

SOME SOIL CHEMICAL AND FERTILITY ASPECTS OF THE LAND DISPOSAL OF A  
WATER TREATMENT RESIDUE ON SELECTED SOILS OF KWAZULU-NATAL,  
SOUTH AFRICA

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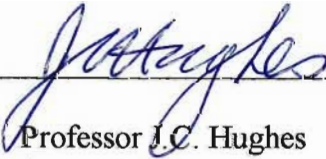
2005

**DECLARATION**

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

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Nala! Ndokose! kuni Zibhekuza. Sonwabile kuba ngeNtando yenu Sixhamle, Sihlomle. Ingathi oku ingayintshayelelo yokuba aMaMpembathi waxa ukwAkhaka Nokwakha kuthi.

## ABSTRACT

The environmental and agricultural viability of land disposal of a water treatment residue (WTR) from the Midmar Water Treatment Works of Umgeni Water was investigated by determining answers to four broad questions:

1. What effects would the application of the WTR have on plants growing on the treated soils?
2. What effects would application of the WTR have on soil chemical properties?
3. What effects would the WTR have on the soil solution composition (and by implication the quality of the groundwater)?
4. Could this material be used to reduce solubility of potential pollutants ?

To answer these questions, the following experiments were set up, and their respective results are reported.

1. Effects of the water treatment residue on plant growth

This was investigated in a pot experiment and two field experiments.

In the pot experiment five soils, two Huttons (Hu-M and Hu-T), an Inanda (Ia-C), a Namib (Nb-F) and a Shortlands (Sd) were used to grow perennial ryegrass (*Lolium perenne*). All samples were fertilized with a basal dressing of N, P, K, Mg and S. Two lime levels were added to the Ia-C and Nb-F soils, the higher calculated to reduce acid saturation to 1%, and the lower being half of that. The WTR was applied at rates of 0, 40, 80 and 120 Mg ha<sup>-1</sup>. All treatments were in triplicate. Eight cuts in all were made of the perennial ryegrass.

The dry matter (DM) yield of perennial ryegrass grown in the pot experiment increased with the WTR applied in all five soils although the highest increase was with the acidic Ia-C and Nb-F soils. The fact that the highest yields were on the strongly acid soils suggests that the liming effect of the WTR could have contributed, more so considering that lime also increased yields in these soils. It was, however, clear that no one factor was responsible for the increase in yield as the liming effect could not explain the results of the other three soils.

At the two field experiments perennial ryegrass was grown at Brookdale Farm from 1998 to 2001, after which the site was re-seeded with tall fescue (*Festuca arundinaceae*). At Ukulinga Farm tall fescue was grown from the outset in 2000. In the two field experiments with both perennial ryegrass and tall fescue, no significant increase in yield was apparent. Importantly, however, from an environmental point of view there was no decrease in yield whether the WTR was incorporated or applied as a mulch. This was observed even at the highest rates of application, namely 1280 Mg ha<sup>-1</sup>. The growth on the mulched plots was often observed to be better than any of the other treatments, including the control.

Analysis of the plant material from both pot and field experiments indicated that the WTR neither



induced deficiencies nor created toxicities of heavy metals in the tissues.

## 2. Effects of the water treatment residue on soil chemical properties

This aspect was investigated in a pot experiment with perennial ryegrass as the test crop, an incubation experiment at ambient temperatures in the laboratory, and also at the two field experiments.

In the pot experiment, changes in chemical properties included an increase in extractable calcium and pH, and a decrease in extractable acidity. In the Ia-C soil, pH (KCl) increased from 4.25 to 5.37 whilst the acid saturation decreased from 27 to 1% at 120 Mg ha<sup>-1</sup>. For the Nb-F soil under the same conditions the pH increase was from 3.91 to 6.46 and the acid saturation declined from 37 to 1%. Fractionation of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn showed that the WTR increased the inactive forms of these elements. The same was established from fractionation of P.

Two incubation experiments were run separately. In the first, the five soils used in the pot experiment plus four more were used. These were another Hutton (Hu-F), another Namib (Nb-A), a Valsrivier (Va) and a Westleigh (We). The Hu-F and We samples were from the field experiments at Brookdale and Ukulinga, respectively. Rates of application of the WTR were 0, 40, 80, 120, 320 and 1280 Mg ha<sup>-1</sup>. Samples were incubated at ambient temperature for about three months. The second incubation experiment involved only two strongly acid soils which were chosen to specifically test the liming effect of the WTR. These were an Avalon (Av) and an Inanda (Ia-W). The WTR rates were 0, 20, 40, 60, 80, 100, 120, 320 and 1280 Mg ha<sup>-1</sup>. Sub-samples were taken during the incubation period for pH analysis and, in the second incubation experiment, acidity analysis. Monitoring of the pH showed that the reaction of the WTR with all the soils was complete within seven days. Trends in the measured properties were the same as found from the pot experiment.

Soil samples were taken periodically from the two field sites and analysed to monitor any effects. Unlike in the pot and incubation experiments, the WTR in the field did not cause any major changes in pH, Ca, Mg and P levels in soil samples from the plots with the highest rate of 1280 Mg ha<sup>-1</sup>.

Analysis of Ca and Mg from depth samples taken at 200 mm intervals to 1200 mm from the Brookdale experiment showed that no serious migration of these elements had occurred after three years following application of the WTR. The same results were noted in depth samples from the Ukulinga site. Except for Mn, exchangeable forms of the eight heavy metals were low or undetectable. Also, there was no indication of redistribution of these metals to lower layers.

## 3. Possible effects of the water treatment residue on groundwater pollution

Analysis of water extracts from the incubated soil samples established that the ions which increased with application of the WTR were calcium, chloride and nitrate. Fractionation of heavy metals from the pot experiment and incubated soils showed that application of the WTR residue increased mostly the immobile forms of the metals. Laboratory experiments therefore indicated that there could be

pollution of the groundwater by nitrates. However, analysis of saturated pastes from soils at both field experiments showed that the levels of nitrate were increased by application of the WTR in only the fallow plots.

#### 4. The water treatment residue as a possible pollutant-reducing agent

The effect of the water treatment residue on the sorption of P and heavy metals (Cd, Ni and Zn) was studied in the laboratory. Soils treated with WTR were equilibrated for 6 hours in 0.005 M calcium chloride solution containing a known concentration of each element.

For the coarse-textured soils, initial P concentrations ranged from 0 to 1000 mg kg<sup>-1</sup> as opposed to 0 to 1800 mg kg<sup>-1</sup> for the clay soils. Treatments of WTR used were 0, 80, 320 and 1280 Mg ha<sup>-1</sup>, both incubated and non-incubated. At high initial P solution concentrations, the WTR increased the extent of sorption in the coarser textured soils (Hu-T, Nb-A, Nb-F, Va and We), and decreased it in highly sorbing Av, Hu-M, Ia-C and Ia-W soils. In general though, the WTR greatly reduced soluble P.

For Cd, Ni and Zn only one concentration, 50 mg kg<sup>-1</sup>, was studied using the incubated soil samples as affected by WTR rates from 0 to 1280 Mg ha<sup>-1</sup>. For all three metals, the amount sorbed increased with increase in amount of WTR for the nine soils studied, namely the Av, Hu-F, Hu-M, Hu-T, Ia-C, Ia-W, Nb-F, Va and We. In many cases the sorption was so high that more than 40 mg kg<sup>-1</sup> of the initial concentration was removed from solution. Even for those soils with high sorption capacity e.g. the Va and We, the WTR still increased sorption by up to an average of more than 25% for Cd and more than 40% for Ni and Zn. Because for the Av and Ia-W soils liming also increased sorption, it could be assumed that the accompanying increase in pH as a result of the addition of WTR promoted precipitation of metals, and/or the resultant increase in negative charge increased their adsorption.

These results show that where excess concentrations of soluble heavy metals may occur (especially in coarse-textured soils), and where there is concern about run-off with high P concentrations then this WTR could be considered to immobilize these elements and render them less harmful to the environment.

#### General comments and management guidelines

Based on the results reported above, it is apparent that the WTR can be safely disposed of onto land. It has been demonstrated in the current investigation that rates of application can be as high as 1280 Mg ha<sup>-1</sup>. Rates of application to land higher than 1280 Mg ha<sup>-1</sup> could probably be acceptable - this was the highest rate tested in this investigation - where the residue is produced in large amounts at the plant, and land for disposal is somewhat limited.

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## CHAPTER 1

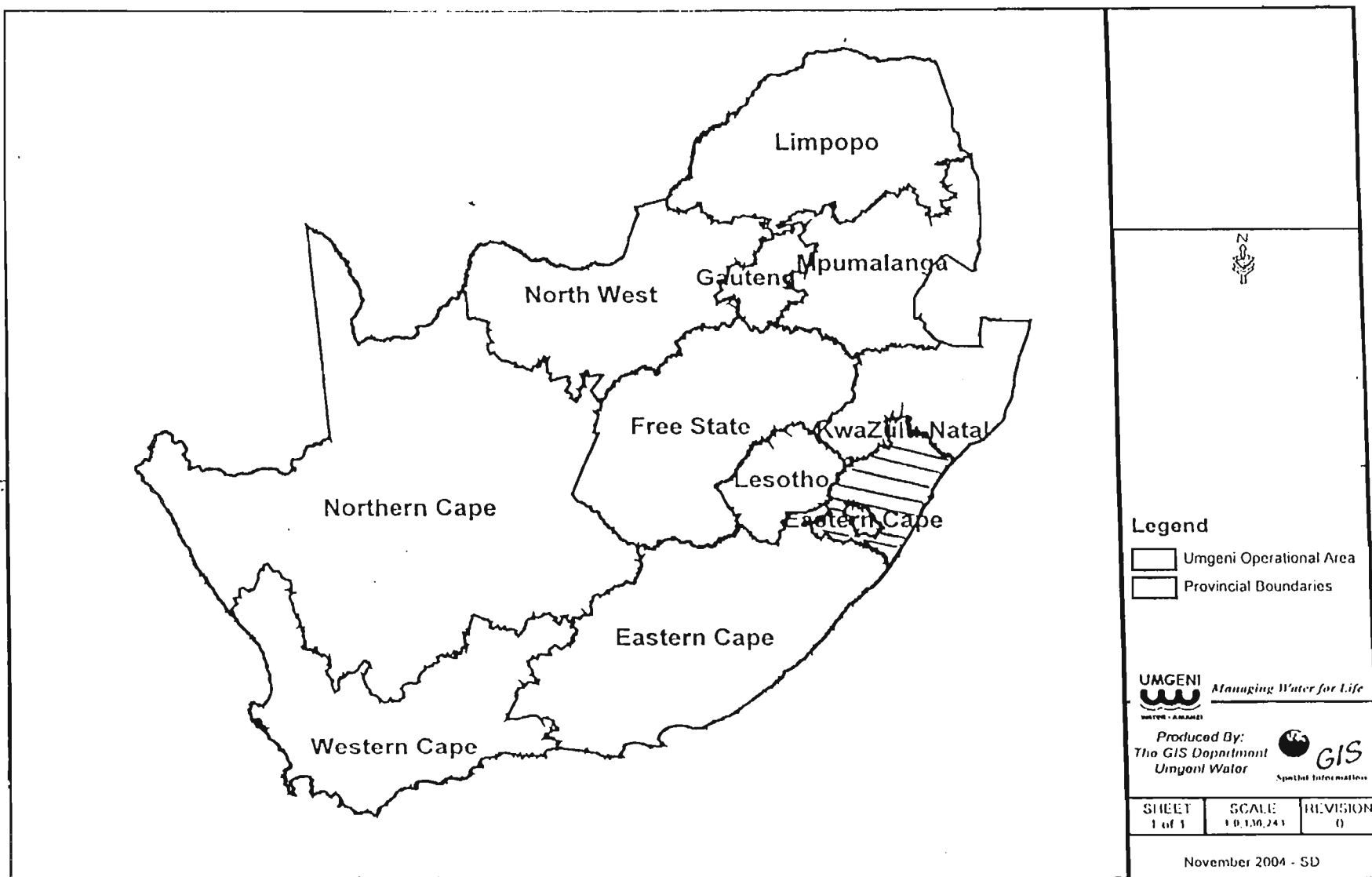
### PRODUCTION OF WATER TREATMENT RESIDUE AND CONSIDERATIONS FOR ITS DISPOSAL: GENERAL INTRODUCTION

#### 1.1 Water treatment residue: source, terminology and production

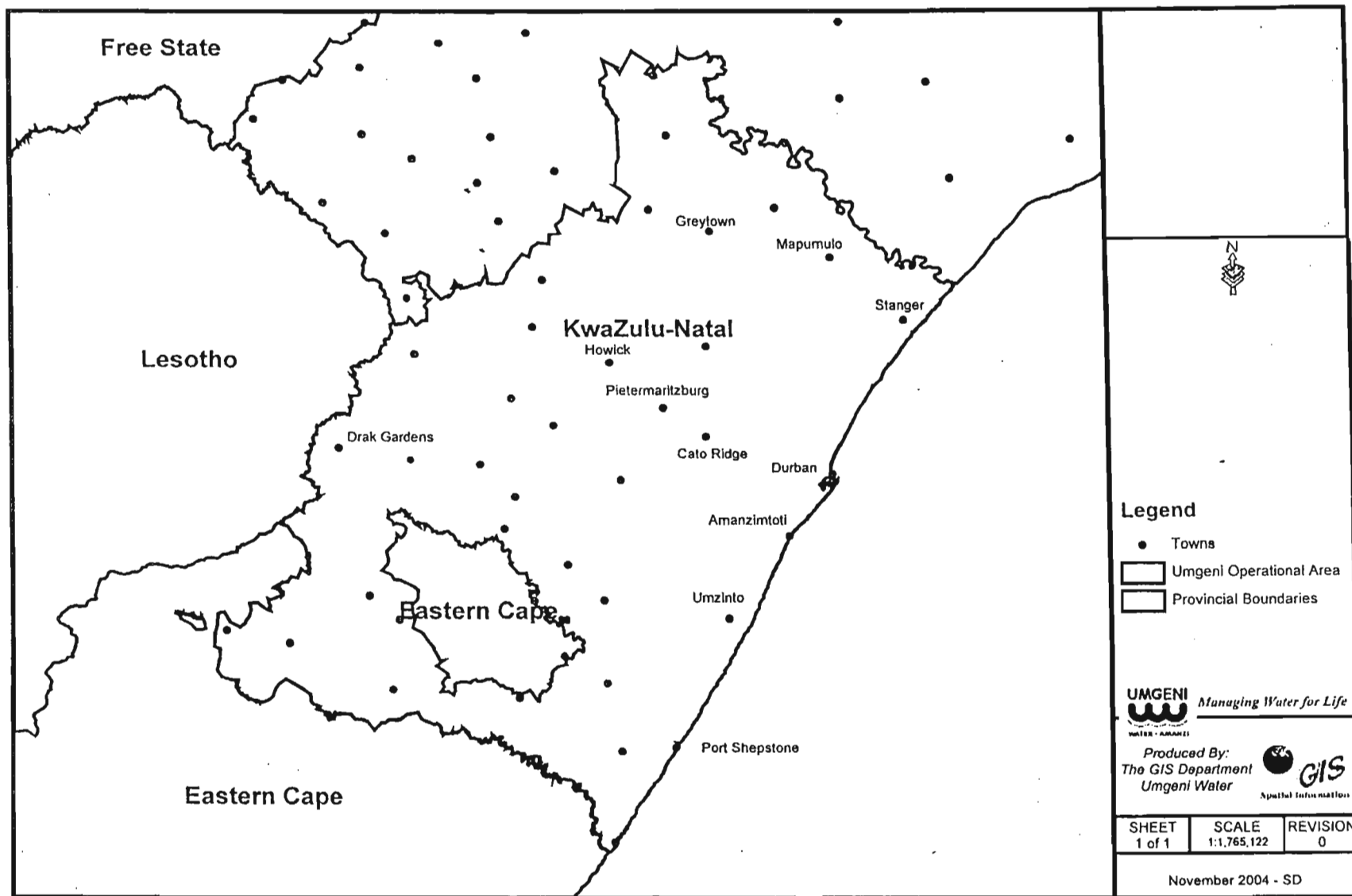
The water treatment residue of concern in this investigation is produced by Umgeni Water, a water purification company in the midlands region of the KwaZulu-Natal province of South Africa, with its head office in Pietermaritzburg. According to its web site (<http://www.umgeni.co.za/HomePage1.aspx>) Umgeni Water, established in 1974, supplies 340 million kL of safe, clean drinking water to 4.8 million people annually, making it the largest bulk water supplier in KwaZulu-Natal. Umgeni Water's area of operation, spanning 24 thousand km<sup>2</sup> (<http://www.umgeni.co.za/Operational%20area242.aspx>), is shown on Map 1.1 of South Africa. From the enlarged version (Map 1.2), it can be seen that the supply area stretches between Greytown, Stanger and surrounding areas in the north and Eastern Cape province in the south, and is bordered by the Indian Ocean in the east and the Drakensberg Mountains in the west. The official boundaries are given as the Tugela and Mooi Rivers in the north, and the Mkomazi and Mzimkulu Rivers in the south (<http://www.umgeni.co.za/company/operationalarea/Index.htm>). These investigations relate to the material produced in the Midmar Water Treatment Works at Howick about 30 km north of Pietermaritzburg.

