alkaline conditions inhibit the action of Fe-oxidising bacteria (Carrucio *et al.*, 1988) perhaps assisting in reducing acid generation. Consideration could also be given to the effects of using wet (as opposed to dry) RWTR. The material used here was collected dry, but it originates as a slurry from the water treatment process. The use of wet material could have different impacts on both soil chemical and physical properties. The wet material may contain electrolytes and polymers that have not reacted or bonded with material in the raw water. These unreacted bonds may then be available to react with the soil matrix altering the physical

(Moodley, 2001), and possibly chemical behaviour of the soil.

These aspects can be further examined by means of leaching and incubation studies, under a variety of controlled conditions. These types of studies can give insight into detailed chemical (and physical) changes in the materials, so indicating dissolution rates and equilibrium states.

The final aspect to be investigated would be field testing. The establishment of field trials enable one to study how the materials behave at field-scale in the environment. While a number of factors cannot be controlled, field experimentation shows what the outcomes will be under natural conditions. Furthermore, it allows *in situ* measurements of parameters that cannot be successfully determined in pot experiments, such as changes in compaction, bulk density, leaching parameters and general hydrology. Plant dynamics can also be better investigated, and multi-species systems used to test species preferences and plant dynamics over a longer time frame e.g. from germination, through establishment to full production. This is especially so for perennial species.

Similar investigations are proposed for the use of the FWTR on sandy soils. However, in this instance careful consideration would be given to other crops, to determine the potential of introducing toxic elements into food destined for human consumption. Methods to reduce this transfer would need to be considered and would include encouraging a change in the chemicals used in the treatment process as well as considering possible ameliorative techniques that would either remove or immobilise these toxic elements. A better understanding of this, together with the development of treatment and disposal protocols, will help design engineers develop and plan water treatment works using technology that is fit-for-purpose and compatible with the disposal options available for WTRs.

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Appendices

Appendix 1 The questionnaire distributed to water treatment authorities to determine raw water treatment and water treatment residue disposal practices in South Africa. The questionnaire was developed before the decision to use the term ‘water treatment residue’, hence the use of the term ‘sludge’

Questionnaire.

This questionnaire is to obtain information from as many drinking water treatment works as possible. If there is more than one plant under your management or forming part of your organisation, please complete a separate questionnaire for each plant.

Contact person:

Details: Address:

.....

.....

(Tel).....

(Fax).....

(e-mail).....

1) Where is/are the source/s of abstraction of the facility’s raw water? (if more than one, list in order of greatest volume taken).....
.....
.....
.....
.....
.....
.....
.....

2) What volume of sludge is produced seasonally?
Winter:.....
Summer:.....
(If possible please also include annual trends)

3) What chemicals and flocculants are added to purify the raw water? (tick where applicable):
Lime: ☐ Bentonite: ☐
 $Al_2(SO_4)_3$: ☐
 $FeCl_3$: ☐
Polyelectrolytes ☐ Type (please specify):.....
Activated Silica ☐
Other (please specify):
.....

4) What are the dosage rates of chemicals added? (Give as ppm or mg/L if possible)
Lime:..... Bentonite:.....
 $Al_2(SO_4)_3$:.....
 $FeCl_3$:.....
Polyelectrolytes:.....
Activated Silica:.....
Other (from question 3):.....
.....

5) How is the sludge thickened?
Centrifugation ☐
Chemical additives ☐ (please specify):.....
Settling ponds ☐
Other (please specify):.....

6) What is the approximate solids content of the sludge produced?

7) How is the sludge currently disposed of?
Landfill ☐ Land treatment ☐ Sewer discharge ☐
River discharge ☐
Other (please specify):.....

8) How is the sludge transported to the disposal site?
Road (truck, trailer, etc.) ☐
Pipeline ☐
On site disposal ☐
Other:.....

9) What is the approximate distance to the disposal site?
.....

10) Have any studies been conducted that are related to the disposal or use of the sludge?
Yes ☐ No ☐

11) If Yes, are these studies available in the public domain?
Yes ☐ No ☐

12) If Yes, where can these studies be accessed?
.....
...

13) Are there any potential sites for rehabilitation and/or land treatment (amelioration) in the vicinity of the water treatment facility and surrounding areas? (Please give details).
.....
.....
.....
.....

14) Would your company be interested in supporting this study?
Logistically ☐ Financially ☐ Both ☐

15) Would you send us a sample of the requested quantity of waste material?
Yes ☐
Yes, if we arrange transport ☐
No ☐

Appendix 2 Method for determining extractable Ca, Mg, K and Na and cation exchange capacity in the water treatment residues and other materials

2.5 g of air dry (<2mm) sample were placed in a 100 mL plastic centrifuge tube and 25 mL 0.1M SrCl_2 solution added. The tubes were capped and shaken on a reciprocating shaker for 30 minutes and subsequently centrifuged at a R.C.F of 1535 x g. for 4 minutes. The supernatant was then filtered through Whatman 541 filter paper into 100 mL volumetric flasks. This was repeated a further 3 times with the shaking time reduced to 15 minutes. The solution was then made to volume with 0.1M SrCl_2 .

The residue was then washed with 70% ethanol, followed by 3 more washes with 50% ethanol. Each time the solution was centrifuged as before and the supernatant discarded. The residue was then treated with 4 x 25 mL aliquots of 1M ammonium acetate, following the same shaking and centrifuging procedure as for the SrCl_2 treatment.

Calcium, Mg and Sr were measured by atomic absorption spectrophotometry and Na and K by flame emission spectrometry, using a Varian SpectrAA-200. Exchangeable cations (Mg, Ca, K and Na) were measured in the SrCl_2 solution. Calcium, Mg and Na were measured by diluting an aliquot with a K solution to give a final concentration of 2 000 mg K L^{-1} . Potassium was measured by taking an aliquot and diluting with a Cs solution to give a final concentration of 1 200 mg Cs L^{-1} . Strontium (estimating total CEC) was measured in the ammonium acetate solution. An aliquot was diluted with a K solution to give a final concentration of 2 000 mg K L^{-1} . These additional solutions were added as ionisation suppressants, as indicated by the instrument's operating manual. Results are expressed as $\text{cmol}_c \text{ kg}^{-1}$ of air-dry material.

Appendix 3 Method used for particle size analysis (adapted from Gee and Bauder, 1986)

Air dry (<2mm) material was dispersed by the addition of 10 mL Calgon (35.7 g sodium hexametaphosphate and 7.9 g sodium carbonate per litre) and 20 mL distilled water with subsequent ultrasound treatment (400 watt, Labsonic 2000) for 3 minutes. The dispersed sample was passed through a 0.053 mm sieve into a 1 L sedimentation cylinder and made up to the 1 000 mL mark with distilled water.

The >0.053 mm fraction (sand) was dried at 105°C and the <0.053mm fraction in the cylinders was brought into suspension by agitation with a custom-made plunger. The coarse silt (0.02-0.053 mm), fine silt (0.002-0.02 mm) and clay (<0.002mm) were determined by sedimentation and pipette sampling after appropriate settling times for each size fraction, according to Stokes Law. The pipetted sample was dried overnight at 105°C. Separate subsamples of all <2mm materials were dried at 105°C overnight for moisture content determination. All fractions are given as a mass percentage of oven-dry soil, after correcting for moisture content of air-dry samples. Two replicates were measured on each sample. Texture classes were assigned according to the Soil Classification Working Group (1991).

Appendix 4 List of water treatment facilities that returned partially and completely filled questionnaires. Includes source of raw water and chemical dosing rates (where supplied)

| Water Authority | Water source | Dosing rates of chemicals (mg L ⁻¹) ¹ | | | | | | | | |
|--|------------------------------------|--|-----|------|-------|-------------------|-----------|-------|------|-------|
| | | Lime | Ben | AlSO | FeSO | FeCl ₃ | LCP | ActSi | NaAl | Other |
| Albany Coast Water | Desalinisation Plant | | | | | | | | | |
| Amatola Water | Nahoon Dam | 8 | | | | | 6-12 | | | |
| Bloemfontein Water³ | | | | | | | | | | |
| Plant 1 | Hennie Steyn bridge | 7.34 | | | | 0.8 | 13.3 | | | |
| Plant 2 | Gariiep Dam wall | 2.56 | | | | | 4.88 | | | |
| Plant 3 | Sterkfontein bridge | 3.43 | | | | 2 | 2.9 | | | |
| Bushbuckridge Water Board³ | | | | | | | | | | |
| Plant 1 | Shatale River | * | | | | | | * | | |
| Plant 2 | N'warhelo River | * | | | | | * | | | |
| Plant 3 | Edinburgh Dam | * | | | | * | * | | | |
| Plant 4 | Mutlumuvi/Sand River Pump stations | * | | | | | * | | | |
| Plant 5 | Not specified | * | | | | | * | | | |
| Plant 6 | Sand River canal | | | | | | * | | * | |
| Cape Metropolitan Council³ | | | | | | | | | | |
| Blackheath | Theewaterskloof Dam | 5.6 | | 1.6 | | | | | | |
| Brooklands | Kleinplaas/Lewis Gay/Rawson Dams | 60 | | 8 | | | 0.1 | | | |
| Constantia Nek | Table Mountain Dams | 47.6 | | 5.3 | | | | 6 | 3.1 | |
| Faure | Theewaterskloof/Palmiet | 40-45 | | | 7-15 | | | | | |
| Kloofnek | Hely Hutchinson/Woodhead Dams | 42 | | 5 | | | | | 2.5 | 22 |
| Voelvlei | Voelvlei Dam | 16.2 | | | 4.7-7 | | 0.02-2.25 | | | 5.3 |
| Wemmershoek | Wemmershoek/Theewaterskloof Dam | 30-36 | | 65 | | | | | | 16 |

Appendix 4 (continued) List of water treatment facilities that returned partially and completely filled questionnaires. Includes source of raw water and chemical dosing rates (where supplied)

| Water Authority | Water source | Dosing rates of chemicals (mg L ⁻¹) ¹ | | | | | | | | |
|----------------------------------|----------------------------|--|---------|-------|------|-------------------|---------|-------|------|-------|
| | | Lime | Ben | AlSO | FeSO | FeCl ₃ | LCP | ActSi | NaAl | Other |
| Khara Hais Municipality | Orange River | 5 | | | | | 0.1-1 | | | 5-15 |
| Lepelle Northern Water | Olifants River | | | | | | 0.29 | | | |
| Midvaal Water Company | Middle Vaal River | 15 | | 10 | | 10-23 | 0.4-10 | | | |
| Rand Water | Vaal Dam | 60-80 ² | | | | 1.5-7 | 8 | 3 | | |
| Rustfontein Water | Modder River | 9 | | | | | 2 | | | |
| Umgenti Water³ | | | | | | | | | | |
| Amazimtoti | Niengwane Dam | 6-12 | 0.5-2.5 | | | | 5-17 | | | |
| Craigieburn | Umkomaas River | 4 | | | | | 1-7 | | | |
| Durban Heights | Nagle/Inanda Dams | 4-6 | | | | | 2-3 | | | |
| DV Harris | Midmar Dam | 8-8.2 | 3-3.5 | | | | 1.3 | | | |
| Hazelmere | Hazelmere Dam | 10-12 | | | | | | | | |
| Imfume | Boreholes | | | | | | 57 | | | |
| Ixopo | Solly Bux Dam/borehole | 4 | | 33-45 | | | | | | |
| Midmar | Midmar Dam | 5.3-8.2 | 2.1-2.9 | | | | 1.1-1.4 | | | |
| Mtwalume | Mtwalume River | 4-7 | | 33 | | | 10 | | | |
| Ogunjini | River abstraction | | | | | | * | | | |
| Umbumbulu | Nugwane Dam | 6-12 | 0.5-2.5 | | | | 5-17 | | | |
| Umlaas Rd | Midmar Dam | 5.3 | 2.4-3.4 | | | | 2.1 | | | |
| Umzinto | JG Smith Dam/Umzinto River | 10-12 | | | | | 8-14 | | | |
| Wiggins | Inanda Dam | 2-2.5 | 1-2 | | | | 1.5-2 | | | |

¹ Lime - lime, Ben – bentonite, AlSO - Al₂(SO₄)₃·14H₂O, FeSO - Fe₂(SO₄)₃, FeCl₃ - FeCl₃, LCP – long-chain organic polymer, ActSi - activated silica, NaAl - sodium aluminate, Other - activated charcoal and CO₂.

² Added as CaO (Rand Water).

³ Water treatment authorities with more than one water treatment facility.

* These treatment facilities indicated the use of these chemicals, but did not supply dosing rates.

Appendix 5 X-ray fluorescence analysis of the water treatment residues discussed in Chapter 2, the spoil, soil and ash used in Chapter 3, and the Longlands sand used in Chapter 4

| Sample | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | MnO | MgO | CaO | Na ₂ O | K ₂ O | TiO ₂ | P ₂ O ₅ | Total | LOI ¹ |
|-----------------|------------------|--------------------------------|--------------------------------|------|------|-------|-------------------|------------------|------------------|-------------------------------|--------|------------------|
| | (%) | | | | | | | | | | | |
| Midmar | 54.57 | 22.60 | 11.95 | 1.53 | 1.92 | 4.20 | 0.15 | 1.47 | 0.86 | 0.24 | 99.49 | 23.91 |
| Midvaal | 53.07 | 22.36 | 14.24 | 0.41 | 1.83 | 4.45 | 0.33 | 1.89 | 0.74 | 0.47 | 99.79 | 27.70 |
| Amatola | 52.59 | 29.06 | 10.31 | 0.07 | 1.82 | 1.55 | 0.43 | 2.98 | 0.86 | 0.12 | 99.79 | 25.63 |
| Rand | 24.36 | 9.89 | 4.85 | 0.66 | 5.25 | 53.19 | 0.61 | 0.82 | 0.31 | 0.09 | 100.03 | 36.93 |
| Faure 1 | 29.93 | 8.70 | 53.80 | 0.96 | 0.72 | 3.15 | bd ³ | 0.93 | 0.78 | 0.39 | 99.36 | 43.07 |
| Spoil | 73.02 | 19.00 | 2.82 | 0.03 | 0.59 | 1.39 | 0.33 | 1.09 | 1.03 | 0.09 | 99.57 | 26.93 |
| Soil | 87.65 | 7.16 | 2.32 | 0.03 | 0.22 | 0.19 | 0.35 | 1.41 | 0.36 | 0.01 | 99.70 | 4.52 |
| Ash | 56.14 | 29.93 | 3.87 | 0.03 | 1.27 | 5.55 | 0.24 | 0.78 | 1.51 | 0.38 | 99.70 | 1.61 |
| Lo ² | 89.91 | 2.59 | 3.84 | 0.07 | 0.08 | 0.16 | bd | 0.16 | 2.80 | 0.03 | 99.64 | 2.81 |

| | Cd | Co | Cr | Cu | Ni | Pb | Zn | S | Sr | As | V | U |
|---------|------------------------|-------|--------|-------|--------|-------|--------|---------|--------|-------|--------|-------|
| | (mg kg ⁻¹) | | | | | | | | | | | |
| Midmar | 4.00 | 39.00 | 161.00 | 44.00 | 53.00 | 37.00 | 84.00 | 720.00 | 71.00 | 17.00 | 154.00 | bd |
| Midvaal | nd ⁴ | 32.00 | 246.60 | 53.20 | 117.70 | 26.00 | 142.10 | 2402.00 | 66.20 | 5.00 | 187.80 | 0.20 |
| Amatola | nd | 19.00 | 134.30 | 23.00 | 39.70 | 36.00 | 84.50 | 911.00 | 91.40 | 11.00 | 175.80 | 3.80 |
| Rand | nd | 3.50 | 77.30 | 5.40 | 22.90 | 5.80 | 33.10 | 700.00 | 273.40 | 1.70 | 61.10 | 2.10 |
| Faure 1 | nd | nd | 43.00 | bd | 21.00 | nd | 182.00 | 2500.00 | nd | nd | 93.00 | nd |
| Spoil | nd | 22.10 | 248.60 | 34.40 | 52.10 | 14.00 | 51.60 | 10800 | 164.30 | 13.80 | 222.40 | 2.50 |
| Soil | nd | 12.60 | 152.30 | 15.40 | 25.70 | 6.90 | 30.80 | 100.00 | 48.40 | 5.10 | 98.10 | 0.50 |
| Ash | nd | 12.60 | 201.50 | 49.80 | 47.40 | 45.90 | 40.30 | 2900.00 | 990.00 | 24.00 | 151.70 | 12.20 |
| Lo | nd | nd | 146.00 | 4.00 | 4.00 | nd | 16.00 | 235.00 | nd | nd | nd | nd |