In order to provide potable drinking water to communities, water suppliers add materials to the raw water to remove suspended solid particles and contaminants. Some of the various materials that can be added to the turbid water to promote flocculation are alum (aluminium sulphate), ferric chloride, organic polymers and lime. At the Midmar plant, Umgeni Water uses a combination of cationic organic polymers and lime (calcium carbonate) to remove the turbidity from the source water. A more comprehensive description of the water treatment process is given in Hughes, Titshall, Buyeye, Johnston, Moodley and Pecku (2005). Although this residue has been called water treatment sludge,





Map 1.1 Umgeni Water operational area (striped) in KwaZulu-Natal, South Africa



Map 1.2 Umgeni Water operational area and surroundings

the term which will be used in this document is water treatment residue (WTR) in order to avoid confusion with sewage sludge. Freshly produced WTR is a slurry-filter cake of about 23% solids (Umgeni Water, 1994). Typical amounts of the WTR produced are indicated in Table 1.1. The period March 2003 to April 2004 has been chosen to indicate the rate at which the WTR is produced at Umgeni Water's Midmar Water Treatment Works. From Table 1.1 the average rate of production of the freshly produced (wet) material, is about  $4624 \text{ m}^3 \text{ yr}^{-1}$  which on an air dry basis (solids only) is equivalent to about 1018 Mg or  $1062 \text{ m}^3 \text{ yr}^{-1}$ . Practically and economically the figure for the filter cake, that is  $4624 \text{ Mg yr}^{-1}$ , is the one to consider as it is in this state that the material is likely to be disposed of in landfill sites.

**Table 1.1** Monthly production rates of water treatment residue at the Midmar Water Treatment Works for the period April 2003 to March 2004

	April 2003	May 2003	June 2003	July 2003	Aug. 2003	Sept. 2003	Oct. 2003	Nov. 2003	Dec. 2003	Jan. 2004	Feb. 2004	Mar. 2004
a	208	236	400	336	280	280	280	596	540	444	420	604
b	48	54	92	77	64	64	64	137	124	102	97	139
c	46	52	88	74	61	61	61	132	119	98	93	133

a Figures in  $\text{m}^3$ , acquired from Umgeni Water and represent filter cake of 23 % solids

b Figures in  $\text{m}^3$ , calculated for air-dry, less than 2 mm aggregates

c Figures in Mg, calculated based on a  $960 \text{ kg m}^{-3}$  sample density of air-dry, less than 2 mm aggregates

## 1.2 Unwanted materials from processing: terminology

In the process of preparing certain products, materials other than the desired product may be produced. This substance might be readily referred to as a byproduct, although Miller and Miller (2000) have another idea about the meaning of this term. Citing Powers (1998), they consider a byproduct to be a material, derived from agricultural or industrial activities, that has positive growth effects on plants, and no adverse environmental impact. Where it has a neutral or no effect upon land application, Miller and Miller (2000) consider such material to be waste. In South Africa there is

legal reference to litter and waste (The Environment Conservation Act 73 of 1989). Litter, a form of waste, is any object or matter discarded by the person in whose possession or control it was, whilst waste is “matter . . . identified as an undesirable or superfluous byproduct, emission, residue or remainder of any process or activity”. This definition thus stops at the production stage and does not consider what might happen to this material; it also does not include any harmful property that the waste might possess, or harm that it might cause. The National Water Act (Act 36 of 1998) classifies a waste as including “any solid material or material that is suspended, dissolved or transported into a water resource in such volume, composition or manner as to cause, or to be reasonably likely to cause, the water resource to be polluted”. Although concerned with pollution of water resources, this description of waste does not necessarily mean that the material has to be physically placed in a water source to cause concern; in other words it does not exclude the possibility of such a pollution occurring via another source of placement of the material, like land or landfill.

Four classes of environmental problems are recognised i.e., degradable waste, persistent wastes, wastes of reversible biological and geophysical impact, and those of irreversible biological and geophysical impact (Fuggle, 1994). It is advisable to determine to which of these categories any waste or byproduct belongs, as this would help with developing or adopting safer or appropriate means of disposal.

### **1.3 Disposal of unwanted materials: options**

In South Africa Lombard, Botha and Rabie (1994) list thermal treatment, isolation from the environment, recycling and physico-chemical treatment as some of the disposal options for unwanted material. They are supported in the recognition of thermal treatment (referred to as incineration) by Cameron, Di and McLaren (1997), who also highlighted the option of discharge to water when considering the disposal of wastes from New Zealand and Australia. These options generally have limitations including not being suitable for all kinds of waste, being costly and causing atmospheric pollution (notably incineration; Cameron *et al.*, 1997). However, most of these options will generate residues that would still need ultimate disposal to landfill sites (Lombard *et al.*, 1994). Lombard *et*

*al.* (1997) do, however, concede that suitable sites for disposal will become scarcer and therefore more costly. Besides, some landfills might also allow seepage, and produce volatile and flammable gases (Cameron *et al.*, 1997). Also, landfill sites might be specific for a certain kind of material, and co-disposal might not be allowed since it might initiate mobilization and migration of certain chemical species (Cameron *et al.*, 1997). Land disposal, another means of disposal, is thus an option to be investigated. There is more information on disposal options in Hughes *et al.* (2005).

#### **1.4 Perspective on land disposal: policy and views**

According to the Environment Conservation Act, 1992 (section 9 of Act 79 of 1992, substituting Section 20 of Act 73 of 1989), a disposal site may not be established, provided or operated without a permit issued by the Minister of Environmental Affairs and Tourism. The practice of disposal of material thus has legal connotations.

Three forms of disposal of waste material onto land may be recognised, namely land application (King, 1982; Geertsema, Knocke, Novak and Dove, 1994; Lucas, Dillaha, Reneau, Novak and Knocke, 1994; Cameron *et al.*, 1997; Miller and Miller, 2000) defined by Miller and Miller (2000) as addition of byproducts to benefit crop growth; land treatment (Hughes, 1988; Miller and Miller, 2000) which is regarded as disposal in general (Miller and Miller, 2000); and littering, which implies leaving litter on any place to which the public has access, except at a place set apart for such purpose (Lombard *et al.*, 1994). Of the mentioned authors only Miller and Miller (2000) make a point of differentiating between land application and land treatment. For the purpose of this investigation there will be no attempt to distinguish between the two. This is because it is not considered that any benefits for crop growth are of more importance than environmental harmlessness of the material being disposed of. In view of this, both land application and land treatment will be taken to mean the activity of land disposal of waste material such that effects on the environment are monitored, and that there is a commitment to safe-guarding the health of living organisms. This is in contrast to land disposal in the form of littering where it is considered that waste is disposed of regardless of consequences, in other words an act of merely transferring the problem to another 'owner' and environment. Although

control of littering is regulated through local by-laws (Lombard *et al.*, 1994), it is a fact that dumping or discarding of unwanted material anywhere is a common occurrence.

### 1.5 Motivation for the study

According to the Umgeni Water (1994) report, the landfill site at Howick, where their Midmar Works is located, was too small to accommodate the quantities of the WTR produced. Transportation to the nearest larger landfill site in Pietermaritzburg would be expensive, as would co-disposal with municipal sewage sludge. The Department of Water Affairs and Forestry has expressed concern about re-circulation to water bodies; this is a further discouragement to this latter option. Elliott and Singer (1988) are also against the disposal of WTR into the municipal sewage system as they regard the practice as merely transferring the burden of ultimate disposal. Such problems are not unique to KwaZulu-Natal; essentially the same disposal constraints are experienced in other parts of the world as indicated by Basta, Zupancic and Dayton (2000). Pumping the WTR back into surface waters would cause sedimentation which would unfavourably reduce water depths, detrimentally increase water turbidity, produce an ecological imbalance via eutrophication, and possibly cause pollution to this environment by heavy metals.

The production of large quantities of WTR is unavoidable. The current quantities produced are likely to increase as the number of urban inhabitants increases, as Umgeni Water (and other water purification companies) make inroads into rural areas, as metropolitan councils incorporate previously tribal authorities which will force them to supply more potable water, and because of demands for healthy water in rural areas to avoid health hazards. Conventional disposal of such quantities of WTR in landfill sites might in the near future no longer be a viable option due to the reduced availability of landfill sites and economics of transportation.

As it is certain that increasing quantities of water treatment residues will continue to be produced by the various waterworks in the country, and because other disposal options are either currently not viable or might be questionable in the future, it is logical that disposing of the material onto land be

investigated. As Logan (1990) puts it: “land has the final solution to many of society’s waste disposal problems ...”. It was with such an idea in mind that Umgeni Water bought land in close proximity to their Midmar Water Treatment Works for disposal of this WTR.

## **1.6 Aims and objectives**

Whilst WTRs have been deemed by some to be environmentally benign (e.g. Elliott and Singer, 1988), no such decision has yet been taken in South Africa where this material is classified as a ‘waste’. This means WTRs are classified together with sewage sludges (biosolids). Whilst biosolids might be considered degradable wastes because of organic matter, and persistent wastes because of heavy metals, the same may not expressly be said about WTRs. It still needs to be established whether it is fair and practical to consider WTR as waste.

Water treatment residues might also have an agricultural influence that needs to be established. On the other hand, once it is in intimate contact with the soil in a favourably moist environment, then the WTR might no longer be the harmless material it is perceived to be on its own. It cannot just be assumed that its innocuousness would persist in the soil, taking into account the extremely complex nature of the soil medium; the residue and soil might react to yield products or results of environmental concern. Besides this scientific outlook, it might be argued that any unknown and unproven material should be considered a potential hazard until established otherwise.

Cameron *et al.* (1997) raised the question of whether soil is an appropriate dumping ground for all kinds of waste. For this investigation, it was thus important to establish whether it would be appropriate for Umgeni Water to continue applying WTR on the land ear-marked for disposal (some minimal disposal had taken place for the past seven years on small areas of the land), and to test whether other soils could safely accommodate this activity. According to Cox, Camberato and Smith (1997), the suitability of the WTR for land treatment would be determined by its composition and subsequent effects on soil properties (once it has been applied).

The broad objectives of the investigation were therefore as follows:-

- to review literature on WTR to investigate its potential for land application;
- to characterize the WTR to establish its properties;
- to determine the influence of the WTR on growth of cover plants;
- to establish the possible chemical effects of the WTR on the soil environment; and
- to investigate the possibility of using the WTR as an environment-cleansing material.



## CHAPTER 2

### WATER TREATMENT RESIDUE AND LAND USE HISTORY: A REVIEW

#### 2.1 Water treatment residue and plant growth: setting the scene

Rengasamy, Oades and Hancock (1980) in South Australia tested WTR on maize (*Zea mays*) in a greenhouse study. Using alum residue (produced with aluminium sulphate as the main flocculent) at rates of 2 and 20 Mg ha<sup>-1</sup> applied as a dry solid or a suspension to three soils, i.e., a strongly sodic clay soil, a leached podzolic lateritic sand and a hard-setting red-brown earth, with and without fertilizer, they achieved mixed responses with respect to dry mass (DM) yield. The lower rate increased yield with respect to the zero application in all three soils irrespective of the form in which the WTR was applied, and whether fertilizer was added or not. This increase in DM yield was most noticeable when the three soils were fertilized, and in the unfertilized hard-setting red-brown earth compared to the other two soils.

Although the main thrust of these investigators' study was on soil structural properties, P uptake by the maize plants was also considered, and this increased in almost all soils and treatments at the 2 Mg ha<sup>-1</sup> rate. Despite the yields at the higher WTR rate being greater than the control, they were lower than those at the 2 Mg/ha rate except for the fertilized podzol and red-brown earth soils. Lower uptake of P was observed with this WTR rate compared to the control and the lower rate, and this was ascribed to the sorption of this nutrient by disordered aluminium-rich products in the WTR.

From these results some observations can be made with respect to the effects of application of WTR to soil. Such an investigation should include the influence of WTR on both chemical/fertility and physical properties of soils. The effects of the material depend, amongst other factors, on WTR rate, soil type and soil fertility. Further, a decrease in uptake of P by plants does not necessarily mean a reduction in dry mass yield, notably where improved soil physical properties provide an environment for better plant performance. In addition, less uptake of P does not necessarily translate to a deficiency.

Other factors to consider are the type of plant, type of WTR and whether one is dealing with glasshouse or field experiments.

## **2.2 Water treatment residue and plant growth: a global tale of different results**

### **2.2.1 Use of water treatment residue with different plants**

Since Rengasamy *et al.* (1980) reported the results of their investigation on WTR effects on plant growth, other workers, mostly from other parts of the world, have utilised a variety of plants. Amongst those studied have been sorghum-sudan grass by Heil and Barbarick (1989) in Colorado, fescue grass (Lucas *et al.*, 1994) in Virginia, lawn grass in Southern Australia (Ahmed, Grant and Oades, 1997), blue gramma and western wheatgrass (Ippolito, Barbarick and Redente, 1999) in Colorado and, in Oklahoma with bermudagrass (Basta *et al.*, 2000). This interest in the influence of WTR on cover plants has a bearing, not only from an agricultural point of view, but also from an environmental one, as it affects aspects such as soil erosion.

In Connecticut, Bugbee and Frink (1985) investigated the effects of WTR on the growth of sugar maple and hemlock. Geertsema *et al.* (1994) researched pine trees in Virginia. This research has an economic as well as an environmental implication because some trees, like certain pine species, can be used in reclamation activities (Logan, 1992).

Amongst investigators with field crops were Skene, Oades and Kilmore (1995) who worked with beans in Southern Australia, Cox *et al.* (1997) in South Carolina with wheat, and Wang, Coullaird, Auclair and Campbell (1998) with barley in Canada. Another agronomic consideration was provided by researching the response of vegetable plants, namely tomatoes by Elliott and Singer (1988) in Pennsylvania and by Dayton and Basta (2001) in Oklahoma. Ornamental/horticultural plants in the form of marigold have also received attention from Bugbee and Frink (1985) and Ahmed *et al.* (1997).

### 2.2.2 Plant response to water treatment residue: effects of soil chemical and fertility conditions

Positive responses by plants in terms of increased foliar mass were reported by Elliott and Singer (1988), Heil and Barbarick (1989), Ahmed *et al.* (1997) and Ippolito *et al.* (1999). All of these were pot experiments except for those of Ahmed *et al.* (1997) which were also conducted as field experiments. These positive results were explained by an increase in soil pH (Elliott and Singer, 1988; Heil and Barbarick, 1989), improved availability of Fe (Heil and Barbarick, 1989) following application of ferric chloride residue, and N supply by the WTR (Elliott and Singer, 1988; Ahmed *et al.*, 1997). Differences in plant species and time of growth were proposed by Ippolito *et al.* (1999) as the possible reasons for a positive response from blue gramma, and an indifferent one from western wheat grass that was grown later.

In field experiments conducted by Bugbee and Frink (1985) and Geertsema *et al.* (1994), application of the WTR did not cause any significant changes to plant uptake of elements, element migration or growth of the trees. Whilst such results are agronomically disappointing, they are encouraging from an environmental viewpoint if the concern is disposal only and not economic in terms of increasing yield.

Lucas *et al.* (1994), Cox *et al.* (1997) and Wang *et al.* (1998) reported unequivocal negative plant growth responses. Other workers (Elliott and Singer, 1988; Heil and Barbarick, 1989) had negative and positive responses in the same experimental set-up. The results of Heil and Barbarick (1989) confirmed those of Rengasamy *et al.* (1980) who established that relatively high levels of the WTR decreased yields with respect to the lower ones, as increased sorption of P by the material reduced this nutrient's uptake by plants. Phosphate sorption was also given as the reason for the negative results of Lucas *et al.* (1994) and Cox *et al.* (1997). On the other hand, Wang *et al.* (1998) reported low pH and increased Al activity as the reasons for the inhibited growth of barley they observed with WTR application. This is seen as an isolated case as other workers who have used alum residue have reported results contrary to these, notably Heil and Barbarick (1989), Skene *et al.* (1995) and Ippolito *et al.* (1999). Skene *et al.* (1995) established that both alum and polymer types of WTR resulted in

similar Al concentrations in plant tissue that were actually less than in the control. The results of Ippolito *et al.* (1999) established that Al shoot concentration actually decreased with increase in WTR addition. The anomalous results of Wang *et al.* (1998) could be because of the strongly acidic nature of their WTRs; one had a pH as low as 3.9. To explain observed decreases in yield following application of a ferric chloride residue, Elliott and Singer (1988) proposed precipitation of magnesium ammonium phosphate (struvite) in the created alkaline conditions.