| | Nb | Ce | Nd | Zr | Y | Sc | Th | Ba | La | Rb | Ga |
|---------|------------------------|--------|-------|--------|-------|-------|-------|---------|--------|--------|-------|
| | (mg kg ⁻¹) | | | | | | | | | | |
| Midmar | 11.00 | 96.00 | 25.00 | 126.00 | 27.00 | 33.00 | 10.00 | 1007.00 | 19.00 | 94.00 | 20.00 |
| Midvaal | 7.80 | 51.00 | 24.00 | 101.60 | 23.10 | 30.70 | 7.90 | 438.70 | 5.40 | 109.20 | 19.00 |
| Amatola | 10.60 | 71.00 | 38.00 | 105.10 | 29.40 | 30.10 | 16.10 | 705.70 | 30.60 | 171.50 | 23.00 |
| Rand | 2.70 | 5.10 | bd | 32.20 | 38.10 | 13.50 | 5.00 | 398.40 | bd | 38.10 | 8.90 |
| Faure 1 | nd | nd | nd | nd | nd | nd | nd | nd | 38.00 | nd | nd |
| Spoil | 12.30 | 95.00 | 36.50 | 196.60 | 24.20 | 34.60 | 15.30 | 538.70 | 30.80 | 33.20 | 14.90 |
| Soil | 5.10 | 36.80 | 13.50 | 230.10 | 14.50 | 20.00 | 9.60 | 448.40 | 31.20 | 58.40 | 9.30 |
| Ash | 34.60 | 169.50 | 76.90 | 389.10 | 71.70 | 36.50 | 45.80 | 1117.40 | 100.60 | 40.50 | 38.70 |
| Lo | nd | nd | nd | nd | nd | nd | nd | nd | 10.00 | nd | nd |

1 Loss on ignition.
2 Longlands sand.
3 below detection.
4 not determined.

Appendix 6 Mean (3 replicates) electrical conductivity (mS m⁻¹) and pH for the first, second and third leachates collected from the soil and spoil treatments at Rand water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹. Coefficient of variation (%) values are given for pH and EC for each leachate

| Waste | Grass | RWTR rate (g kg ⁻¹) | Leachate 1 | | Leachate 2 | | Leachate 3 | |
|-------|-------------------|---------------------------------------|------------|------|------------|------|------------|------|
| | | | EC | pH | EC | pH | EC | pH |
| Soil | <i>E.teff</i> | 0 | 91.5 | 7.03 | 87.6 | 7.29 | 152.3 | 6.40 |
| Soil | <i>E.teff</i> | 50 | 100.9 | 7.50 | 318.0 | 7.92 | 458.3 | 8.08 |
| Soil | <i>E.teff</i> | 100 | 127.5 | 7.99 | 155.3 | 7.29 | 408.3 | 7.62 |
| Soil | <i>E.teff</i> | 200 | 143.0 | 7.87 | 192.6 | 8.28 | 650.0 | 8.19 |
| Soil | <i>E.teff</i> | 400 | 275.0 | 7.36 | 288.3 | 8.21 | 519.6 | 8.08 |
| | | CV(%) | 11.3 | 1.6 | 11.6 | 1.8 | 12.5 | 2.0 |
| Soil | <i>D.eriantha</i> | 0 | 76.2 | 6.62 | 46.3 | 5.69 | 57.0 | 5.40 |
| Soil | <i>D.eriantha</i> | 50 | 231.3 | 7.82 | 314.6 | 7.92 | 492.0 | 8.26 |
| Soil | <i>D.eriantha</i> | 100 | 289.0 | 7.39 | 336.0 | 7.98 | 624.3 | 8.24 |
| Soil | <i>D.eriantha</i> | 200 | 319.0 | 7.89 | 708.3 | 7.75 | 850.6 | 8.23 |
| Soil | <i>D.eriantha</i> | 400 | 411.6 | 7.59 | 550.3 | 7.98 | 704.3 | 8.32 |
| | | CV(%) | 9.1 | 1.2 | 16.4 | 0.8 | 14.9 | 1.8 |
| Soil | <i>C.ciliaris</i> | 0 | 114.8 | 6.09 | 166.3 | 5.86 | 202.3 | 5.86 |
| Soil | <i>C.ciliaris</i> | 50 | 122.7 | 7.84 | 273.6 | 7.97 | 594.0 | 7.66 |
| Soil | <i>C.ciliaris</i> | 100 | 215.6 | 7.99 | 287.0 | 8.14 | 700.0 | 7.82 |
| Soil | <i>C.ciliaris</i> | 200 | 254.3 | 7.78 | 356.6 | 8.15 | 767.0 | 7.88 |
| Soil | <i>C.ciliaris</i> | 400 | 282.2 | 7.93 | 371.0 | 8.19 | 657.0 | 8.62 |
| | | CV(%) | 13.3 | 2.1 | 30.1 | 0.4 | 18.0 | 3.5 |
| Spoil | <i>E.teff</i> | 0 | 281.3 | 7.27 | 275.0 | 6.92 | 343.6 | 6.69 |
| Spoil | <i>E.teff</i> | 50 | 351.3 | 7.20 | 446.0 | 7.45 | 402.3 | 7.98 |
| Spoil | <i>E.teff</i> | 100 | 492.6 | 7.41 | 621.0 | 7.56 | 563.6 | 8.01 |
| Spoil | <i>E.teff</i> | 200 | 665.3 | 7.60 | 680.0 | 7.93 | 653.0 | 7.92 |
| Spoil | <i>E.teff</i> | 400 | 632.0 | 7.94 | 779.3 | 7.93 | 619.3 | 8.23 |
| | | CV(%) | 7.8 | 1.9 | 3.1 | 2.0 | 21.0 | 0.8 |
| Spoil | <i>D.eriantha</i> | 0 | 265.3 | 7.22 | 309.0 | 6.77 | 221.3 | 6.53 |
| Spoil | <i>D.eriantha</i> | 50 | 401.6 | 7.51 | 529.3 | 7.57 | 498.3 | 7.32 |
| Spoil | <i>D.eriantha</i> | 100 | 392.0 | 7.68 | 688.0 | 7.62 | 636.6 | 8.03 |
| Spoil | <i>D.eriantha</i> | 200 | 445.0 | 7.61 | 730.3 | 7.61 | 665.3 | 8.26 |
| Spoil | <i>D.eriantha</i> | 400 | 473.6 | 7.47 | 846.0 | 7.67 | 827.3 | 8.13 |
| | | CV(%) | 6.4 | 3.0 | 5.4 | 0.5 | 14.2 | 3.3 |
| Spoil | <i>C.ciliaris</i> | 0 | 289.0 | 7.39 | 261.3 | 6.89 | 237.0 | 6.37 |
| Spoil | <i>C.ciliaris</i> | 50 | 327.6 | 7.60 | 387.3 | 7.62 | 434.0 | 8.05 |
| Spoil | <i>C.ciliaris</i> | 100 | 467.6 | 7.66 | 512.0 | 7.77 | 459.0 | 8.21 |
| Spoil | <i>C.ciliaris</i> | 200 | 619.0 | 7.88 | 824.6 | 7.87 | 745.0 | 8.04 |
| Spoil | <i>C.ciliaris</i> | 400 | 607.6 | 7.54 | 1086.6 | 7.63 | 945.3 | 7.84 |
| | | CV(%) | 7.9 | 2.3 | 10.0 | 1.4 | 23.5 | 0.6 |

Appendix 7 ANOVA tables for (a) *Eragrostis teff*, (b) *Digitaria eriantha* and (c) *Cenchrus ciliaris* grown in the soil material and (d) *Eragrostis teff*, (e) *Digitaria eriantha* and (f) *Cenchrus ciliaris* grown in the spoil material when treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹. Raw yield data are available from the author subject to suitable confidentiality agreements

(a)

| Source of variation | d.f. ¹ | SS ² | MS ³ | VR ⁴ | F Probability |
|------------------------------|-------------------|-----------------|-----------------|-----------------|---------------|
| Block (replicate) | 2 | 13.25 | 6.62 | 1.16 | <0.001 |
| RWTR application rate | 4 | 605.27 | 151.32 | 16.61 | |
| Residual | 8 | 45.50 | 5.69 | | |
| Total | 14 | 664.01 | | | |
| Coefficient of variation (%) | 8.7 | | | | |

(b)

| SOV | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|--------|--------|-------|---------------|
| Block (replicate) | 2 | 31.37 | 15.68 | 2.03 | <0.001 |
| RWTR application rate | 4 | 546.80 | 136.70 | 17.72 | |
| Residual | 8 | 61.72 | 7.72 | | |
| Total | 14 | 639.89 | | | |
| Coefficient of variation (%) | 17.2 | | | | |

(c)

| SOV | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|--------|-------|------|---------------|
| Block (replicate) | 2 | 4.78 | 2.39 | 0.36 | 0.005 |
| RWTR application rate | 4 | 231.13 | 57.78 | 8.62 | |
| Residual | 8 | 53.64 | 6.71 | | |
| Total | 14 | 289.55 | | | |
| Coefficient of variation (%) | 4.8 | | | | |

(d)

| SOV | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|--------|-------|------|---------------|
| Block (replicate) | 2 | 62.47 | 31.23 | 2.74 | 0.534 |
| RWTR application rate | 4 | 38.55 | 9.64 | 0.85 | |
| Residual | 8 | 91.23 | 11.40 | | |
| Total | 14 | 192.25 | | | |
| Coefficient of variation (%) | 19.4 | | | | |

(e)

| SOV | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|--------|-------|------|---------------|
| Block (replicate) | 2 | 38.35 | 19.17 | 1.19 | 0.197 |
| RWTR application rate | 4 | 125.19 | 31.30 | 1.94 | |
| Residual | 8 | 128.94 | 16.12 | | |
| Total | 14 | 292.48 | | | |
| Coefficient of variation (%) | 8.1 | | | | |

(f)

| SOV | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|--------|-------|------|---------------|
| Block (replicate) | 2 | 85.60 | 42.80 | 0.64 | 0.430 |
| RWTR application rate | 4 | 286.99 | 71.75 | 1.07 | |
| Residual | 8 | 535.48 | 66.93 | | |
| Total | 14 | 908.06 | | | |
| Coefficient of variation (%) | 11.5 | | | | |

1 d.f. degrees of freedom.

2 SS sum of squares.

3 MS mean sum of squares.

4 VR variance ratio.

Appendix 8 Mean yields (\pm SE, 3 replicates) for the first, second and third harvests for *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil and spoil treated with Rand water treatment residue at application rates of 0, 50, 100, 200 and 400 g kg⁻¹. Where significant ANOVA F-statistics were obtained, LSD_{5%} comparisons were made. LSD_{5%} values and coefficients of variation (CV) are presented for each harvest. Raw yield data are available from the author subject to suitable confidentiality agreements

| Waste | Grass | RWTR rate (g kg ⁻¹) | Harvest 1 | | Harvest 2 (g pot ⁻¹) | | Harvest 3 | |
|-------|--------------------|---------------------------------------|---------------------|------|-------------------------------------|------|-----------|------|
| | | | mean | SE | mean | SE | mean | SE |
| Soil | <i>E. teff</i> | 0 | 10.16a ¹ | 0.41 | 12.24a | 4.40 | 2.46a | 0.70 |
| Soil | <i>E. teff</i> | 50 | 8.56ab | 1.79 | 3.16b | 0.88 | 2.47a | 1.31 |
| Soil | <i>E. teff</i> | 100 | 7.80ab | 2.50 | 1.14b | 0.89 | 2.17a | 1.32 |
| Soil | <i>E. teff</i> | 200 | 7.10bc | 1.18 | 0.88b | 0.46 | 1.52ab | 0.49 |
| Soil | <i>E. teff</i> | 400 | 4.65c | 0.92 | 1.20b | 0.37 | 0.50b | 0.41 |
| | | LSD _{5%} | 2.53 | | 4.00 | | 1.16 | |
| | | CV(%) | 12.5 | | 21.6 | | 41.3 | |
| Soil | <i>D. eriantha</i> | 0 | 4.11a | 0.81 | 10.65a | 1.29 | 7.26a | 0.54 |
| Soil | <i>D. eriantha</i> | 50 | 1.87b | 1.02 | 3.84b | 3.41 | 2.23b | 1.45 |
| Soil | <i>D. eriantha</i> | 100 | 0.11c | 0.19 | 5.09b | 2.67 | 2.56b | 2.15 |
| Soil | <i>D. eriantha</i> | 200 | 0.31c | 0.16 | 5.02b | 0.41 | 3.77b | 2.28 |
| Soil | <i>D. eriantha</i> | 400 | 0.00c | 0.00 | 2.13b | 0.76 | 2.55b | 1.40 |
| | | LSD _{5%} | 1.24 | | 3.89 | | 3.00 | |
| | | CV(%) | 4.7 | | 17 | | 24.5 | |
| Soil | <i>C. ciliaris</i> | 0 | 7.08a | 0.24 | 6.97 | 1.79 | 6.11 | 0.66 |
| Soil | <i>C. ciliaris</i> | 50 | 5.51ab | 0.93 | 4.13 | 2.66 | 6.49 | 0.73 |
| Soil | <i>C. ciliaris</i> | 100 | 4.54abc | 3.19 | 3.44 | 0.77 | 5.31 | 1.78 |
| Soil | <i>C. ciliaris</i> | 200 | 3.19bc | 2.95 | 5.36 | 5.20 | 6.09 | 3.27 |
| Soil | <i>C. ciliaris</i> | 400 | 1.72c | 0.27 | 3.47 | 1.63 | 2.92 | 1.29 |
| | | LSD _{5%} | 3.38 | | NS | | NS | |
| | | CV | 26.9 | | 16.5 | | 10.4 | |
| Spoil | <i>E. teff</i> | 0 | 2.00a | 1.01 | 7.98 | 1.93 | 3.01 | 1.47 |
| Spoil | <i>E. teff</i> | 50 | 2.52a | 0.69 | 8.73 | 3.71 | 2.05 | 1.11 |
| Spoil | <i>E. teff</i> | 100 | 2.77a | 0.28 | 11.10 | 3.12 | 1.69 | 0.94 |
| Spoil | <i>E. teff</i> | 200 | 4.30b | 1.00 | 5.62 | 2.50 | 1.29 | 0.37 |
| Spoil | <i>E. teff</i> | 400 | 4.21b | 0.83 | 5.93 | 4.35 | 1.08 | 0.64 |
| | | LSD _{5%} | 1.43 | | NS | | NS | |
| | | CV(%) | 13.8 | | 24.4 | | 41.4 | |
| Spoil | <i>D. eriantha</i> | 0 | 0.46a | 0.25 | 9.91 | 1.62 | 16.54 | 2.04 |
| Spoil | <i>D. eriantha</i> | 50 | 0.41a | 0.25 | 9.30 | 1.57 | 17.34 | 3.43 |
| Spoil | <i>D. eriantha</i> | 100 | 0.72a | 0.05 | 9.48 | 1.65 | 14.79 | 4.29 |
| Spoil | <i>D. eriantha</i> | 200 | 0.49a | 0.41 | 9.73 | 1.39 | 10.52 | 6.33 |
| Spoil | <i>D. eriantha</i> | 400 | 0.10b | 0.18 | 9.95 | 1.02 | 10.43 | 3.40 |
| | | LSD _{5%} | 0.31 | | NS | | NS | |
| | | CV(%) | 48.0 | | 12.0 | | 20.7 | |
| Spoil | <i>C. ciliaris</i> | 0 | 0.77a | 0.34 | 9.68 | 3.97 | 12.43 | 5.56 |
| Spoil | <i>C. ciliaris</i> | 50 | 1.58b | 0.19 | 11.00 | 3.10 | 9.32 | 3.64 |
| Spoil | <i>C. ciliaris</i> | 100 | 1.92b | 0.11 | 9.22 | 4.22 | 10.81 | 6.61 |
| Spoil | <i>C. ciliaris</i> | 200 | 2.94c | 0.51 | 11.56 | 5.04 | 12.72 | 7.92 |
| Spoil | <i>C. ciliaris</i> | 400 | 2.24bc | 0.62 | 17.20 | 1.09 | 13.83 | 2.67 |
| | | LSD _{5%} | 0.73 | | NS | | NS | |
| | | CV(%) | 10.9 | | 15.9 | | 9.9 | |

¹ Letters that are different indicate significant differences ($p < 0.05$) within a single harvest for a treatment and grass type (NS - non significant F-statistic).