Based on the results they obtained with WTR experiments, some workers came to the conclusion that the strong binding effect of this material for P might be temporary. Thirty months after the residue was applied to soil, Geertsema *et al.* (1994) observed no significant differences in bioavailable and total P between the control and WTR-treated soils in field experiments. These results were partially supported by those of Ahmed *et al.* (1997) who, in some subsequent cuts of lawn grass grown in pot experiments, observed an increase in P uptake per pot at a WTR rate of 400 Mg ha<sup>-1</sup>. From this they concluded that with ageing and exposure to wetting and drying this material released more of this nutrient. They thus proposed that WTR could serve a dual purpose i.e., it could be used to sorb P from polluted waters, which it can do (Macks, Grant, Murray and Drew, 1998), and then act as a slow release P fertilizer. Essentially the same suggestion was made by Butkus, Grasso, Schulthess and Wijnja (1998), namely that WTR could act as a P supplier in soil by being amended with it prior to land application.

Although reduced availability of P induced by addition of the WTR seems to be the main chemical/fertility problem that might reduce the agronomic potential of this material, Dayton and Basta (2001) also considered nitrite toxicity to be a factor in some conditions. Growing tomatoes directly on the WTR, these workers found that out of 14 of these residues used, five generated toxic levels of nitrite. Because the pH of the WTRs was deemed not high enough to cause accumulation of nitrite, it was speculated that low availability of P in the affected WTRs could have prevented oxidation of nitrite to nitrate as suggested by Purchase (1974).

Micronutrients have also received attention concerning their relationship with plant growth following

addition of the WTR. Elliott and Singer (1988) reported reduced uptake of Cd, Cu, Ni and Zn by tomatoes grown in pots, which was attributed to the high pH. Growing sorghum-sudangrass on two soils in glasshouse studies, Heil and Barbarick (1989) established that the concentrations of the metals Cu, Mn, Ni, Pb and Zn were within acceptable ranges in plants grown on both soils. There were mixed results with Cd where one soil produced plants with relatively high concentrations of this metal. In this soil the WTR-treated soil had a pH of 5.1 which was judged low enough to increase the solubility of this element. Although Lucas *et al.* (1994) and Cox *et al.* (1997) reported increased uptake of Cu and Mn by fescue, and Mn by wheat, respectively, these increased tissue concentrations were within acceptable limits. Also, the increase in concentration was not associated with the yield response of plants grown. In the same experiment, however, Lucas *et al.* (1994) established that tissue concentrations of Fe and Zn were not significantly affected by application of WTR. Similar results were reported by Ahmed *et al.* (1997) where concentrations of Cu and Mn in lawn grass tissue were at optimal levels, and were not influenced by the rate of application of WTR. Growing bermudagrass directly on a WTR, Basta *et al.* (2000) established that tissue concentrations of Cd, Cu, Fe, Mn and Zn were not different from those of plants grown on soil. Whilst it is evident that the response of plants to metals will depend on experimental conditions, it can nevertheless be accepted that WTRs neither release these in quantities that are toxic to plants, nor do they change soil conditions such that this happens.

### 2.2.3 Plant response to water treatment residue: effects of soil physical condition

The soil physical condition of a soil sometimes has a bearing on the soil's chemical and fertility properties. Soil physical properties determine the rate and extent of water infiltration into, and percolation through soils, which in turn govern solute redistribution and leaching. In fact Skene *et al.* (1995) concluded that the physical properties of a WTR are more important than its chemical properties when it comes to plant growth. As was shown by the results of Rengasamy *et al.* (1980), addition of WTR to soils can affect plant yield through changes in chemical or physical properties. Considering soil physical properties, these workers associated increase in dry matter yield with a decrease in dispersion (or improved aggregation) of the soils. Consistent with these findings of

Rengasamy *et al.* (1980), Heil and Barbarick (1989) also reported improved physical conditions brought about by WTR and thus an improvement in plant growth. This was in a soil where chemical (pH) and fertility (N) properties were ruled out as having contributed to the observed positive plant response.

Other research by Bugbee and Frink (1985), Skene *et al.* (1995) and Ahmed *et al.* (1997) has established that WTRs can be favourably used as ingredients in plant growth media/potting mixtures. In a mixture of three or all of the residue, peat, perlite and soil, Bugbee and Frink (1985) found negative growth of lettuce and marigold (ascribed to P deficiencies) in all treatments except those without soil. This positive response was attributed to the WTR improving the aeration and moisture holding capacity in the growth mixture. Generally similar reasons were given for results achieved with beans in a WTR-sand-fertilizer mixture (Skene *et al.*, 1995), and with marigold grown in mixtures containing the residue, peat moss and pine bark (Ahmed *et al.*, 1997). This mixture performed as well as two commercially available mixtures in terms of number of flowers and shoot mass of the marigold plants.

### **2.3 Environmental consideration of water treatment residues**

From a chemical point of view, not only highly soluble species like nitrate might be of concern to environmental pollution, but also those with generally low solubility like P and heavy metals.

There are two notable routes by which P in agricultural lands can reach water bodies, i.e., by surface drainage (e.g. McDowell, Drewry, Paton, Carey, Monaghan and Condon, 2003; Zhang, Zhu, Guo and Liu, 2004) and subsurface drainage (e.g. Djodjic, Börling and Bergstrom, 2004; Van Es, Schindelbeck and Jokela, 2004). By either pathway, P could end up in surface waters, notably from soils which are over fertilized (Carefoot and Whalen, 2003). With its sorptive nature, loss of P from land is associated with sediment transport (McDowell *et al.*, 2003), and so its movement could be as colloidal P as established by McDowell *et al.* (2003), Toor, Condon, Di and Cameron (2004) and Turner, Kay and Westermann (2004). Enhancing runoff losses of this element is surface application

of P sources (Tarkalson and Mikkelsen, 2004). Flow mechanisms associated with rapid preferential flow increases leaching of P compared to a matrix flow (Nash and Halliwell, 1999; Siemens, Ilg, Lang and Kaupenjohann, 2004; Van Es *et al.*, 2004).

This possibility of using WTR for environmental cleansing or protection based on its P sorption propensity has received recognition by certain workers. Applied to soils, WTR was found to be effective in reducing the amount of soluble P in runoff water (Peters and Basta, 1996; Gallimore, Basta, Storm, Payton, Huhnke and Smolen, 1999) and in reducing excessive amounts of extractable P (Haustein, Daniel, Miller, Moore and McNew, 2000). The residue is thus able to prevent or reduce eutrophication, whether it occurs via external drainage or internal drainage water. Also, with its ability to stabilize aggregates (Rengasamy *et al.*, 1980) it could reduce colloidal transportation losses of P. The principle has also been successfully extended to co-application of WTR with biosolids (sewage sludge) with the aim of reducing the high active P levels in the sludge (Ippolito *et al.*, 1999).

Other potential pollution from agricultural lands is from heavy metals. Mobilization of these metals has been associated, amongst others, with application of sewage sludge (McBride, Richards, Steenhuis and Spiers, 1999; McBride, Martinez, Topp and Evans, 2000; McLaren, Clucas, Taylor and Hendry, 2004) which usually contains high amounts of these elements, and organic matter that facilitates leaching of some as metal-organic matter complexes (McBride *et al.*, 1999). Leaching of metals is also effected by macropore flow (McLaren *et al.*, 2004) or preferential flow (McBride and Evans, 2002) which bypasses interaction with the soil (McLaren *et al.*, 2004). Whilst WTRs are different from sewage sludges, they nevertheless contain heavy metals, and there is no unanimous consensus regarding the behaviour of these residues with respect to these elements (Section 2.2.2).

For use as a soil substitute, WTR has received recommendation by Basta *et al.* (2000) with bermudagrass but not by Dayton and Basta (2001) who experienced poor growth of tomatoes. Both groups of workers grew the plants directly on the residue. Dayton and Basta (2001) considered nitrite toxicity and P deficiency to have been the cause of the poor performance but also suggested that low available water and low bulk density of the material might limit its use in this regard. The factor of

the different responses of different plants becomes an issue here as the success of the experiment of Basta *et al.* (2000) indicated that the residue could be used as a soil substitute for re-vegetation of degraded lands.

Whether application of WTRs will have any effects on the environment would be determined in part by their chemical/fertility and physical properties in association with the properties of the soils, and also of other materials applied.

## **2.4 Conclusions**

As shown in the literature, WTR can be of both agronomic and environmental use if judiciously used. This would depend, amongst other factors, on the nature of the WTR and soil properties, both chemical and physical. Although some negative results have been reported, they can generally be explained and are mostly attributed to reduction in P availability at high WTR loadings. Also, most of these negative results have been experienced in pot experiments where nutrient balancing and unrealistic plant populations tend to be additional problems. The fact that no negative results have been reported in field experiments, either with respect to element uptake, element migration or plant growth suggests the relative safety of land disposal. Also heavy metals, which can be pollutants in excess concentrations, have not been reported to be of concern. In South Africa, all these observations still have to be established or disputed. An investigation thus is needed to test the influence of a WTR in the South African context.



## **CHAPTER 3**

### **CHARACTERIZATION OF THE WATER TREATMENT RESIDUE AND SOILS**

#### **3.1 Introduction**

Water treatment residues from different water works are not expected to be similar, except if, by coincidence, the raw waters and additives for purification are essentially similar. In fact, even WTRs from the same plant could be different depending on the season and flocculants added. To test the possible effects of any WTR on soils and plants, it is thus important to determine its properties.

Soils to be used for disposal of WTRs, if such an activity were to be approved, might be determined more by convenience of location with respect to the water works than any beneficial effects on crop growth. It is with this view in mind that it was decided that it was important to test the material on a variety of soils.

Soils used in different aspects of the study, and the WTR sampled from the Midmar Water Treatment Works, Howick, were characterized by determining some of their properties.

#### **3.2 Materials and methods**

##### **3.2.1 Water treatment residue**

Small samples of the WTR were collected over time from the above-mentioned water works and analysed for a range of elements. As there was virtually no variation of properties with years and season, a bulk sample of the material was then collected, dried, milled to pass through a 2 mm sieve and stored for all future use.

### 3.2.2 Soils

Twelve topsoils in all, chosen to represent a wide range of properties, and to complement a companion study on soil physical quality (Moodley, 2001), were used in the different experimental aspects of the investigation (See Map 3.1 for location of sampling sites). Soil form names, as classified by the Soil Classification Working Group (1991), were used to identify the soils. One was an Avalon (Av) soil from Geluksburg at a KwaZulu-Natal Department of Agriculture experimental site. There were three Hutton (Hu) soils, i.e., one from the field experiment at Brookdale Farm, Howick, about 40 km north of Pietermaritzburg (Hu-F), the second from a site adjacent to the water works at Midmar (Hu-M), and the third from Mangosuthu Technikon about 20 km south of Durban (Hu-T). Two of the soils were of the Inanda (Ia) form, one from an experimental site of the KwaZulu-Natal Department of Agriculture at Cedara (Ia-C) and the other (Ia-W) from Hilton, both north of Pietermaritzburg. From Adams Mission south of Durban came a Namib (Nb) soil (Nb-A), another Namib (2 samples) from a disused Mission Farm (Nb-F and Nb-F1) and a Shortlands (Sd). Completing the twelve were a Valsrivier soil (Va) from Muden, near Greytown north of Pietermaritzburg, and a Westleigh (We) from the field experiment at the University of KwaZulu-Natal's Ukulinga Research Farm, about 5 km from Pietermaritzburg. The soils were also classified according to the Soil Survey Staff (1975) (Table 3.1a).

### 3.2.3 Analysis of the water treatment residue and soils

The pH of all samples (soils and WTR), which had been air-dried and milled to pass a 2 mm sieve, was measured in a suspension of 10 g soil in 25 mL of both distilled water and 1M KCl solution. Acidity, Ca and Mg were extracted with 1M KCl solution on an end-over-end shaker for 10 minutes at a soil to solution ratio of 1:10. To determine cation exchange capacity, samples were first extracted with 0.1 M  $\text{SrCl}_2$  solution in a 1:10 ratio with the four sequential extracts being pooled before analysis (Hughes and Girdlestone, 1994). Cation exchange capacity (CEC) was then determined by extracting the resultant Sr-saturated soil with 1M ammonium acetate solution at a 1:10 ratio (Hughes and Girdlestone, 1994). Phosphorus was extracted with a solution (pH = 8) containing 0.25 M ammonium

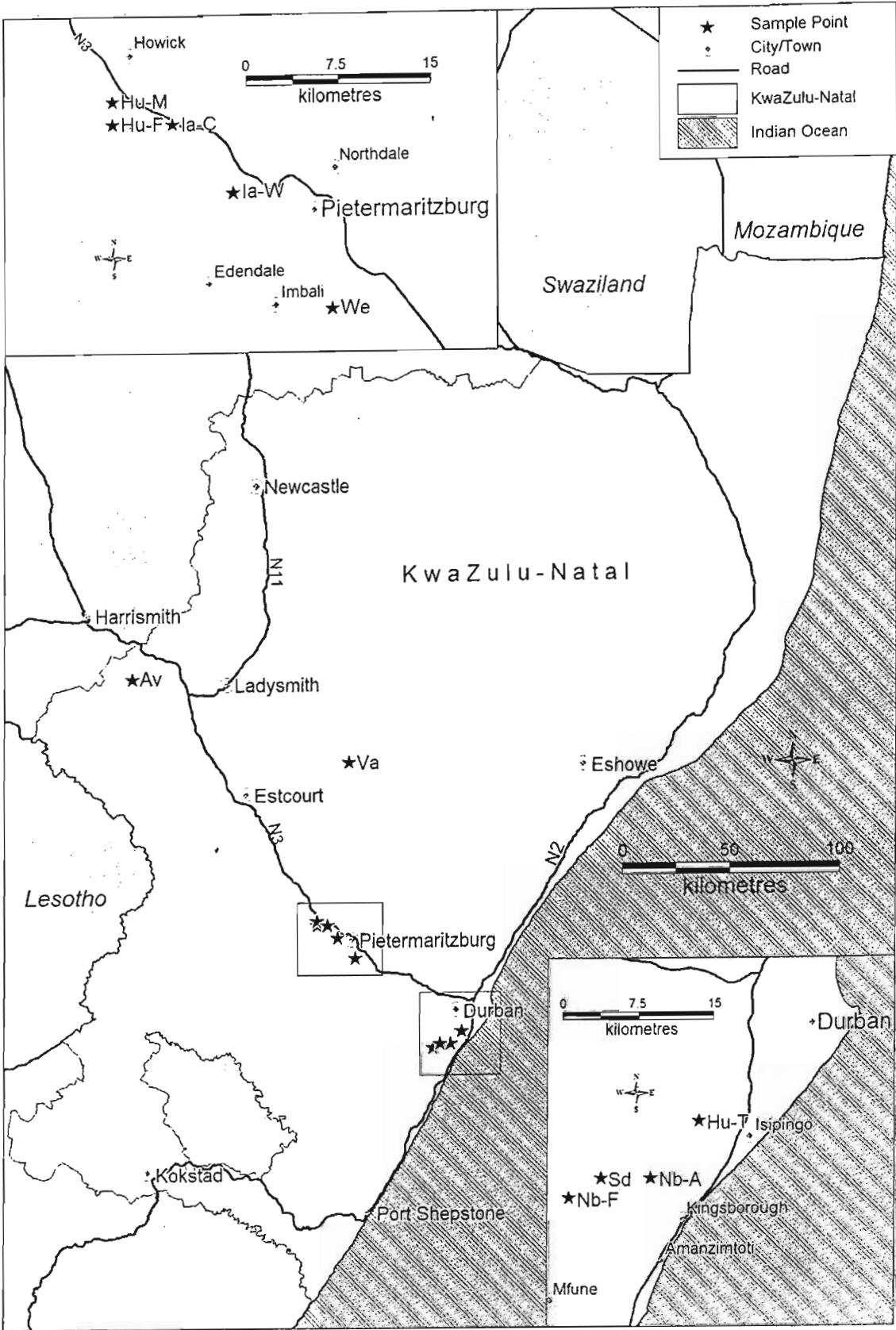
bicarbonate, EDTA disodium salt and 0.01 M ammonium fluoride (The Non-Affiliated Soil Analysis Work Committee, 1990), i.e., the Ambic extracting solution as used by the Fertilizer Advisory Service of the KwaZulu-Natal Department of Agriculture. It was then analysed by the molybdenum blue method of Murphy and Riley (1962). All the above solutions were filtered through Whatman no. 1 paper. Organic matter was determined by the Walkley-Black method (Walkley, 1947). All extractions were done on an end-over-end shaker. Particle size analysis was done by the pipette method following dispersion in sodium hexametaphosphate and sodium carbonate solution (Gee and Bauder, 1986).

Other salt solutions were also used to extract cations from the WTR on an end-over-end shaker, i.e., 0.5M buffered (Thomas, 1982) and 0.1M unbuffered (Gillman, 1979)  $\text{BaCl}_2$  solutions at a ratio of 1:10. This was done to investigate the isolation of an extractant that would be suitable in the presence of non-reacted lime in the material, as well as to be convenient for a single extraction. In another approach, the four sequential  $\text{SrCl}_2$  extractions mentioned earlier in this section were also analysed separately (instead of being pooled) to gauge the extent of cation recovery in the four steps.