Appendix 9 Fertility analyses for *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil and spoil treated with Rand water treatment residue at application rates of 0, 50 100, 200 and 400 g kg⁻¹. The numbers 1, 2 and 3 refer to the first, second and third harvests, respectively. Typical nutrient levels for turf grasses (Bennett, 1993) and *Festuca arundinacea* and *Eragrostis curvula* (Miles, undated) are given, where available

| | | RWTR | Ca | | | Mg | | | K | | | Na | | | P | | | N | | |
|----------------|--------------------|-----------------------|-------------|------|------|-------------|------|------|-------------|------|------|-------|-------|-------|-------------|------|------|-------------|------|------|
| | | rate | (%) | | | | | | | | | | | | | | | | | |
| Waste | Grass | (g kg ⁻¹) | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Soil | <i>E. teff</i> | 0 | 0.29 | 0.35 | 0.26 | 0.18 | 0.28 | 0.28 | 1.76 | 1.75 | 2.29 | 0.023 | 0.023 | 0.025 | 0.42 | 1.18 | 1.56 | 1.30 | 2.59 | 2.80 |
| Soil | <i>E. teff</i> | 50 | 0.46 | 0.41 | 0.52 | 0.30 | 0.42 | 0.51 | 1.42 | 1.74 | 2.70 | 0.021 | 0.031 | 0.053 | 0.39 | 0.44 | 0.75 | 1.36 | 2.86 | 3.71 |
| Soil | <i>E. teff</i> | 100 | 0.37 | 0.37 | 0.46 | 0.35 | 0.71 | 0.69 | 1.41 | 1.69 | 2.95 | 0.030 | 0.047 | 0.065 | 0.34 | 0.63 | 0.75 | 1.26 | 3.17 | 3.93 |
| Soil | <i>E. teff</i> | 200 | 0.41 | 0.35 | 0.33 | 0.45 | 0.75 | 0.79 | 1.89 | 1.64 | 2.99 | 0.032 | 0.023 | 0.027 | 0.36 | 0.57 | 0.73 | 1.93 | 3.01 | 3.79 |
| Soil | <i>E. teff</i> | 400 | 0.35 | 0.23 | 0.28 | 0.75 | 0.90 | 1.08 | 2.53 | 1.55 | 2.57 | 0.037 | 0.049 | 0.058 | 0.45 | 0.34 | 0.68 | 3.51 | 3.05 | nd |
| | | | | | | | | | | | | | | | | | | | | |
| Soil | <i>D. eriantha</i> | 0 | 0.73 | 0.55 | 0.41 | 0.39 | 0.56 | 0.55 | 3.76 | 3.29 | 4.09 | 0.035 | 0.025 | 0.049 | 0.97 | 1.80 | 0.69 | 2.49 | 2.54 | 3.22 |
| Soil | <i>D. eriantha</i> | 50 | 0.66 | 0.72 | 0.77 | 1.19 | 1.29 | 0.94 | 3.83 | 4.21 | 4.62 | 0.039 | 0.044 | 0.075 | 0.71 | 2.42 | 1.38 | 3.21 | 2.77 | 3.71 |
| Soil | <i>D. eriantha</i> | 100 | 1.68 | 0.67 | 0.63 | 1.50 | 1.72 | 1.28 | 3.89 | 4.24 | 4.55 | 0.066 | 0.033 | 0.048 | 0.62 | 2.70 | 1.52 | nd | 2.53 | 3.69 |
| Soil | <i>D. eriantha</i> | 200 | 0.77 | 0.38 | 0.28 | 1.38 | 1.66 | 1.27 | 3.23 | 3.60 | 3.92 | 0.033 | 0.023 | 0.038 | 0.52 | 1.77 | 1.02 | nd | 2.70 | 3.44 |
| Soil | <i>D. eriantha</i> | 400 | nd | 0.33 | 0.72 | nd | 2.17 | 1.85 | nd | 3.66 | 3.65 | nd | 0.025 | 0.029 | nd | 2.30 | 1.29 | nd | 2.96 | 3.44 |
| | | | | | | | | | | | | | | | | | | | | |
| Soil | <i>C. ciliaris</i> | 0 | 0.13 | 0.21 | 0.18 | 0.07 | 0.33 | 0.27 | 3.19 | 3.06 | 4.06 | 0.025 | 0.026 | 0.023 | 0.67 | 1.81 | 0.61 | 1.24 | 2.28 | 3.05 |
| Soil | <i>C. ciliaris</i> | 50 | 0.17 | 0.53 | 0.46 | 0.25 | 0.70 | 0.61 | 4.19 | 3.88 | 4.85 | 0.095 | 0.074 | 0.024 | 0.40 | 0.54 | 0.53 | 1.67 | 2.64 | 3.12 |
| Soil | <i>C. ciliaris</i> | 100 | 0.23 | 0.38 | 0.26 | 0.29 | 0.71 | 0.66 | 3.91 | 3.54 | 4.68 | 0.102 | 0.143 | 0.039 | 0.32 | 0.37 | 0.53 | 1.97 | 2.33 | 2.95 |
| Soil | <i>C. ciliaris</i> | 200 | 0.16 | 0.31 | 0.16 | 0.30 | 0.73 | 0.78 | 4.12 | 3.57 | 4.54 | 0.086 | 0.043 | 0.053 | 0.27 | 0.29 | 0.59 | 2.66 | 1.77 | 2.84 |
| Soil | <i>C. ciliaris</i> | 400 | 0.16 | 0.18 | 0.13 | 0.56 | 0.80 | 0.92 | 5.89 | 3.80 | 4.85 | 0.087 | 0.040 | 0.064 | 0.34 | 0.21 | 0.49 | 4.42 | 1.72 | 2.73 |
| | | | | | | | | | | | | | | | | | | | | |
| Spoil | <i>E. teff</i> | 0 | 0.45 | 0.67 | 0.56 | 0.24 | 0.44 | 0.35 | 1.67 | 2.58 | 3.51 | 0.027 | 0.038 | 0.078 | 0.70 | 0.97 | 0.85 | 1.61 | 3.54 | 4.15 |
| Spoil | <i>E. teff</i> | 50 | 0.36 | 0.55 | 0.61 | 0.29 | 0.56 | 0.57 | 1.66 | 2.34 | 3.29 | 0.028 | 0.024 | 0.058 | 0.56 | 0.88 | 0.77 | 1.45 | 3.08 | 4.06 |
| Spoil | <i>E. teff</i> | 100 | 0.33 | 0.42 | 0.48 | 0.28 | 0.65 | 0.69 | 1.42 | 2.51 | 2.99 | 0.017 | 0.018 | 0.063 | 0.50 | 0.81 | 0.77 | 1.69 | 3.22 | 4.05 |
| Spoil | <i>E. teff</i> | 200 | 0.33 | 0.32 | 0.36 | 0.35 | 0.63 | 0.77 | 1.94 | 1.90 | 2.91 | 0.021 | 0.023 | 0.066 | 0.55 | 0.48 | 0.66 | 1.74 | 3.05 | 3.91 |
| Spoil | <i>E. teff</i> | 400 | 0.34 | 0.29 | 0.26 | 0.56 | 0.86 | 0.96 | 2.11 | 2.06 | 2.96 | 0.032 | 0.012 | 0.047 | 0.42 | 0.62 | 0.85 | 3.14 | 3.38 | 4.20 |
| | | | | | | | | | | | | | | | | | | | | |
| Spoil | <i>D. eriantha</i> | 0 | 0.35 | 0.47 | 0.49 | 0.27 | 0.51 | 0.53 | 2.94 | 4.11 | 3.71 | 0.028 | 0.030 | 0.055 | 0.92 | 0.71 | 0.82 | 2.14 | 2.74 | 2.71 |
| Spoil | <i>D. eriantha</i> | 50 | 0.97 | 0.41 | 0.41 | 0.88 | 0.84 | 0.97 | 3.34 | 3.84 | 3.64 | 0.024 | 0.014 | 0.060 | 0.48 | 0.63 | 0.54 | nd | 3.18 | 2.57 |
| Spoil | <i>D. eriantha</i> | 100 | 0.82 | 0.31 | 0.36 | 0.88 | 1.15 | 0.91 | 3.29 | 3.67 | 3.58 | 0.035 | 0.014 | 0.058 | 0.37 | 0.74 | 0.47 | 2.47 | 3.17 | 2.55 |
| Spoil | <i>D. eriantha</i> | 200 | 0.81 | 0.25 | 0.2 | 1.33 | 1.13 | 0.79 | 3.41 | 3.18 | 3.57 | 0.024 | 0.012 | 0.033 | 0.35 | 0.60 | 0.39 | 3.89 | 2.85 | 2.52 |
| Spoil | <i>D. eriantha</i> | 400 | 1.38 | 0.26 | 0.14 | 1.80 | 1.22 | 1.11 | 2.94 | 3.15 | 3.37 | 0.049 | 0.014 | 0.051 | 0.28 | 0.61 | 0.47 | nd | 2.96 | 2.38 |
| | | | | | | | | | | | | | | | | | | | | |
| Spoil | <i>C. ciliaris</i> | 0 | 0.41 | 0.24 | 0.36 | 0.29 | 0.28 | 0.31 | 5.02 | 3.87 | 4.23 | 0.087 | 0.047 | 0.061 | 0.86 | 0.60 | 0.59 | 1.73 | 2.55 | 2.74 |
| Spoil | <i>C. ciliaris</i> | 50 | 0.22 | 0.18 | 0.28 | 0.30 | 0.36 | 0.37 | 4.73 | 3.18 | 3.82 | 0.080 | 0.031 | 0.069 | 0.52 | 0.39 | 0.27 | 1.55 | 2.41 | 2.62 |
| Spoil | <i>C. ciliaris</i> | 100 | 0.21 | 0.24 | 0.21 | 0.31 | 0.48 | 0.52 | 4.58 | 3.30 | 3.79 | 0.081 | 0.035 | 0.055 | 0.42 | 0.33 | 0.42 | 1.54 | 2.44 | 2.58 |
| Spoil | <i>C. ciliaris</i> | 200 | 0.20 | 0.16 | 0.18 | 0.38 | 0.55 | 0.69 | 4.73 | 3.32 | 3.72 | 0.075 | 0.025 | 0.029 | 0.31 | 0.35 | 0.45 | 1.83 | 2.15 | 2.70 |
| Spoil | <i>C. ciliaris</i> | 400 | 0.22 | 0.13 | 0.11 | 0.59 | 0.68 | 0.77 | 6.47 | 3.56 | 3.31 | 0.115 | 0.020 | 0.027 | 0.34 | 0.38 | 0.44 | 4.01 | 2.72 | 2.50 |
| Bennett (1993) | | | 0.50 - 1.20 | | | 0.20 - 0.60 | | | 1.00 - 2.50 | | | - | | | 0.10 - 0.40 | | | 2.80 - 3.50 | | |
| Miles | | <i>E. curvula</i> | 0.22 - 0.31 | | | 0.07 - 0.14 | | | 0.90 - 1.60 | | | - | | | 0.16 - 0.21 | | | 1.80 - 2.30 | | |
| (undated) | | <i>F. arundinacea</i> | 0.10 - 0.25 | | | 0.20 - 0.36 | | | 2.20 - 3.50 | | | - | | | 0.25 - 0.35 | | | 2.80 - 3.50 | | |

nd not determined.

Appendix 9 (continued) Fertility analyses for *Eragrostis teff*, *Digitaria eriantha* and *Cenchrus ciliaris* grown in the soil and spoil treated with Rand water treatment residue at application rates of 0, 50 100, 200 and 400 g kg⁻¹. The numbers 1, 2 and 3 refer to the first, second and third harvests, respectively. Typical nutrient levels for turf grasses (Bennett, 1993) and *Festuca arundinacea* and *Eragrostis curvula* (Miles, undated) are given

| Waste | Grass | RWTR rate (g kg ⁻¹) | Zn | | | Cu | | | Mn (mg kg ⁻¹) | | | Fe | | | B | | |
|----------------|--------------------|---------------------------------------|----|----|----|--------|----|----|------------------------------|-----|-----|----------|-----|-----|---------|-----|----|
| | | | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| | | | | | | | | | | | | | | | | | |
| Soil | <i>E. teff</i> | 0 | 33 | 31 | 42 | 4 | 10 | 11 | 536 | 639 | 436 | 67 | 128 | 48 | 38 | 4 | 4 |
| Soil | <i>E. teff</i> | 50 | 19 | 14 | 23 | 4 | 4 | 6 | 98 | 51 | 69 | 143 | 94 | 130 | 36 | 4 | 4 |
| Soil | <i>E. teff</i> | 100 | 23 | 16 | 23 | 6 | 6 | 9 | 74 | 72 | 80 | 114 | 142 | 169 | 42 | 4 | 4 |
| Soil | <i>E. teff</i> | 200 | 25 | 12 | 19 | 11 | 8 | 16 | 89 | 99 | 93 | 148 | 258 | 237 | 42 | 6 | 6 |
| Soil | <i>E. teff</i> | 400 | 23 | 10 | 21 | 23 | 14 | 15 | 140 | 80 | 155 | 283 | 303 | 405 | 43 | 8 | 13 |
| | | | | | | | | | | | | | | | | | |
| Soil | <i>D. eriantha</i> | 0 | 46 | 19 | 41 | 13 | 8 | 8 | 310 | 481 | 631 | 191 | 124 | 76 | nd | 8 | 4 |
| Soil | <i>D. eriantha</i> | 50 | 34 | 10 | 19 | 17 | 10 | 9 | 93 | 77 | 88 | 151 | 164 | 144 | nd | 12 | 8 |
| Soil | <i>D. eriantha</i> | 100 | 41 | 10 | 29 | 33 | 16 | 10 | 140 | 99 | 96 | 769 | 311 | 196 | nd | 14 | 13 |
| Soil | <i>D. eriantha</i> | 200 | 22 | 10 | 50 | 29 | 16 | 12 | 117 | 66 | 71 | 312 | 174 | 130 | nd | 8 | 6 |
| Soil | <i>D. eriantha</i> | 400 | nd | 12 | 29 | nd | 27 | 18 | nd | 78 | 61 | nd | 217 | 162 | nd | 8 | 8 |
| | | | | | | | | | | | | | | | | | |
| Soil | <i>C. ciliaris</i> | 0 | 32 | 12 | 18 | 6 | 4 | 5 | 148 | 165 | 223 | 82 | 108 | 170 | 46 | 6 | 4 |
| Soil | <i>C. ciliaris</i> | 50 | 19 | 10 | 16 | 8 | 6 | 6 | 70 | 53 | 53 | 136 | 338 | 95 | 36 | 8 | 6 |
| Soil | <i>C. ciliaris</i> | 100 | 30 | 25 | 18 | 11 | 6 | 7 | 60 | 53 | 39 | 192 | 227 | 119 | 43 | 8 | 6 |
| Soil | <i>C. ciliaris</i> | 200 | 34 | 12 | 12 | 13 | 8 | 8 | 73 | 71 | 43 | 198 | 590 | 117 | nd | 8 | 8 |
| Soil | <i>C. ciliaris</i> | 400 | 33 | 12 | 12 | 17 | 6 | 12 | 107 | 67 | 50 | 405 | 263 | 161 | nd | 6 | 6 |
| | | | | | | | | | | | | | | | | | |
| Spoil | <i>E. teff</i> | 0 | 78 | 89 | 90 | 8 | 12 | 12 | 195 | 220 | 174 | 76 | 85 | 94 | nd | 71 | 63 |
| Spoil | <i>E. teff</i> | 50 | 64 | 61 | 62 | 4 | 8 | 10 | 109 | 59 | 62 | 66 | 77 | 97 | nd | 53 | 79 |
| Spoil | <i>E. teff</i> | 100 | 67 | 51 | 55 | 6 | 10 | 6 | 84 | 60 | 51 | 69 | 99 | 101 | nd | 33 | 57 |
| Spoil | <i>E. teff</i> | 200 | 57 | 37 | 36 | 8 | 8 | 7 | 59 | 43 | 38 | 70 | 82 | 99 | nd | 25 | 30 |
| Spoil | <i>E. teff</i> | 400 | 34 | 31 | 32 | 11 | 12 | 8 | 49 | 43 | 55 | 104 | 117 | 140 | 36 | 10 | 19 |
| | | | | | | | | | | | | | | | | | |
| Spoil | <i>D. eriantha</i> | 0 | 67 | 55 | 47 | 11 | 9 | 10 | 143 | 183 | 257 | 124 | 115 | 81 | nd | 224 | 95 |
| Spoil | <i>D. eriantha</i> | 50 | 52 | 45 | 43 | 13 | 6 | 7 | 96 | 69 | 85 | 96 | 143 | 80 | nd | 175 | 76 |
| Spoil | <i>D. eriantha</i> | 100 | 57 | 35 | 33 | 13 | 8 | 5 | 83 | 71 | 58 | 94 | 149 | 89 | nd | 88 | 79 |
| Spoil | <i>D. eriantha</i> | 200 | 66 | 39 | 18 | 15 | 6 | 3 | 81 | 53 | 31 | 134 | 125 | 63 | nd | 74 | 43 |
| Spoil | <i>D. eriantha</i> | 400 | 54 | 31 | 20 | 19 | 8 | 6 | 88 | 51 | 47 | 224 | 133 | 86 | nd | 63 | 18 |
| | | | | | | | | | | | | | | | | | |
| Spoil | <i>C. ciliaris</i> | 0 | 43 | 31 | 42 | 9 | 4 | 6 | 139 | 72 | 84 | 93 | 110 | 90 | 30 | 94 | 63 |
| Spoil | <i>C. ciliaris</i> | 50 | 41 | 29 | 40 | 9 | 4 | 2 | 93 | 41 | 29 | 83 | 108 | 92 | 35 | 49 | 42 |
| Spoil | <i>C. ciliaris</i> | 100 | 38 | 24 | 40 | 9 | 4 | 4 | 66 | 35 | 29 | 89 | 222 | 86 | 49 | 47 | 27 |
| Spoil | <i>C. ciliaris</i> | 200 | 30 | 25 | 29 | 9 | 4 | 5 | 39 | 29 | 27 | 99 | 104 | 84 | 35 | 22 | 29 |
| Spoil | <i>C. ciliaris</i> | 400 | 35 | 20 | 23 | 11 | 6 | 4 | 35 | 22 | 20 | 128 | 122 | 113 | 39 | 10 | 8 |
| Bennett (1993) | | | - | | | 5 - 20 | | | 25 - 150 | | | 35 - 100 | | | 10 - 60 | | |