Free carbonates in the WTR were determined by back titration with sodium hydroxide after addition of excess HCl (Allison and Moodie, 1965). Nitrogen was analysed by the Kjeldahl procedure (Forster, 1995). Total element concentrations were analysed by X-ray fluorescence spectroscopy (XRF).

Soluble cations and anions from the WTR were determined in 1:2 and 1:5 WTR:distilled water extracts after shaking for an hour (Rhoades, 1996). Extracts were filtered through Whatman no. 42 paper.

In all samples, Ca, K, Mg, Na and Sr were determined by atomic absorption spectrophotometry,  $\text{NH}_4$  by the method of Forster (1995), P by UV/visible spectrophotometry, S by the turbidimetric method of Verma, Swaminathan and Sud (1977), and bicarbonate, carbonate and chloride by titration (United States Salinity Laboratory Staff, 1954).



Map 3.1 Sampling sites for the soils used in the study

### 3.3 Results and discussion

#### 3.3.1 General

The particle size distribution of the WTR is 84% clay, 10% silt and 6% sand. It also contains 3.8% free carbonates and 0.01 % N. The pH of the WTR, as measured in both water and KCl, is slightly basic (Table 3.1b). This, coupled with 3.8% free carbonates, implies that at high rates of application the WTR has the potential to act as a liming material. From an agronomic point of view, this material would thus mostly be suitable for disposal on strongly acid soils. The amount of extractable basic cations and the relatively high cation exchange capacity further support the benefits the WTR could have if used in infertile soils.

Although the oxidizable organic C is high and might suggest some benefits from mineralization, the low concentration of N indicates otherwise. The classification results of the soils are in Table 3.1a. The soils cover a range of clay percentages and chemical properties as desired (Tables 3.1a and b). The Nb-F1 sample of the Namib form was sampled first. Because it had a high content of extractable P, another sample from a less fertilized part of the field was acquired, hence sample Nb-F.

#### 3.3.2 Extractants

Considering the extractants (Table 3.2a), the highest amount of cations extracted from the WTR was  $45.6 \text{ cmol}_c \text{ kg}^{-1}$  by the sequential extraction with 0.1M  $\text{SrCl}_2$ , which is approximately twice the CEC of  $23.8 \text{ cmol}_c \text{ kg}^{-1}$  (Table 3.1b). This difference is possibly explained by extraction of free carbonates and a significant amount of soluble cations by the sequential extraction, as well as incomplete extraction of Sr by ammonium acetate in the determination of the cation exchange capacity. A further test in the laboratory showed the last to be the case, a second extraction of Sr soil with ammonium acetate producing about  $6 \text{ cmol}_c \text{ kg}^{-1}$ . The difference in the effectiveness of the extractants (single extractions) is not that marked. It would thus seem that a single extraction recovers virtually only the soluble and (some) exchangeable cations whilst leaving the carbonates intact. This is based on the fact that they compare to the amount of cations extracted by buffered barium chloride which does not

**Table 3.1a** Soil classification and particle size analysis of the soils used

Soil form*	Soil family*	USDA**	Sample name	Sand <sup>a</sup>	Silt <sup>b</sup>	Clay <sup>c</sup>
(g 100g <sup>-1</sup> )						
Avalon	Blackmoor	Plinthic Paleudult	Av	6	10	84
Hutton	Stella	Typic Haplustult	Hu-F	12	50	38
Hutton	Hayfield	Typic Haplustult	Hu-M	30	30	40
Hutton	Hayfield	Typic Ustochrept	Hu-T	66	13	21
Inanda	Himeville	Humic, Rhodic, Kandiodox	Ia-C	10	27	63
Inanda	Mayfield	Humic, Rhodic, Kandiodox	Ia-W	40	13	47
Namib	Nortier	Typic Psammaquent	Nb-A	80	10	10
Namib	Nortier	Typic Psammaquent	Nb-F, Nb-F1	84	10	6
Shortlands	Bayala	Typic Haplustalf	Sd	12	31	57
Valsrivier	Slykspruit	Typic Haplargid	Va	56	19	25
Westleigh	Helena	Typic Plinthaquept	We	18	50	32

\* Soil Classification Working Group (1991), \*\* Soil Survey Staff (1975)

a=particles between 0.053 and 2.00 mm in diameter, b=particles between 0.002 and 0.053 mm in diameter,

c=particles less than 0.002 mm in diameter

**Table 3.1b** Some properties of the water treatment residue and soils used in the study

Sample name	pH (KCl)	pH (H <sub>2</sub> O)	P	Acidity	Ca	Mg	CEC	Acid sat.	Org. C
			(mg kg <sup>-1</sup> )	(cmol <sub>c</sub> kg <sup>-1</sup> )				(g 100g <sup>-1</sup> )	
WTR	7.62	7.71	26	0.01	20.6*	8.3*	23.8*	0.0	3.47
Av	3.77	4.03	30	3.45	0.3	0.1	1.4	89.6	1.35
Hu-F*	4.22	5.21	22	0.86	5.1	8.6	8.6	8.1	3.35
Hu-M	4.60	5.89	30	0.01	10.5	16.5	16.5	0.1	3.43
Hu-T	4.79	5.63	25	0.04	6.0	7.8	7.8	0.5	1.55
Ia-C	4.25	5.34	20	1.51	2.5	7.9	7.9	26.5	4.74
Ia-W	3.77	4.19	11	3.33	0.3	1.9	1.9	87.0	5.92
Nb-A	4.28	5.35	5	0.04	0.7	1.3	1.3	3.0	0.48
Nb-F1	3.77	4.81	338	0.46	0.5	3.9	3.9	39.7	0.59
Nb-F	4.53	5.82	7	0.02	1.4	0.3	1.0	1.2	0.46
Sd	4.75	5.95	7	0.01	12.4	16.1	16.1	0.1	1.85
Va*	5.91	6.81	19	0.06	6.7	10.5	10.5	0.5	1.27
We*	4.90	5.91	14	0.01	6.0	9.8	9.8	0.6	2.17

\* From Moodley (2001)

dissolve carbonates. Barium chloride would thus seem the most convenient extractant. It is more efficient than strontium chloride, easier to prepare than the buffered barium chloride and can be used to measure extractable K, unlike potassium chloride. The electrical conductivity of the water extract (1:2) indicates a significant amount of soluble salts, with the dominant cations being calcium and (to some extent) magnesium, and the anions chloride and bicarbonate (to some extent) (Table 3.2b). Migrating solutes in WTR-treated soils would be expected to be dominated by these ions although none of them is particularly environmentally harmful, either directly or indirectly.

**Table 3.2a** Analysis of salt extracts of the water treatment residue

Extractant	Ca	K	Mg	Na	NH <sub>4</sub>	Sum
	(cmol <sub>c</sub> kg <sup>-1</sup> )					
1M KCl	20.6	nd	8.3	1.7	0.7	31.3
0.1M BaCl <sub>2</sub>	23.7	0.7	9.2	1.3	0.5	35.4
0.5M BaCl <sub>2</sub> -TEA	22.7	0.8	9.0	1.8	0.2	34.5
0.1M SrCl <sub>2</sub> (4x)	35.7	0.7	8.0	0.9	0.3	45.6
0.1M SrCl <sub>2</sub> (1)	21.7	0.4	5.4	0.5	0.4	28.4
0.1M SrCl <sub>2</sub> (2)	8.6	0.2	1.5	0.3	0.1	10.7
0.1M SrCl <sub>2</sub> (3)	4.4	0.1	0.6	0.4	0.1	5.6
0.1M SrCl <sub>2</sub> (4)	3.9	0.1	0.3	0.3	0.1	4.7
0.1M SrCl <sub>2</sub> (1+2+3+4)	38.6	0.8	7.8	1.5	0.7	49.4

Considering the concentration of total trace elements (Table 3.2c), Cl is one of the most abundant. It is thus not surprising that this element would dominate the soil solution, especially as it is an indifferent ion. Overall though, the element levels are relatively low, and much lower in comparison to the ferric chloride residue of Elliott and Singer (1988). Amongst others, this residue had high concentrations of Cr (432.2 mg kg<sup>-1</sup>), Mn (4826.8 mg kg<sup>-1</sup>) and Ni (306.8 mg kg<sup>-1</sup>), yet it was beneficial to tomatoes grown in a greenhouse up to a 10% (m/m) rate of application. Thus from the point of view of heavy metal toxicity and pollution, it would seem that the WTR under consideration here is not likely to be problematic. This is more so considering its basic pH which will reduce the mobility of such heavy metals.

**Table 3.2b** Analysis of water extracts of the water treatment residue

Soil:water	EC	pH	Ca	K	Mg	Na	NH <sub>4</sub>	Sum	Cl	HCO <sub>3</sub>	NO <sub>3</sub>	SO <sub>4</sub>	Sum
	(dS m <sup>-1</sup> )		(mmol <sub>e</sub> kg <sup>-1</sup> )						(mmol <sub>e</sub> kg <sup>-1</sup> )				
1:2	1.69	7.26	5.1	0.8	3.1	1.0	0.6	10.6	12.7	5.4	0.3	0.6	19.0
1:5	0.70	7.41	2.9	0.4	1.7	0.8	0.4	6.2	5.4	2.8	0.1	0.4	8.7

EC = electrical conductivity

**Table 3.2c** Concentrations of some major and trace elements in water treatment residue as determined by XRF

Sample date	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	LOI	
	(%)											
May 1998	52.30	23.93	4.65	13.91	1.60	1.36	0.84	0.11	0.32	0.81	22.90	
August 2000	54.57	22.60	4.20	11.95	1.47	1.92	1.53	0.15	0.24	0.86	23.91	
Sample date	As	Ba	Cd	Ce	Cl	Co	Cr	Cu	Ga	La	Nb	Nd
	(mg kg <sup>-1</sup> )											
May 1998	20	891	nd	88	nd	45	138	42	18	34	nd	31
August 2000	17	1007	4	96	1575	39	161	44	20	19	11	25
Sample date	Ni	Pb	Rb	S	Sc	Sr	Th	U	V	Y	Zn	Zr
	(mg kg <sup>-1</sup> )											
May 1998	56	17	104	810	40	157	17	2	205	29	101	123
August 2000	53	37	94	720	33	71	10	0	154	27	84	126

LOI = loss on ignition



### 3.4 Conclusions

The properties of the WTR indicate an apparently environmentally-friendly material. From its low amount of pollutants namely heavy metals and N, to its high clay content and basic pH which would assist in the deactivation of most chemical species, it can, on its own, be regarded as a relatively harmless material. In addition, an analysis of a WTR sample by Umgeni Water (Pietermaritzburg) tested negative for both *Salmonella* species and *Escherichia coli* (Hughes *et al.*, 2005). Its properties of basic pH and presence of free carbonates map out an investigation involving strongly acid soils. The pH and high clay content suggest inclusion of strongly sorbed substances like P and heavy metals in the study. The concern for its effects on the environment to which it is introduced requires that the behaviour of chemical species following its application be established, and that the growth of vegetation following land treatment be investigated.

## CHAPTER 4

### WATER TREATMENT RESIDUE AND GROWTH OF PERENNIAL RYEGRASS: POT EXPERIMENT

#### 4.1 Introduction

From the literature review (Chapter 2) it was seen that the effects of WTR on plant growth in pot experiments are not clearly defined but depend on a number of factors, amongst which are WTR type/properties (Heil and Barbarick, 1989; Skene *et al.*, 1995), soil type (Rengasamy *et al.*, 1980; Heil and Barbarick, 1989), plant species (Ippolito *et al.*, 1999) and WTR application rates (Rengasamy *et al.*, 1980; Elliott and Singer, 1988; Heil and Barbarick, 1989).

Using three types of WTR, Heil and Barbarick (1989) found the best response with the ferric-based material for sorghum-sudan grass grown under greenhouse studies in an iron-deficient soil. On the other hand, Skene *et al.* (1995) found a polymer WTR to be a superior growth medium for beans than alum-based material because of better K and N supply. It is in soils with low fertility that the material is likely to provide a nutritional benefit (Cox *et al.*, 1997) and where there is a benefit from its liming effect (Elliott and Singer, 1988; Heil and Barbarick, 1989). When it comes to the WTR rate of application, rather conservative amounts up to a maximum 2.5% (m/m) have generally been suggested or indicated by results obtained (Heil and Barbarick, 1989; Geertsema *et al.*, 1994; Lucas *et al.*, 1994), a figure equivalent to approximately 44 Mg ha<sup>-1</sup>. Some workers have exceeded this rate and still achieved results better than the control. Elliott and Singer (1988) observed a significant response to tomatoes grown in the greenhouse with a WTR rate of 10% (m/m), although the highest yield was obtained at a rate of 6% (m/m). Ahmed *et al.* (1997), with a rate of 1600 Mg ha<sup>-1</sup>, reported positive results with lawn grass in both field and greenhouse experiments. Other workers have grown plants directly on the residue, and measured an increase in yield relative to sand (Skene *et al.*, 1995) and soil (Basta *et al.*, 2000). It would seem then that the rate factor is not conclusive and would have to be established for particular plant species and soil conditions.

The results of the above-mentioned investigations are an indication of the agronomic usefulness of WTR, in spite of some negative reports of plant response which were mostly attributed to relatively large quantities of this material reducing P availability and thus reducing yields. Even in these instances it was found that application of P with the WTR eliminated the problem (Bugbee and Frink, 1985; Lucas *et al.*, 1994).

Polymer residues as considered in this work have not been widely investigated, probably because they are considered even more innocuous than the alum-based product which has been the subject of most investigations. There is thus a need for the polymer WTR produced by Umgeni Water at its Midmar plant in Howick to be tested for its effects on plant growth.

The objectives of this chapter are as follows:-

- to determine the effects of application of WTR on the growth of a test plant on different soils; and
- to establish changes in soil chemical properties following application of the WTR.

## 4.2 Materials and methods

### 4.2.1 Soils

Five of the 12 soil samples were used i.e., the Hu-M, Hu-T, Ia-C, Nb-F1 and Sd (see Tables 3.1a and 3.1b). This aspect of the investigation was the first to be carried out, before the project was expanded to include the other 6 soils. The Hu-M, Hu-T and Sd soils are moderately acid whereas the Ia-C and Nb-F1 soils are strongly acid.

### 4.2.2 Pot experiment

The WTR was applied at rates of 0, 40, 80 and 120 Mg ha<sup>-1</sup> to triplicate 1 kg soil samples which had been air-dried, milled and passed through a 2 mm sieve. The highest of these rates corresponded to 65.57, 62.50, 80.00, 57.55 and 68.38 mg kg<sup>-1</sup> for the Hu-M, Hu-T, Ia-C, Nb-F1

and Sd soils, respectively. These rates were chosen such that the highest exceeded the safe disposal rate of 80 Mg ha<sup>-1</sup> given in the Umgeni Water (1994) report. In the Ia-C and Nb-F1 soils the WTR was applied with three lime levels. The highest level was the amount of calcitic lime calculated to reduce the acid saturation percent of the respective soil to 5%, and the lower one was half of that. Assuming field incorporation to a depth of 200 mm, these rates were equivalent to 9 and 4.5 Mg ha<sup>-1</sup> in the Ia-C soil, and 5 and 2.5 Mg ha<sup>-1</sup> for the Nb-F1 soil. All experimental samples received a basal dressing of N (150 mg kg<sup>-1</sup> as ammonium dihydrogen phosphate which was also the P source, and ammonium nitrate to provide the balance), P (75 mg kg<sup>-1</sup>), K (50 mg kg<sup>-1</sup> as potassium chloride), Mg (37.5 mg kg<sup>-1</sup>) and S (50 mg kg<sup>-1</sup>) - the last two being provided by hydrated magnesium sulphate.

Perennial ryegrass (*Lolium perenne*) was chosen as the test crop for two reasons. One reason was that an exhaustive extraction of nutrients was desired so that even if the effects of the WTR were masked by the initially high fertility, their role might become apparent once inadequacy of nutrients was experienced. The other reason for the choice of ryegrass was the desire to test a cover plant from the point of view of possible rehabilitation of degraded landscapes. Nutrient depletion was ensured by cutting plants after tillering and allowing them to regrow. Eight cuts in all, the last of which was the final harvesting, were made in a period spanning about 12 months. The dates of the cuts were 10.12.97, 07.01.98, 29.01.98, 20.03.98, 30.04.98, 17.07.98, 01.09.98 and 22.10.98. Plant samples were kept for analysis. Soils were maintained at the desired moisture contents by weighing and watering every day. At the termination of the experiment, soil samples were kept for chemical analyses.