nd not determined.

Appendix 10 Overview of possible causes and mechanisms of grass nutrient uptake and responses when grown in Rand water treatment residue mixed with spoil or soil (expanded from Section 3.4.3)

In some instances Ca uptake appeared to be associated with low yield, possibly due to a concentration effect, although this trend was not consistent enough to be shown conclusively. Bennett (1993) reports an adequate Ca concentration of from 0.5 to 1.2% for turf grasses. This is generally higher than the levels reported here, but can be viewed in the light of the nature of these grasses. Turf grasses typically require higher nutrient levels due to continuous herbage removal (mowing). Although there appears to be little information on sufficiency levels for grasses other than those found in cropping systems, Miles (undated) has reported an adequate range for *E. curvula* to be from 0.1 to 0.25%, and 0.22 to 0.31% for *F. arundinacea*. These values suggest that the Ca concentrations reported here may be adequate. Furthermore, there was little visual indication of Ca deficiencies during the course of the pot experiment.

A clear pattern for Mg uptake was evident. In almost all cases there was an increase in Mg uptake with increasing rate of RWTR. Bennett (1993) indicates that generally Mg concentrations are lower than Ca in grasses. This trend is reversed for these data, with the treatments with higher RWTR application rates tending to have higher Mg:Ca ratios. Marschner (1986) reports that when two nutrients are near the deficiency range, an increase of one nutrient may stimulate growth, leading to a deficiency of the other induced by the dilution effect. While it may be plausible that in some instances the elevated concentrations of Mg induced low levels of Ca, frequently high levels of Mg were not associated with improved yield of a particular treatment or grass. In addition it would appear that generally Ca was at adequate concentrations to prevent this effect.

Concentrations of K tended to be high. Wilkinson *et al.* (2000) report that excessive K uptake may inhibit Mg translocation to aerial tissue in plants, due to competitive effects in the roots of plants. It would appear that this has not occurred here, due to adequate Mg and K, even in the control treatments.

Uptake of Na tended to show marginal increases with increasing RWTR additions, but concentrations were negligible. While some authors have reported on essentiality of Na by some plants species, halophytes in particular (Marschner, 1986), little evidence exists for the

necessity in grasses and adequacy values are not available. It has also been reported that under certain conditions Na may substitute for K in plant tissue (Marschner, 1986). Of more concern in this discussion is the potential of Na to induce deficiencies of other elements. Levy (2000) reports that Na may induce K, Mn, Zn and Cu deficiencies in plants, as well as creating unsuitable growing environments, such as under sodic conditions.

As P was added to the pots, it was unlikely that P deficiencies would occur, even though it was indicated that the RWTR had a high P sorbing capacity. Apart from additional fertiliser added at 80 DAE to correct apparent N and P deficiencies, the plants did not show typical P deficiency symptoms, indicating that adequate P was available.

Nitrogen concentrations did not show a consistent pattern for any of the treatments. Generally the second and third harvests showed higher N uptake, but this was probably due to increased N applications after the first harvest to correct for apparent deficiencies. *Eragrostis teff* grown in the spoil showed high N concentrations for the third harvest. This is attributed to a very poor yield, leading to a concentration effect. A similar comment could be made about *E. teff* grown in the soil, although it is not as evident as for the spoil treatment. The increase in uptake by *C. ciliaris* and *D. eriantha* may be due to the plants being able to access more nutrients as root mass increased within the pots.

Trace nutrient uptake was variable. Zinc uptake tended to decrease with increasing RWTR additions regardless of treatment. Changes across the harvests were not clear, though. The decrease with increasing RWTR additions may be associated with an increase in pH, where Zn is immobilised and becomes plant unavailable (Mortvedt, 2000). This effect is also reported for Cu, Mn and Fe (Mortvedt, 2000).

Manganese uptake showed a similar pattern to that of Zn, but the concentrations were considerably greater. *Eragrostis teff* grown in the soil showed markedly high Mn concentrations ($>400 \text{ mg kg}^{-1}$), but this decreased considerably with RWTR additions. The other grasses and those grown in the spoil did not show such high control concentrations, but the same pattern was evident. While it is unlikely that the ranges found in this investigation would be problematic, they may lead to imbalances and antagonistic effects of other elements essential for plant growth.

Iron concentrations showed a sharp increase in tissue concentrations, especially for the soil treatments. While it is reported that Fe deficiencies may occur in calcareous (or over-limed) media (Mortvedt, 2000), it was not apparent here. A number of possibilities exist that may help explain this behaviour. Firstly, both the RWTR and spoil show moderate levels of plant available Fe, even though the pH was high for both materials. The RWTR has FeCl_3 added during treatment, while coal spoil typically has a high Fe content (pyritic materials). Another possibility is the widely reported interaction between Fe and Mn (Pendias and Pendias, 1984; Adriano, 1986). These authors indicate that Fe and Mn are generally interrelated in their metabolic functions and that a Fe/Mn ratio of 1.5 to 2.5 should exist for healthy plant growth. It is reported that high levels of Mn may antagonise and reduce Fe uptake in plants. This may be what was observed in the control treatments for the soil and spoil. When RWTR is added, Mn availability may be reduced due to an increase in pH. As the RWTR has moderate concentrations of available Fe, the availability of this element may be improved, hence increasing the uptake by the grasses. While the Fe/Mn ratio of between 1.5 to 2.5 was seldom observed for these grasses, there was little evidence of either a Mn or Fe toxicity when the ratio was below 1.5 or over 2.5. It may be argued that the apparent N deficiencies were rather a result of Fe chlorosis, but this was discounted as N applications remedied the symptoms.

Copper concentrations in the grasses tended to increase with increasing RWTR additions in the soil material. This trend was apparent only for the first and second harvest in the spoil material, and then showed a reverse trend for the third harvest. It was expected that plant uptake of Cu would decrease with increasing RWTR additions, due to increasing pH, but the reverse pattern of uptake was evident.