#### 4.2.3 Chemical analysis of soils

Air-dried, <2mm soil samples (1 from each replicate) were analysed for pH, and extractable acidity, Ca, Mg and Na in 1M KCl extracts (1:10 soil:solution ratio on an end-over-end shaker for 10 minutes). Phosphorus, extracted by the Ambic solution (Section 3.2.3), was analysed colorimetrically (Murphy and Riley, 1962) with a UV/visible spectrophotometer.

#### 4.2.4 Chemical analysis of plant tissue

Oven-dried (70°C) samples (1 from each replicate) were sent to the KZN Department of Agriculture and Environmental Affairs where they were digested and analysed (Ca, K, Mg, N, P, Cu, Mn, Zn) by the procedure of Riekert and Bainbridge (1998).

#### 4.2.5 Statistical analysis

Three samples of DM yield, plant tissue and soil, from each of the three replicates, were chemically analysed, and results statistically analysed using one-way analysis of variance (at  $p < 0.05$ ).

### 4.3 Results and discussion

#### 4.3.1 Dry matter yields

In Figures 4.1 to 4.5c it can be seen that the pattern of dry matter (DM) yield over the different cuts is essentially the same in all five soils with, in general, the DM peaking at cuts 2 and 6. Exceptions are the Nb-F1 soil with no WTR applied, where the peak at cut 6 is not prominent (Figures 4.5a to 4.5c). This observation was true even in the soils where cut 1 yields were relatively high, namely the Hu-T soil (Figure 4.2), the Sd soil (Figure 4.3) and the Nb-F1 soil where lime was applied (Figures 4.5b and 4.5c).

Two factors could be affecting this pattern of response within the same soil, namely nutrient levels and time between cuts. At the second cut the amount of available nutrients was still relatively high, so although growth was only for 22 days after the first cut, the DM yield was the highest. At cut 6, where the second highest yield was obtained, the cutting was done 78 days after the fifth one which was the longest period between cuts. This lengthy period obviously allowed the plants to accumulate the high mass.

A similar pattern in the yield response to WTR as discussed above was also observed with lime in the strongly acid Ia-C and Nb-F1 soils (Figures 4.6a to 4.7d). The maxima at cuts 2 and 6 are again prominent at all lime and WTR levels, except in the Nb-F1 soil where either no lime or WTR was applied. There is overall a similarity to the yield pattern of perennial ryegrass in response to WTR and agricultural lime. Looking at the Nb-F1 soil in particular, the creation of a yield peak once either the lime or WTR is applied further implies that there is something common to their effects. Both of them introduce Ca to the soil, and because of the presence of free carbonates the WTR could be expected to have a liming effect as well. It can be argued that the positive response of perennial ryegrass to either lime or WTR in the Nb-F1 soil was partly due to the introduction of Ca. The Ia-C soil, with a higher Ca content, showed more prominent maxima, and liming does not noticeably make these more defined.

Considering total DM yield response to applied WTR (Figure 4.8), the highest increases occurred in the Ia-C and Nb-F1 soils. For the Hu-M, Hu-T, Ia-C, Nb-F1 and Sd soils the highest yield increases were 2.38 g, 3.30 g, 4.66 g, 4.32 g and 2.74 g, respectively, and all these increases were significant ( $p < 0.05$ ). These masses represented increases of 18.9%, 21.9%, 18.2%, 35.2% and 62.8%, respectively. The better response in the Ia-C and Nb-F1 soils suggests that the liming effect of the WTR was in operation, and/or that Ca nutrition made an improvement to growth. Elliott and Singer (1988) and Heil and Barbarick (1989) have also suggested that an increase in pH owing to WTR application could improve yields. Not easy to explain is the increase in the other three soils which had pH values between 5.5 and 7.0 and fairly high extractable Ca. It is even difficult to invoke the argument of Rengasamy *et al.* (1980) and Skene *et al.* (1995) of improved physical properties as these three soils have good physical properties. The results nevertheless tend to confirm that this material should be looked at broadly as many factors are involved in its impact.

In Figures 4.9 and 4.10 the total DM yield of the two strongly acid soils in response to applied WTR is considered at different lime levels. Even in the presence of lime the increases in yields are significant in both soils at low rates of WTR application, indicating a complementary effect between the two materials. At higher rates of application of the WTR, there is an indication of some

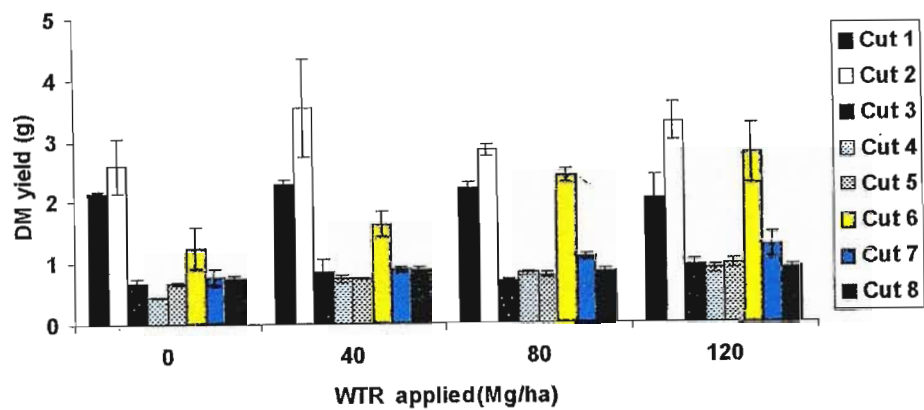


Figure 4.1 DM yield of perennial ryegrass grown on the Hu-M soil as affected by amount of WTR applied

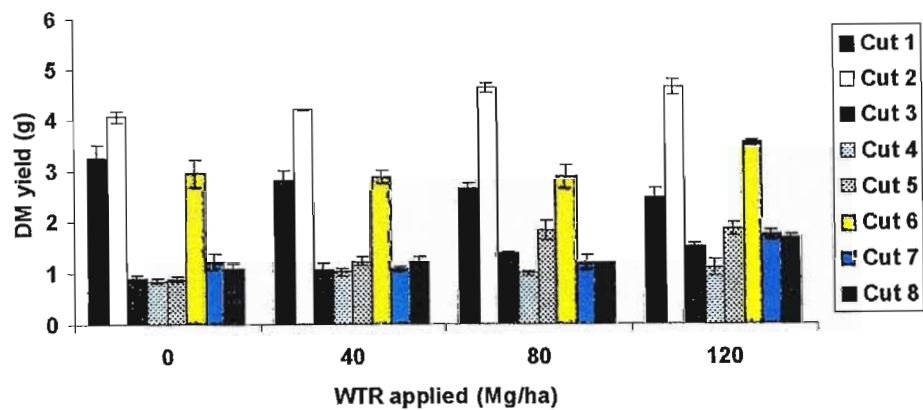


Figure 4.2 DM yield of perennial ryegrass grown on the Hu-T soil as affected by amount of WTR applied

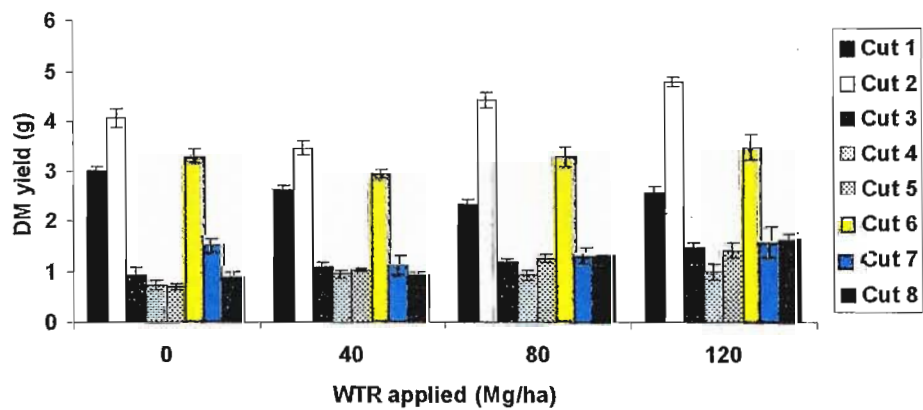


Figure 4.3 DM yield of perennial ryegrass grown on the Sd soil as affected by amount of WTR applied

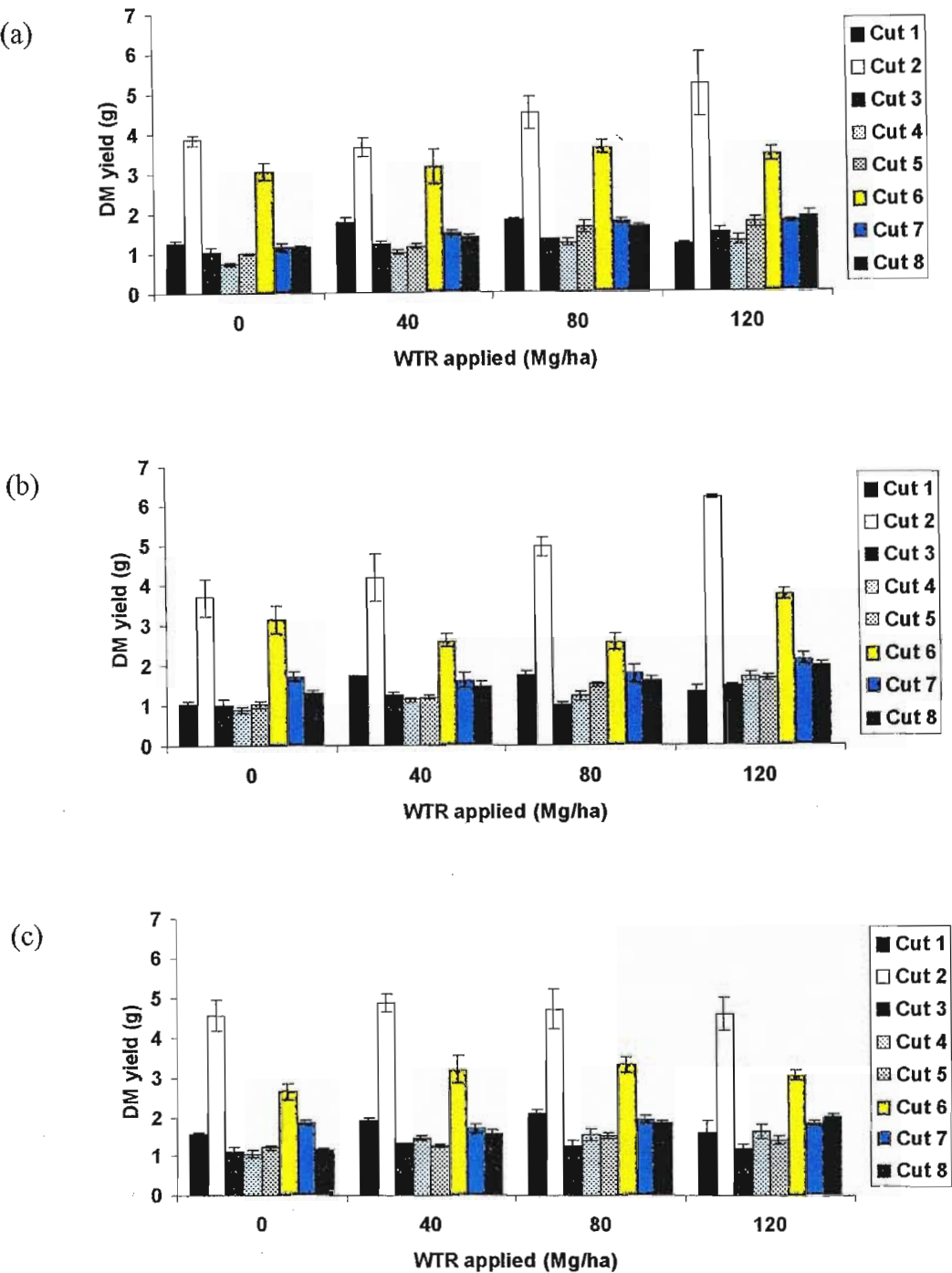


Figure 4.4 DM yield of perennial ryegrass grown on the Ia-C soil at line level (a) 0, (b) 1 and (c) 2 as affected by amount of WTR applied



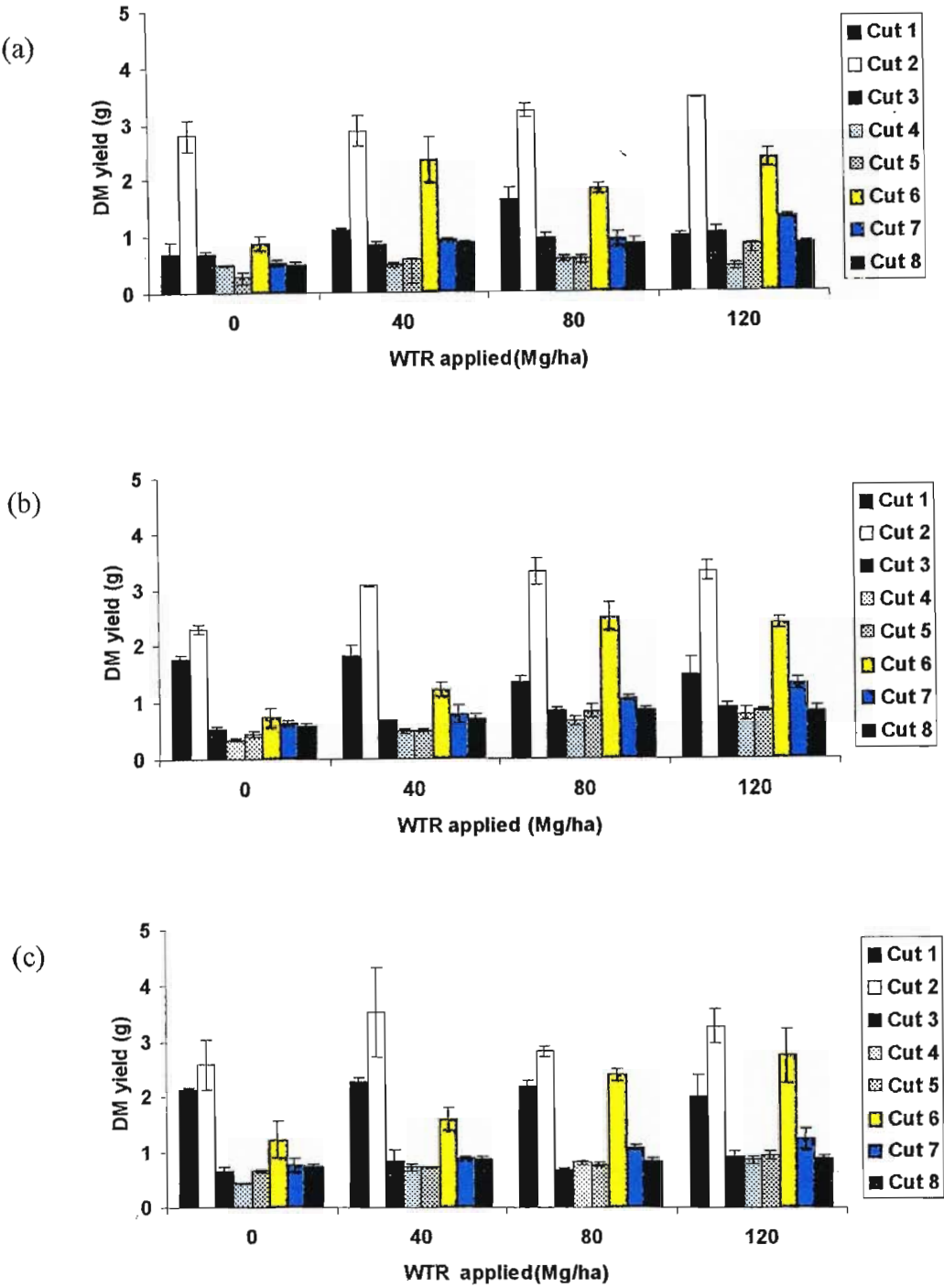


Figure 4.5 DM yield of perennial ryegrass grown on the Nb-F1 soil at lime level (a) 0, (b) 1 and (c) 2 as affected by amount of WTR applied

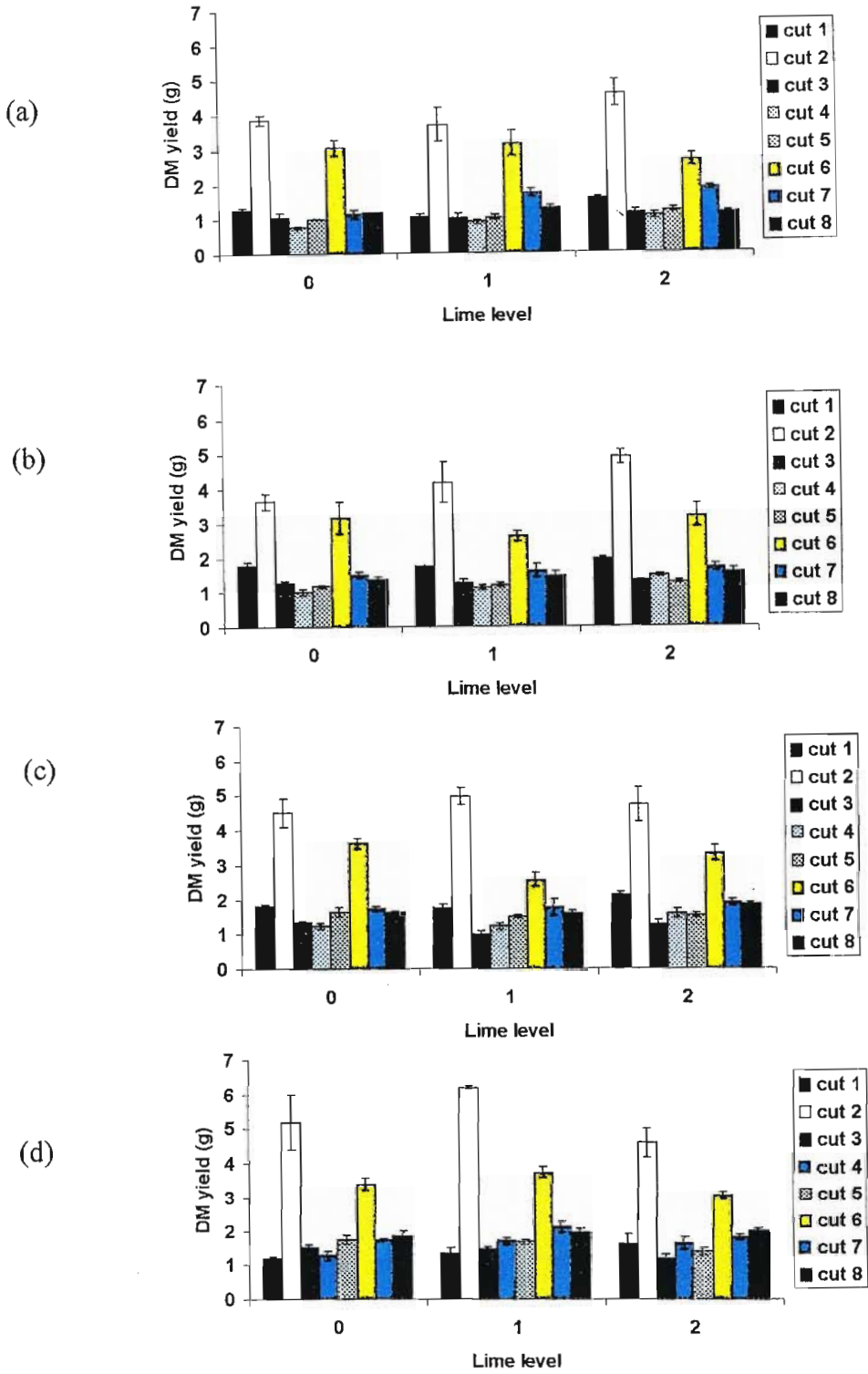


Figure 4.6 DM yield of perennial ryegrass grown at (a) 0, (b) 40, (c) 80 and (d) 120 Mg ha<sup>-1</sup> WTR on the Ia-C soil as affected by lime level

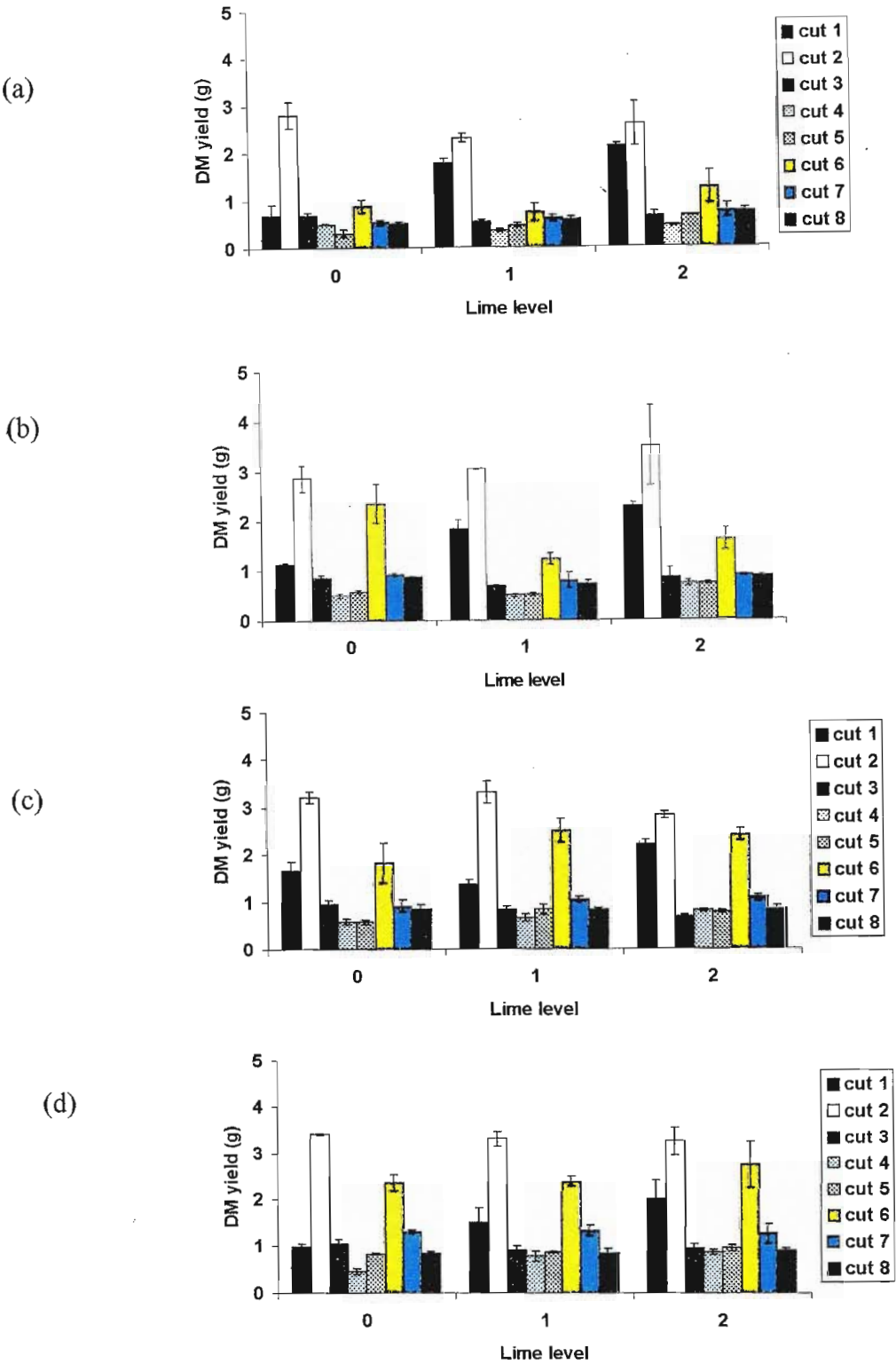


Figure 4.7 DM yield of perennial ryegrass grown at (a) 0, (b) 40, (c) 80 and (d) 120 Mg ha<sup>-1</sup> WTR on the Nb-F1 soil as affected by lime level

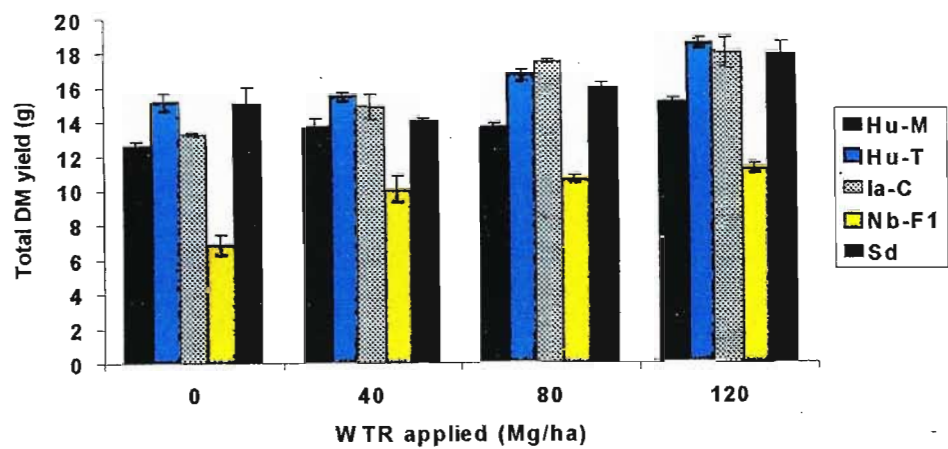


Figure 4.8 Total DM yield of perennial ryegrass grown on the five soils at different WTR levels

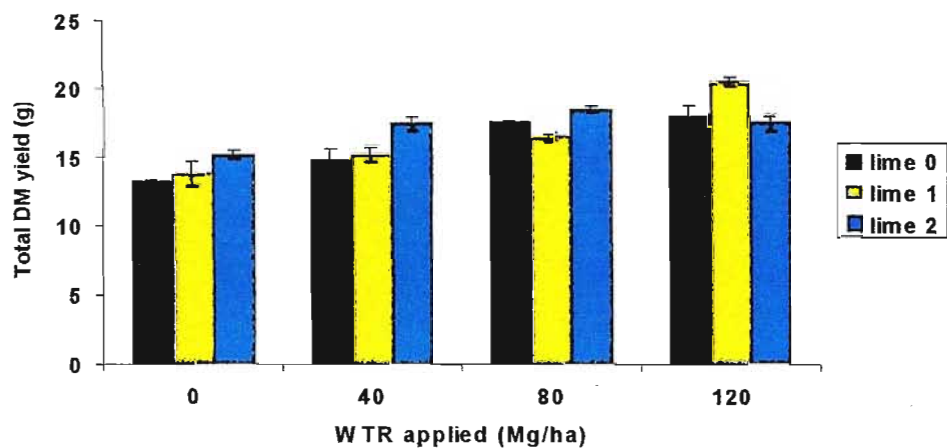


Figure 4.9 Total DM yield of perennial ryegrass grown on the Ia-C soil at different WTR and lime levels

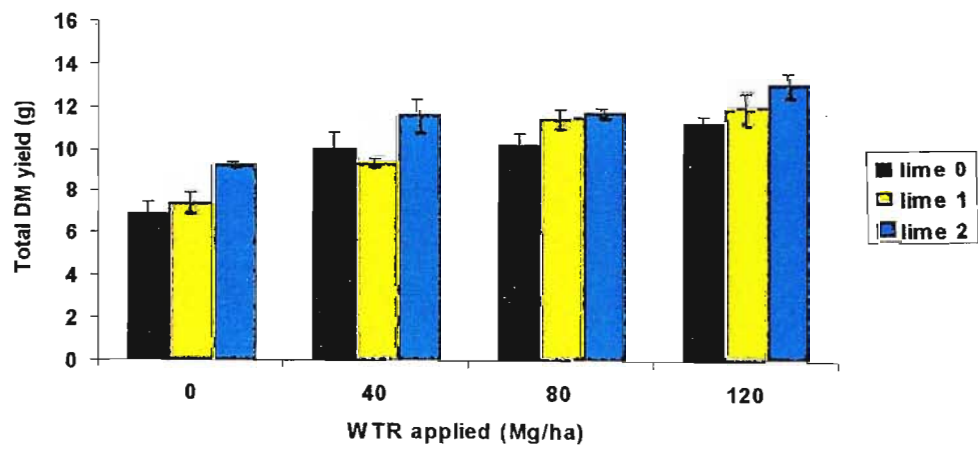


Figure 4.10 Total DM yield of perennial ryegrass grown on the Nb-F1 soil at different WTR and lime levels

supplementary (Figure 4.10; Appendix 1.5) and even negative (Figure 4.9; Appendix 1.4) effects. Isolating the effects of lime at similar rates of WTR shows that the increases are not as high as those of the WTR (at similar lime levels). In the Ia-C soil the highest increase due to WTR application was 6.43 g whereas that of lime was 2.32 g; the corresponding figures for the Nb-F1 soil were 4.49 and 2.50 g. These observations indicate that the suggested liming effect is not the only cause of the increase in DM yield (see also Section 6.3.2).

#### 4.3.2 Nutrient levels in plant tissue

These data are presented in Appendices 1.1 to 1.5 for cuts 1, 2, 4 and 8. These cuts were selected to represent the first, middle and final harvests.

In almost all soils and all cuts analysed, tissue Ca increased significantly with amount of WTR applied. This was especially true for the Hu-M, Hu-T and Sd, all being soils to which no lime was applied. In the two soils to which lime was added, there were a few instances where response of Ca tissue concentrations to increase in WTR was not statistically different, notably in the Ia-C soil.

Increase in tissue Ca with amount of WTR applied was expected as this material had a high amount of extractable Ca. Although this might indicate that this nutrient could contribute to an increase in yield as suggested for the Nb-F1 soil above, the data do not confirm this. It is in fact in the higher yielding cut 2 that Ca is in lower concentrations compared to the lower yielding cuts 4 and 8. It might then be that Ca is not a factor in the yield response, or that there is a reduction in its concentration with increase in yield. This dilution effect would not be entirely expected though, since there was an input of plant-available Ca through the WTR, and also by liming in the Ia-C and Nb-F1 soils.

Concentrations of Mg are largely unaffected. With the WTR containing extractable Mg (Section 3.3.2), the uptake of this element would have been expected to increase with increase in application rates of the material. The application levels of the WTR were apparently not high enough to increase

uptake of Mg by plants.

Tissue P does not show any trend, which is an unexpected response. Not only does the material contain P, it also was expected to sorb P (Rengasamy *et al.*, 1980; Lucas *et al.*; 1994; Cox *et al.*, 1997) and so reduce its availability. It has, however, been pointed out that polymer WTR have lower P sorption capacities than, for example, alum WTR (Skene *et al.*, 1995).

Levels of Mn tended to decrease as the rate of WTR applied increased except in the Nb-F1 soil where it tended to increase. Zinc and Fe did not show any definite pattern of response.

#### 4.3.3 pH and extractable elements in the soils

These results are given in Appendix 2.1. Measured pH values show an increase in both KCl and water in all soils, confirming that the residue has a liming effect. This is further confirmed by the reduction in extractable acidity and acid saturation, notably in the Ia-C and Nb-F1 soils. In the Ia-C soil the acid saturation drops from 27% to 1%, and from 37% to 1% in the Nb-F1 soil. Extractable Ca increases as expected, whilst Mg is virtually unaffected. This soil behaviour of Mg explains to some extent the similar concentrations of this element in plant tissue (Section 4.3.2) at the same cut. Extractable P decreases noticeably in the Nb-F1 soil and to some extent in the Hu-T soil. These decreases were apparently not enough to cause a corresponding decrease in plant tissue P or reduction in yields. Thus a decrease in the extractable levels of this nutrient does not necessarily lead to deficiencies or reduced levels in plants.

## 4.4 Conclusions

From both agricultural and environmental points of view, the results obtained from the pot experiment are encouraging as perennial ryegrass can be used as feed for animals and protection of land. In all five soils considered there was a significant positive response of DM yield of perennial ryegrass to the application of WTR. Thus whether soils needed lime or not the material was of

benefit to the plant concerned. It can be suggested that the material is not soil specific as different pH values, clay percentages and fertility status were some of the variables involved.

What has been more difficult to identify are the actual causes of the observed response. None of the nutrient levels in plant tissues could help with the explanation as none was consistent with the DM yields. The common factors in all soils after application of the residue were an increase in pH and Ca. However, neither of these could satisfactorily explain the established response. Improvement in soil physical properties would also not be a conclusive explanation, since the Nb-F1 was the only soil with initially poor physical properties.

It is suggested that no single factor can be used to explain the effects of the WTR on the response of perennial ryegrass in this pot experiment. For the acid and infertile Ia-C and Nb-F1 soils, liming and introduction of Ca could have contributed to the increase in dry mass yields, whilst for the other three soils which are moderately acid and relatively fertile there was probably another mechanism at work.

## CHAPTER 5

### WATER TREATMENT RESIDUE AND PERFORMANCE OF PERENNIAL RYEGRASS AND TALL FESCUE: FIELD EXPERIMENTS

#### 5.1 Introduction

The literature review (Chapter 2) revealed that observed negative effects of applied WTR on plant growth have been in greenhouse experiments while no such effects have been reported for field trials. In the field experiments of Geertsema *et al.* (1994) and Ahmed *et al.* (1997) where loading rates of up to about 55 Mg ha<sup>-1</sup> and 1600 Mg ha<sup>-1</sup> were used, there were no negative changes in the growth of pine trees and lawn grass, respectively.

Four possible effects of land-treated WTR need to be considered i.e., agricultural influence (uptake of elements and plant growth), soil properties, composition of drainage water, and impact on the activity of undesirable and/or excessive chemical species in the soil.