Boron uptake was variable, and the first harvest was missing a number of data due to inadequate sample size. Generally the soil treatments had low B concentrations, especially the second and third harvests. The reduction in uptake with increasing RWTR additions is probably associated with an increase in pH, reducing availability (Adriano, 1986). The high concentrations seen for some of the control spoil treatments were of some concern. However, no toxicity symptoms were seen. The upper limit for toxicity to plants is variable and dependant on species and cultivars (Pendias and Pendias, 1984). Adriano (1986) reports a value of $>800 \text{ mg B kg}^{-1}$ as being toxic to pasture grasses, which is above the values reported here.

Appendix 11 ANOVA tables for (a) aboveground yield (b) root biomass in the RWTR layers and (c) root biomass in the ash layer of *Cynodon dactylon* and *Stenotaphrum secundatum* grown in the 20, 40 and 60 mm layers of Rand water treatment residue over a coal combustion ash with two levels of fertiliser. Raw yield data are available from the author subject to suitable confidentiality agreements

(a)

| Source of variation | d.f. ¹ | SS ² | MS ³ | VR ⁴ | F Probability |
|------------------------------|-------------------|-----------------|-----------------|-----------------|---------------|
| Block (replicate) | 2 | 18.23 | 9.11 | 4.02 | |
| Fertiliser application rate | 1 | 38.50 | 38.50 | 16.96 | <0.001 |
| Grass species | 1 | 31.04 | 31.04 | 13.68 | 0.001 |
| RWTR application rate | 2 | 79.37 | 39.69 | 17.48 | <0.001 |
| Fertiliser x grass | 1 | 36.26 | 36.26 | 15.98 | <0.001 |
| Fertiliser x RWTR | 2 | 5.50 | 2.75 | 1.21 | 0.317 |
| Grass x fertiliser | 2 | 2.84 | 1.42 | 0.63 | 0.544 |
| Fertiliser x RWTR x grass | 2 | 0.40 | 0.20 | 0.09 | 0.916 |
| Residual | 22 | 49.93 | 2.27 | | |
| Total | 35 | 262.08 | | | |
| Coefficient of variation (%) | 15.3 | | | | |

(b)

| Source of variation | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|-------|------|-------|---------------|
| Block (replicate) | 2 | 0.32 | 0.16 | 0.38 | |
| Fertiliser application rate | 1 | 0.17 | 0.17 | 0.41 | 0.526 |
| Grass species | 1 | 0.53 | 0.53 | 1.27 | 0.273 |
| RWTR application rate | 2 | 9.35 | 4.68 | 11.27 | <0.001 |
| Fertiliser x grass | 1 | 0.63 | 0.63 | 1.51 | 0.232 |
| Fertiliser x RWTR | 2 | 2.59 | 1.30 | 3.12 | 0.064 |
| Grass x fertiliser | 2 | 4.37 | 2.19 | 5.26 | 0.014 |
| Fertiliser x RWTR x grass | 2 | 0.24 | 0.12 | 0.28 | 0.756 |
| Residual | 22 | 9.13 | 0.42 | | |
| Total | 35 | 27.32 | | | |
| Coefficient of variation (%) | 5.1 | | | | |

(c)

| Source of variation | d.f. | SS | MS | VR | F Probability |
|------------------------------|------|------|------|------|---------------|
| Block (replicate) | 2 | 0.02 | 0.01 | 0.34 | |
| Fertiliser application rate | 1 | 0.01 | 0.01 | 0.49 | 0.493 |
| Grass species | 1 | 0.00 | 0.00 | 0.01 | 0.933 |
| RWTR application rate | 2 | 0.06 | 0.03 | 1.12 | 0.344 |
| Fertiliser x grass | 1 | 0.01 | 0.01 | 0.52 | 0.480 |
| Fertiliser x RWTR | 2 | 0.03 | 0.01 | 0.67 | 0.524 |
| Grass x fertiliser | 2 | 0.01 | 0.01 | 0.27 | 0.770 |
| Fertiliser x RWTR x grass | 2 | 0.07 | 0.03 | 1.34 | 0.282 |
| Residual | 22 | 0.55 | 0.02 | | |
| Total | 35 | 0.76 | | | |
| Coefficient of variation (%) | 53.9 | | | | |

1 d.f. degrees of freedom.

2 SS sum of squares.

3 MS mean sum of squares.

4 VR variance ratio.

Appendix 13 Nutrient concentrations of bean seed grown in a Longlands sand with Faure water treatment residue application rates of 0, 50, 100, 200 and 400 g kg⁻¹ over fertiliser levels of 0, 25, 50, 100 and 150%

| FWTR rate (g kg ⁻¹) | Fertiliser rate (%) | Ca | Mg | K | Na | P | Zn | Cu | Mn | Fe |
|---------------------------------------|---------------------------|----------------|------|------|-------|------|------------------------------------|----|----|-----|
| | | ------(%)----- | | | | | ----- (mg kg ⁻¹) ----- | | | |
| 0 | 0 | 0.17 | 0.17 | 1.37 | 0.017 | 0.34 | 36 | 14 | 28 | 94 |
| 50 | 0 | 0.14 | 0.19 | 1.36 | 0.013 | 0.31 | 31 | 10 | 30 | 85 |
| 100 | 0 | 0.18 | 0.20 | 1.41 | 0.015 | 0.35 | 37 | 12 | 35 | 93 |
| 200 | 0 | 0.19 | 0.18 | 1.29 | 0.014 | 0.25 | 33 | 11 | 35 | 81 |
| 400 | 0 | 0.15 | 0.17 | 1.31 | 0.015 | 0.27 | 40 | 12 | 40 | 107 |
| 0 | 25 | 0.13 | 0.20 | 1.32 | 0.010 | 0.34 | 32 | 12 | 23 | 74 |
| 50 | 25 | 0.17 | 0.21 | 1.25 | 0.013 | 0.33 | 28 | 3 | 24 | 78 |
| 100 | 25 | 0.14 | 0.19 | 1.28 | 0.018 | 0.34 | 33 | 6 | 26 | 85 |
| 200 | 25 | 0.16 | 0.21 | 1.37 | 0.019 | 0.32 | 31 | 5 | 27 | 87 |
| 400 | 25 | 0.13 | 0.20 | 1.43 | 0.016 | 0.35 | 31 | 9 | 32 | 92 |
| 0 | 50 | 0.16 | 0.22 | 1.38 | 0.018 | 0.41 | 34 | 9 | 32 | 89 |
| 50 | 50 | 0.13 | 0.22 | 1.46 | 0.021 | 0.35 | 32 | 8 | 29 | 89 |
| 100 | 50 | 0.15 | 0.20 | 1.40 | 0.012 | 0.37 | 32 | 9 | 27 | 92 |
| 200 | 50 | 0.16 | 0.20 | 1.37 | 0.009 | 0.33 | 29 | 9 | 26 | 80 |
| 400 | 50 | 0.12 | 0.20 | 1.41 | 0.021 | 0.36 | 28 | 9 | 28 | 84 |
| 0 | 100 | 0.18 | 0.20 | 1.39 | 0.006 | 0.43 | 33 | 3 | 37 | 78 |
| 50 | 100 | 0.14 | 0.20 | 1.40 | 0.006 | 0.43 | 39 | 8 | 37 | 74 |
| 100 | 100 | 0.17 | 0.19 | 1.38 | 0.007 | 0.37 | 37 | 8 | 31 | 96 |
| 200 | 100 | 0.14 | 0.19 | 1.42 | 0.010 | 0.40 | 37 | 9 | 31 | 96 |
| 400 | 100 | 0.12 | 0.18 | 1.47 | 0.009 | 0.35 | 46 | 10 | 38 | 80 |
| 0 | 150 | 0.15 | 0.20 | 1.38 | 0.007 | 0.45 | 45 | 11 | 33 | 93 |
| 50 | 150 | 0.12 | 0.20 | 1.45 | 0.006 | 0.48 | 48 | 10 | 44 | 79 |
| 100 | 150 | 0.17 | 0.21 | 1.54 | 0.007 | 0.46 | 51 | 9 | 41 | 82 |
| 200 | 150 | 0.12 | 0.22 | 1.60 | 0.010 | 0.48 | 40 | 9 | 46 | 90 |
| 400 | 150 | 0.09 | 0.22 | 1.60 | 0.015 | 0.47 | 43 | 13 | 63 | 92 |