The agricultural influence refers to phytotoxicity to plants growing on the treated soil, or zootoxicity to animals feeding on treated lands. Buttigieg, Klessa and Hall (1989) pointed out three possible ways by which potentially toxic elements might pose problems to grazing ruminants, i.e., adhering to leaf surfaces during application, ingestion of the material or contaminated soil from the ground, and feeding on herbage that has absorbed the species. Characterization of the WTR (Chapter 3) established that it had a certain amount of heavy metals, some of which are potential toxins in large quantities.

The results of Chapter 4 suggested benefits of application of WTR to growth of perennial ryegrass in a pot experiment, although the mechanisms of this positive response were unclear. Minyi (1989), Hopkins, Adamson and Bowling (1994) and McKenzie and Jacobs (2002) have shown the importance of nutrient adequacy and/or balance in grass herbage. For temperate grasses, which



provide forage to livestock and are also responsible for protection and conservation of soil (Van der Meer and Wedin, 1989), this would be an issue to consider. It is therefore necessary to establish whether land disposal of WTR has an impact on the plant-nutrient relationships.

The objectives of this chapter are as follows:

- to determine the effects of applied WTR on performance of perennial ryegrass (*Lolium perenne*) and Dovey tall fescue (*Festuca arundinaceae*) under field conditions; and
- to establish uptake of elements by these grass species.

## 5.2 Materials and methods

### 5.2.1 Test plants

Perennial ryegrass (*Lolium perenne*) as used in the pot experiment and Dovey tall fescue (*Festuca arundinaceae*) were used to establish the effects of the land disposal of the WTR.

### 5.2.2 Sites and soils: Brookdale and Ukulinga

One experiment was set up at Brookdale Farm near Howick, 36 km north of Pietermaritzburg on a Hutton (Hu-F) soil. This soil is the dominant one on this field of 2% slope (Moodley, 2001), and the farm is an intended site for disposal of the WTR from the Midmar Water Treatment Works. According to Moodley (2001), the site is at an altitude of almost 1066 m; with a mean annual (essentially summer) rainfall of 866.6 mm; and mean annual maximum and minimum temperatures of 22.4°C and 9.9°C, respectively.

The other experiment was established on a Westleigh (We) soil at the University of KwaZulu-Natal Research Farm, Ukulinga. This site was convenient in terms of location, as well as having a soil very different from the Hu-F on which to test the WTR. The field site is situated at an elevation of

775 m and has a 1% slope, Ukulinga Farm has a mean annual rainfall of 735 mm, and mean annual maximum and minimum temperatures of 27.5°C and 8.9°C, respectively (Moodley, 2001).

The greenhouse and field trials were unfortunately not exactly complementary to each other since no common soils were used in both. This was because the field trials were started after the pot trial had been completed, and none of the convenient sites was the source of the soils used in pot trials. However, the Hu-M and Ia-C soils were similar to the Hu-F soil.

### 5.2.3 Experimental design and establishment: Brookdale and Ukulinga

Details of the two field experiments were described by Moodley, Johnston, Hughes and Titshall (2004), from which the following information has been summarized. Profile descriptions of the soils (Moodley, 2001) are given in Appendices 3.1 and 3.2. At both sites plots were 6 m by 4 m, separated from each other by a 2 m wide buffer strip. The variety of treatments applied, and their modes of application, are given in Table 5.1 and Table 5.2 for the Brookdale and Ukulinga trials, respectively. The mulched treatment was included at the Brookdale experiment to simulate disposal without mechanical incorporation which, if successful, would be economically favourable; the incorporation represents the more conventional means of application of waste materials and fertilizers, etc, in agriculture.

The WTR, which had been allowed to air-dry for six months and had broken down to aggregates of mostly 50-80 mm in diameter, was spread evenly (after removal of large chunks) on the soil surface by shovels and then raked over. Lime was broadcast by hand. (For the current study the lime treatment is of particular interest since lime and the WTR are both alkaline sources of Ca). Where application was by incorporation, the material concerned was mixed by discing to a depth of 200 mm.

Setting up the Brookdale experiment was completed in early October 1998. In all, 64 plots were prepared from the 16 treatments which were assigned randomly to the plots. Sixteen plots per

contour were arranged with their longest dimension parallel to the slope of the field. The upper two contours were left fallow, and the lower two were planted with perennial ryegrass. The plots to be seeded with perennial ryegrass (April 1999) were fertilised with 200 kg N ha<sup>-1</sup>, 30 kg P ha<sup>-1</sup> and 185 kg K ha<sup>-1</sup> as limestone ammonium nitrate (LAN), diammonium phosphate (DAP), and potassium chloride (KCl).

At Ukulinga the relevant treatments were applied in the third week of October 1999, although it was only in March 2000 that a stand of Dovey tall fescue could be established because of profuse weed growth. As at the Brookdale trial, there were seeded and fallow plots replicating the same treatments. Fertilizer was added at 400 kg N ha<sup>-1</sup>, 30 kg P ha<sup>-1</sup> and 150 kg K ha<sup>-1</sup> prior to seeding with Dovey tall fescue.

**Table 5.1** Treatments investigated at the Brookdale Farm trial

Treatment	Application rate (Mg ha <sup>-1</sup> )
Water treatment residue (incorporated)	0, 40, 80, 160, 320, 640, 1280
Water treatment residue (mulched)	320, 640, 1280
Gypsum	5, 10
Dolomitic lime	2, 10
Anionic polyacrylamide	15 x 10 <sup>-3</sup> , 30 x 10 <sup>-3</sup>

**Table 5.2** Treatments investigated at the Ukulinga Farm trial

Treatment	Application rate (Mg ha <sup>-1</sup> )
Water treatment residue (incorporated)	0, 80, 320, 1280
Gypsum	10
Dolomitic lime	10
Anion polyacrylamide	30 x 10 <sup>-3</sup>

#### 5.2.4 Field experiment maintenance: Brookdale and Ukulinga

Routine maintenance of both experiments involved keeping the plots and surrounds weed-free by application of a glyphosphate-based herbicide (Roundup<sup>®</sup> and Erase 360 S.L.) on the fallow treatments and Basagran on the grassed treatments when necessary, and regular irrigation and mowing (about every 6-8 weeks) of the grassed treatments.

Maintenance of soil fertility at Brookdale Farm involved application of 50 kg N ha<sup>-1</sup>, 30 kg P ha<sup>-1</sup> and 50 kg K ha<sup>-1</sup> in January of each year with an additional 50 kg N ha<sup>-1</sup> added every 3 months. In March 2001 the experiment was replanted to Dovey tall fescue. The same fertilizer scheme, as used in the maintenance applications, was continued.

At the Ukulinga trial additional N was added every 3 months at 50 kg ha<sup>-1</sup>. In February 2001 maintenance fertilizer (50 kg N ha<sup>-1</sup>, 50 kg K ha<sup>-1</sup> and 30 kg P ha<sup>-1</sup>) was added to the lower half of each grassed plot to investigate the effect of additional fertilizer on the grass, compared to that on the unfertilized section of the same plots. After the April 2001 harvest, N fertilization continued as before over the entire plot.

#### 5.2.5 Grass harvesting: Brookdale and Ukulinga

Grass samples from the two sites were collected on the dates indicated below. Harvesting was done by randomly placing a 0.25 x 0.25 m quadrat in a plot and then cutting the grass in the quadrat with a sheep shear to about 20 mm above the soil surface. Three quadrats were harvested in each plot and the material from these quadrats was bulked before being prepared for analysis.

The perennial ryegrass was harvested at Brookdale as follows: October 1999, December 1999, July 2000 and selected treatments sampled in February 2001. The Dovey tall fescue (which replaced the ryegrass) was harvested as follows: November 2001, February 2002 and October 2002.

The grass was harvested at Ukulinga at the following times:- July 2000, September 2000, February 2001, April 2001 (lower and upper sections of each plot harvested separately), August 2001, November 2001, February 2002, April 2002, November 2002, February 2003 and May 2003.

Dry matter (DM) yields are recorded for (some) sampling dates from the Ukulinga trial but not from the Brookdale trial, the reason being that wild animals had access to the grassed plots so making any measurement of yield meaningless.

Results have not been reported for all harvests in the current study. A general trend of behaviour had appeared from the grass plants in earlier harvests, and the later ones were essentially repetitions. Also, it was the highest treatment of 1280 Mg ha<sup>-1</sup> which was mostly compared with the control, the reason being that the most significant differences would be most likely between these two.

#### 5.2.6 Chemical analysis of grass samples

Except for Cd, Co, Cr, Ni and Pb, all harvests were analysed at the Soil Fertility and Analytical Services Laboratory, KwaZulu-Natal Department of Agriculture and Environmental Affairs, Cedara. Bulked grass samples were dried at 65°C, weighed and then a sub-sample was analysed for Ca, K, Mg, N (in some cases), P, Cu, Mn and Zn (Riekert and Bainbridge, 1998). The procedure was essentially dry digestion followed by dissolving the ash in 1M HCl, and analysis by atomic absorption spectrophotometry. For the analysis of Cd, Co, Cr, Ni and Pb the method of Riekert and Bainbridge (1998) was followed with the difference that instead of the 1g of plant material, 5g were used.

#### 5.2.7 Statistical analysis and comparison of results

All samples were analysed in duplicate and statistically analysed using one-way analysis of variance (at  $p < 0.05$ ). The element levels were compared with research results acquired from the KwaZulu-Natal Department of Agriculture, Cedara (Miles, undated). The comparisons are not directly

appropriate since Miles' research results are based on a date corresponding to 2/3 of canopy for perennial ryegrass 6 to 8 weeks after sowing or 4 weeks regrowth; the corresponding conditions for tall fescue are 5 to 7 weeks regrowth of the green leaf material in the top half of the canopy. They, however, serve as an indication of "ideal" conditions.

### **5.3 Results and discussion**

#### **5.3.1 Observed growth of grass at Brookdale and Ukulinga**

Neither the rate nor the mode of application of the WTR was discerned to cause any negative impact on the growth of the ryegrass (or the tall fescue planted subsequently at Brookdale) with respect to either the density, height or appearance of the grass plants; if anything, the grass appeared to grow better where the material was applied. This was especially true for the highest application rate of 1280 Mg ha<sup>-1</sup>, both incorporated and mulched, and in particular the latter treatments. Such visual improvement was consistently observed throughout the experiment in both the perennial ryegrass and the tall fescue at both sites. The general appearance of the grass is shown in Plates 5.1 and 5.2 for the Brookdale and Ukulinga experiments, respectively.

#### **5.3.2 Brookdale experiment**

##### **5.3.2.1 Perennial ryegrass**

In the October 1999 harvest, no definitive trend appeared as to the effects of either the WTR or the lime on the concentrations of the various elements in plant tissue. Calcium was the only element that seemed to respond to the treatments (Table 5.3a), and that response was to the WTR. Calcium tissue levels increased by 0.08 and 0.13% on the 640 and 1280 Mg ha<sup>-1</sup> mulched treatments relative to the control, but it was only at the higher level that the gain was statistically significant.

A similar trend is observed in the December 1999 harvest. Concentrations of K and Ca increase,



Plate 5.1 Dovey tall fescue grass growing at Brookdale Farm in November 2001



Plate 5.2 Dovey tall fescue grass growing at Ukulinga Farm in November 2001



especially at application rates above 160 Mg ha<sup>-1</sup> although none of the increases is significant for K. In this harvest the increase in tissue Ca occurs at application rates of the WTR over 320 Mg ha<sup>-1</sup> irrespective of its mode of application, but it is again on the 1280 Mg ha<sup>-1</sup> mulched treatment that the result is significant. Both lime treatments also show an insignificant increase for both these elements. It could be expected that tissue Ca would increase with application of the WTR considering its high levels in this material. The results for K are somewhat unexpected as the WTR contains a low K concentration.

**Table 5.3a** Some elements in perennial ryegrass grown at Brookdale Farm in 1999 [means (n = 2) followed by the same letter are not statistically different]

Harvest date	Treatment (Mg ha <sup>-1</sup> )	Ca	K	Mg (g 100g <sup>-1</sup> )	N	P	Cu	Mn (mg kg <sup>-1</sup> )	Zn
October 1999	R0	0.42ab	2.94bc	0.42c	2.68bc	0.26ab	11abc	253e	50ab
	R40i	0.41ab	3.23bc	0.42c	2.75bc	0.29b	12bc	230cde	42ab
	R80i	0.32a	2.14a	0.33ab	1.83a	0.19a	8a	248de	34a
	R160i	0.41ab	2.64ab	0.35abc	2.35ab	0.21a	9ab	226bcde	38ab
	R320i	0.39a	2.82abc	0.38abc	2.79bc	0.23ab	10abc	174ab	42ab
	R640i	0.40a	2.47ab	0.36abc	2.50ab	0.19a	11abc	176abc	46ab
	R1280i	0.40a	2.56ab	0.32a	2.56b	0.19a	11abc	193abc	42ab
	R320m	0.40a	3.09bc	0.39abc	2.81bc	0.25ab	12bc	167a	60b
	R640m	0.50bc	2.88abc	0.40abc	2.73bc	0.24ab	12bc	201abcde	41ab
	R1280m	0.55c	3.48c	0.38abc	3.30c	0.25ab	13c	195abcd	37ab
	<b>LSD(0.05)</b>	<b>0.10</b>	<b>0.76</b>	<b>0.09</b>	<b>0.73</b>	<b>0.08</b>	<b>4</b>	<b>55</b>	<b>25</b>
	L2	0.39	2.58	0.36	2.38	0.22	10	236	35
	L10	0.39	2.60	0.38	2.23	0.22	10	162	37
December 1999	R0	0.38a	2.34a	0.33ab	2.29bcd	0.24a	4a	290ab	27a
	R40i	0.40abc	2.25ab	0.32ab	1.43abc	0.22a	4a	338b	31a
	R80i	0.31a	2.21a	0.28a	1.12a	0.21a	4a	284ab	30a
	R160i	0.31a	2.79ab	0.28a	1.30ab	0.23a	4a	206ab	42a
	R320i	0.41abc	2.98ab	0.33ab	1.71abcd	0.27a	5a	153a	39a
	R640i	0.45bc	2.75ab	0.32ab	1.79abcd	0.24a	5a	164a	39a
	R1280i	0.52cd	2.90ab	0.36ab	2.19abcd	0.26a	7ab	164a	41a
	R320m	0.50bcd	2.91ab	0.35ab	2.39cd	0.28a	9ab	130a	35a
	R640m	0.47bcd	2.93ab	0.30a	2.22bcd	0.27a	8ab	146a	42a
	R1280m	0.60d	3.06b	0.39b	2.55d	0.29a	12b	186ab	37a
	<b>LSD(0.05)</b>	<b>0.14</b>	<b>0.85</b>	<b>0.09</b>	<b>1.09</b>	<b>0.08</b>	<b>5</b>	<b>167</b>	<b>17</b>
	L2	0.41	2.79	0.34	1.58	0.24	5	185	46
	L10	0.46	2.68	0.33	2.16	0.22	7	158	37

R= water treatment residue; L=lime; numbers are rates of application in Mg ha<sup>-1</sup>; i=incorporated; m=mulched

Calcium and Mg levels are within the respective 0.26-1.0% and 0.2-0.5% ranges of adequacy for ryegrass. The concentrations of K were more in the 2.5-6.0% range of adequacy than the 2.0-3.0% range of critical levels. However, N and P are below the adequacy ranges of 3.6-6.0% and 0.25-0.36%, respectively. For N the levels are in fact clearly below the critical 3.5% value whilst for P they are close to the critical concentration of 0.24%. The overall results, where those of the control were no exception to these observations, suggested that it was the low concentrations of these elements in soil rather than the effect of the treatments that caused the inadequate tissue levels.

No trend of response to treatments was observed with respect to minor elements, except possibly for Mn (Table 5.3a) where there was a suggestion of some significant decreases in Mn tissue concentrations with application of WTR or lime. Levels of Cu, Mn and Zn were generally within their adequacy ranges of 6-12, 50-300 and 15-20 mg kg<sup>-1</sup>, respectively. Copper concentrations were sometimes close to or below the lower limit, whilst those of Zn were somewhat elevated compared to the adequacy range. There was, however, no indication that these levels were caused by the application of the WTR since control treatments were similarly affected. The concentrations of both Mn and Zn were well below the 1000 and 300-500 mg kg<sup>-1</sup> DM limits, respectively, suggested by Webber *et al.* (1984; cited by Buttigieg *et al.*, 1989) as the maximum tolerable dietary concentrations for long-term feeding of perennial ryegrass to ruminants.

#### 5.3.2.2 Dovey tall fescue

Neither the major nor the minor elements exhibited any trends with respect to increases in the WTR or the lime applied. Adequate levels for this grass are Ca (0.22-0.31%), K (2.2-3.5%), Mg (0.20-0.36%), and P (0.25-0.35%); the adequate levels for minor elements are not known. Except for K and P in the October 2002 harvest (Table 5.3b), the elements were within these ranges. Even for these exceptions, it was clear that the deficiencies were more a function of the soil conditions at the time than the material applied, as the controls also exhibited similarly low concentrations. Of the micronutrients, it was only the levels of Mn that tended to decrease with application of either the WTR or the lime although some of the differences were statistically non-significant.

### 5.3.3 Dry matter yield of Dovey tall fescue from the Ukulinga experiment

There were no statistical differences between the harvests (Tables 5.4a, 5.4b and 5.4c) except in July 2000 when the 320 and 1280 Mg ha<sup>-1</sup> rates gave significantly higher yields than the other treatments, and in August 2002 when all three rates of WTR yielded significantly higher than the control. Neither the WTR nor the other treatments suppressed the growth of the grass, and in general there were slight increases in yield with application of the WTR.

Where half of the plots were fertilized (April 2001 harvest), the yield was significantly higher than where no fertilization had occurred (Table 5.4b). To ascribe the yield response to increased K content in the plant would only explain the response at 0 and 80 Mg ha<sup>-1</sup> application rates of WTR. It is more that the introduction of all three primary macronutrients improved the performance of the grass. Elliott and Singer (1988) had recommended that introduction of WTRs to croplands should be accompanied by application of N, P and K. A review by Elliott and Dempsey (1991) also established how WTRs had little impact on soil fertility because of their low N contents, no increases in mineralization rates following their application, and their being responsible for reducing plant- available P. After testing the material as a potential plant growth medium, Skene *et al.* (1995) concluded that fertilizer application with WTRs is necessary for optimum plant growth. Results of Rengasamy *et al.* (1980) in pot experiments gave mixed results, with an increase in growth recorded with and without fertilizer application. Application of WTR for agronomic purposes should not make one lose sight of the importance of nutrient balance and adequacy in the soil.

### 5.3.4 Elements in Dovey tall fescue from the Ukulinga experiment

There was no definitive pattern to the uptake of elements in response to the WTR application (Tables 5.4a, 5.4b and 5.4c). Also, although there were some general increases in some elements, they were not significant. As for the ryegrass at Brookdale, it would seem that tall fescue was generally insensitive to the application of either the WTR or the lime as indicated by uptake of elements. Nitrogen (where analysed) was the only element that tended to show increases in response to the WTR. These increases were, however, not statistically significant except in July 2000. These

**Table 5.3b**    Some elements in Dovey tall fescue grown at Brookdale Farm in 2001 and 2002  
[means (n = 2) followed by the same letter are not statistically different]

Harvest date	Treatment (Mg ha <sup>-1</sup> )	Ca	K	Mg	P	Cu	Mn	Zn
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )		
November 2001	R0	0.32a	2.79a	0.35ab	0.24a	9ab	225bcd	29abc
	R40i	0.32a	3.62ab	0.29ab	0.26a	10b	231ad	29abc
	R80i	0.26a	3.35ab	0.28a	0.26a	9ab	251d	30abc
	R160i	0.31a	3.15ab	0.31ab	0.24a	9ab	246d	38c
	R320i	0.27a	3.10ab	0.35ab	0.27a	9ab	199abcd	30abc
	R640i	0.31a	3.47ab	0.32ab	0.24a	8ab	176abcd	29abc
	R1280i	0.34a	3.68ab	0.38b	0.30a	10b	127ab	33bc
	R320m	0.30a	3.03ab	0.33ab	0.23a	6a	163abcd	22a
	R640m	0.30a	3.42ab	0.34ab	0.26a	10b	140abc	28abc
	R1280m	0.28a	3.84b	0.31ab	0.27a	11b	98a	24ab
	<b>LSD(0.05)</b>	<b>0.10</b>	<b>0.99</b>	<b>0.10</b>	<b>0.09</b>	<b>4</b>	<b>95</b>	<b>10</b>
	L2	0.28	3.50	0.35	0.27a	10	201	29
	L10	0.32	3.52	0.33	0.30	9	152	27
February 2002	R0	0.28a	2.10a	0.34a	0.22a	5a	301abc	18a
	R40i	0.30ab	1.97a	0.35a	0.23a	7a	333a	26c
	R80i	0.29ab	2.11a	0.36ab	0.27a	2a	310bc	20ab
	R160i	0.31ab	2.32ab	0.38ab	0.23a	11a	291abc	22abc
	R320i	0.28a	2.08a	0.40ab	0.26a	7a	266abc	24bc
	R640i	0.30ab	2.20a	0.38ab	0.30a	3a	277abc	25c
	R1280i	0.30ab	2.40ab	0.43ab	0.27a	4a	179a	26c
	R320m	0.29ab	2.02a	0.35a	0.28a	2a	209abc	19ab
	R640m	0.33bc	2.80b	0.45ab	0.28a	3aa	188ab	22abc
	R1280m	0.36c	2.31ab	0.47b	0.25a	7a	178a	18a
	<b>LSD(0.05)</b>	<b>0.04</b>	<b>0.58</b>	<b>0.11</b>	<b>0.11</b>	<b>9a</b>	<b>125</b>	<b>5</b>
	L2	0.30	2.04	0.37	0.24	3a	306	19
	L10	0.26	2.02	0.39	0.24	3a	266	19
October 2002	R0	0.33a	1.32a	0.33a	0.19a	4a	331b	19a
	R40i	0.34a	1.54a	0.32a	0.18a	5a	363b	25a
	R80i	0.38a	1.87a	0.32a	0.17a	3a	305ab	21a
	R160i	0.29a	1.43a	0.31a	0.16a	4a	270ab	21a
	R320i	0.32a	1.97a	0.34ab	0.18a	4a	347b	23a
	R640i	0.33a	1.53a	0.30a	0.17a	3a	238ab	21a
	R1280i	0.35a	1.27a	0.41b	0.21a	4a	244ab	21a
	R320m	0.36a	1.91a	0.36ab	0.19a	5a	304ab	22a
	R640m	0.34a	1.46a	0.37ab	0.19a	4a	248ab	19a
	R1280m	0.31a	2.17a	0.35ab	0.22a	5	186a	20a
	<b>LSD(0.05)</b>	<b>0.14</b>	<b>0.09</b>	<b>0.09</b>	<b>0.07</b>	<b>3</b>	<b>144</b>	<b>7</b>
	L2	0.29	0.28	0.28	0.17	4	311	21
	L10	0.37	0.39	0.39	0.23	3	282	19

R= water treatment residue; L=lime; numbers are rates of application in Mg ha<sup>-1</sup> ; i=incorporated; m=mulched

N results tend to correspond with those of the DM yield (Table 5.4a), and this might suggest that N could have contributed to the increase in yield observed in the pot experiment (Section 4.3.1).

From the data, it was clear that the concentrations of the major elements in the grass tissue largely fell in the suggested ranges for adequate levels; and more importantly, application of the WTR did not cause the element levels to be outside these ranges. Of the minor elements, it was again Mn which showed signs of decreasing with application of both the WTR and the lime. Whilst not statistically significant, these decreases were nonetheless consistent.

**Table 5.4a** DM yield and concentration of some elements in Dovey tall fescue grown at Ukulinga Farm in 2000 [means (n = 2) followed by the same letter are not statistically different]

Harvest date	Treatment	DM yield	Ca	K	Mg	N	P	Cu	Mn	Zn
	(Mg ha <sup>-1</sup> )	(Mg ha <sup>-1</sup> )			(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )	
July 2000	R0	1.83a	0.29a	2.32ab	0.30a	1.66a	0.25a	5a	96b	23a
	R80	1.78a	0.29a	1.93a	0.25a	1.62a	0.22a	4a	57a	20a
	R320	2.57ab	0.25a	2.22ab	0.27a	2.34ab	0.23a	5a	71ab	24ab
	R1280	3.48b	0.29a	2.53b	0.33a	3.33b	0.23a	7a	82ab	28b
	LSD(0.05)	0.93	0.24	0.59	0.04	1.11	0.05	3	25	5
	L10		0.27	2.33	0.27	1.80	0.23	5	68	24
September 2000	R0	nd	0.33a	2.99a	0.38b	2.65a	0.28b	8a	159d	33a
	R80	nd	0.33a	2.82a	0.32a	3.08	0.26ab	8a	98ab	28a
	R320	nd	0.33a	2.91a	0.35ab	2.72a	0.28b	8a	87a	29a
	R1280	nd	0.41b	3.35a	0.35ab	3.16a	0.21a	8a	118bc	36a
	LSD(0.05)		0.08	0.80	0.04	0.87	0.06	0.00	20	14
	L10	nd	0.28	3.16	0.30	2.42	0.31	0.00	66	33

R=water treatment residue; L=lime; numbers associated with R and L are rates of application in Mg ha<sup>-1</sup>; nd=not determined

**Table 5.4b** DM yield and concentration of some elements in Dovey tall fescue grown at Ukulinga Farm in 2001 [means (n = 2) followed by the same letter are not statistically different]

Harvest date	Treatment	DM yield	Ca	K	Mg	N	P	Cu	Mn	Zn
	(Mg ha <sup>-1</sup> )	(g)			(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )	
February 2001	R0	2.50a	0.31a	2.41a	0.41a	2.18ab	0.26a	3a	199c	22a
	R80	2.20a	0.34a	2.30a	0.40a	2.07a	0.30a	2a	129ab	29a
	R320	3.60a	0.32a	2.57a	0.37a	2.57bc	0.34a	3a	99a	24a
	R1280	3.25a	0.36a	2.34a	0.40a	3.38d	0.31a	4a	121a	29a
	LSD (0.05)	1.67	0.08	0.69	0.09	0.43	0.11	3	69	15
	L10	3.05	0.35	1.92	0.40	3.10	0.26	3	122	32
April 2001	R0	1.25a	0.40a	1.82a	0.43a	2.41a	0.38a	4a	234b	20a
	R80	1.05a	0.44a	1.68a	0.40a	2.80a	0.37a	4a	207ab	24ab
	R320	1.35a	0.43a	2.22a	0.46a	2.48a	0.50a	4a	114a	24ab
	R1280	1.45a	0.39a	2.27a	0.41a	2.87a	0.41a	4a	126a	26b
	LSD (0.05)	0.59	0.12	0.70	0.08	0.79	0.17	0	105	6
	L10	1.25	0.42	2.23	0.45	1.90	0.46	4	81	22
April 2001*	R0	2.25a	0.32a	2.68a	0.40a	nd	0.36a	3a	155b	40a
	R80	2.60a	0.34a	2.70a	0.40a	nd	0.38ab	5a	93a	25a
	R320	2.40a	0.36ab	2.68a	0.44a	nd	0.43c	4a	86a	25a
	R1280	3.10a	0.45c	2.33a	0.47	nd	0.34a	4a	123ab	40a
	LSD (0.05)	1.41	0.05	0.88	0.07		0.05	3	38	24
	L10	1.90	0.37	2.33	0.47	nd	0.38	4	99	27
August 2001	R0	1.55a	0.42a	2.19a	0.39a	nd	0.30a	7a	289b	43a
	R80	1.30a	0.48a	2.04a	0.38a	nd	0.32a	4a	210ab	39a
	R320	1.80a	0.42a	1.75a	0.39a	nd	0.32a	8a	165a	31a
	R1280	1.40a	0.58a	1.85a	0.42a	nd	0.25a	6a	141a	35a
	LSD (0.05)	1.13	0.41	1.70	0.19		0.21	9	91	26
	L10	1.80	0.42	1.96	0.46	nd	0.34	8	179	40
November 2001	R0	3.10a	0.27a	1.98a	0.33ab	nd	0.29a	4a	194c	16a
	R80	2.20a	0.30a	2.43c	0.31ab	nd	0.32a	3a	134ab	15a
	R320	2.95a	0.31a	1.98a	0.30a	nd	0.29a	3a	94a	15a
	R1280	3.25a	0.37a	1.99ab	0.38b	nd	0.30a	6a	115a	20a
	LSD (0.05)	2.04	0.11	0.36	0.07		0.08	5	56	8
	L10	2.55	0.33	1.61	0.33	nd	0.28	4	95	12

R=water treatment residue; L=lime; numbers associated with R and L are rates of application in Mg ha<sup>-1</sup>

nd=not determined; \* = results from fertilized plots

**Table 5.4c** DM yield and concentration of some elements in Dovey tall fescue grown at Ukulinga Farm in 2002 [means (n = 2) followed by the same letter are not statistically different]

Harvest date	Treatment (Mg ha <sup>-1</sup> )	DM yield (g)	Ca	K	Mg	P	Cu	Mn	Zn
			(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )		
February 2002	R0	2.05a	0.28a	1.47a	0.35a	0.28ab	7a	182b	15ab
	R80	2.30a	0.29a	1.82a	0.30a	0.31ab	5a	115ab	14ab
	R320	3.20a	0.27a	1.54a	0.33a	0.24a	11a	114ab	12a
	R1280	3.20a	0.32a	1.67a	0.36a	0.34a	4a	108a	19b
	LSD (0.05)	1.43	0.09	1.00	0.07	0.08	5	73	7
	L10	2.55	0.30	1.75	0.33	0.29	4	71	14
April 2002	R0	nd	0.48a	1.15ab	0.49a	0.31a	7a	193a	36a
	R80	nd	0.43a	1.50b	0.48a	0.27a	10a	144a	39a
	R320	nd	0.50a	0.79a	0.56a	0.31a	8a	114a	36a
	R1280	nd	0.58a	0.88a	0.55a	0.31a	8a	140a	35a
	LSD (0.05)		0.17	0.54	0.12	0.19	8	116	24
	L10	nd	0.43	1.14	0.50	0.30	6	86	29
August 2002	R0	0.85a	0.51a	0.67a	0.44a	0.21a	4a	197a	24a
	R80	1.50bc	0.51a	0.51a	0.39a	0.20a	7a	184a	34a
	R320	1.45b	0.59ab	0.64a	0.36a	0.21a	4a	106a	24a
	R1280	1.90c	0.65b	0.56a	0.30a	0.19a	5a	128a	29a
	LSD (0.05)	0.42	0.12	0.30	0.13	0.10	6	111	30
	L10	1.10	0.59	0.82	0.46	0.26	3	97	24
November 2002	R0	1.70a	0.35ab	1.27a	0.54c	0.26a	7a	160d	31a
	R80	1.73a	0.34a	1.42a	0.44a	0.27a	6a	111a	24a
	R320	2.24a	0.42ab	0.94a	0.52c	0.27a	7a	120ab	29a
	R1280	2.42a	0.47b	0.90a	0.48b	0.25a	7a	126bc	28a
	LSD (0.05)	1.21	0.12	0.75	0.03	0.04	3	14	12
	L10	2.04a	0.33	1.57	0.50	0.28	7	114	32

R=water treatment residue; L=lime; numbers associated with R and L are rates of application in Mg ha<sup>-1</sup>

nd=not determined

### 5.3.5 Selected heavy metals in grass grown at the two sites

Analytical data for Cd, Co, Cr, Ni and Pb showed that concentrations of Cd were below the detection limit of the method used, and so the results for this element are not reported. For the other

elements the results are presented in Tables 5.5 and 5.6 for the Brookdale and Ukulinga experiments, respectively. In the Brookdale 1999 harvest, Cr and Ni tissue contents significantly decreased with WTR applied at the highest rate, both incorporated and mulched. The concentrations of Co and Pb were essentially unchanged by the application of the WTR. In the mulched treatment of the 2001 harvest, the levels of Co and Cr were significantly higher than those of the control whereas those of Ni and Pb were non-significantly higher.

**Table 5.5** Selected heavy metals in perennial ryegrass (1999) and Dovey tall fescue (2001) grown at Brookdale Farm [means (n = 2) followed by the same letter are not statistically different]

Harvest date	WTR rate (Mg ha <sup>-1</sup> )	Co	Cr	Ni	Pb
		(mg kg <sup>-1</sup> )			
October 1999	0	7.5a	8.9c	7.0d	3.8a
	320i	7.2a	7.6bc	5.3c	3.9a
	1280i	7.9a	6.0b	3.5b	3.8a
	1280m	6.9a	3.0a	1.5a	3.9a
	LSD(0.05)	3.2	1.8	1.2	0.9
November 2001	0	6.9a	3.6ab	2.3ab	3.6ab
	320i	8.2ab	3.3a	2.1a	3.5a
	1280i	7.8a	3.1a	1.7a	3.8ab
	1280m	12.1c	5.8c	3.4b	4.5b
	LSD(0.05)	3.2	1.6	1.3	0.9

i=incorporated; m=mulched

At Ukulinga the Co tissue levels at the 1280 Mg ha<sup>-1</sup> WTR application rate were significantly higher than those of the control. Levels of Cr were unaffected by the rate of WTR in the 2000 harvest and increased (but not significantly) in the 2001 harvest. Nickel and Pb differences were non-significant except for Ni at 1280 Mg ha<sup>-1</sup> in the 2001 harvest. Amounts of Cr and Ni appeared to have increased in the later harvests.

No reason has been found to explain the differences in Cr and Ni concentrations for the comparative



harvests. It should be noted, however, that for the Brookdale results two different grasses were involved; in the Ukulinga data the 2000 harvest was in winter as compared to spring of 2001. Also difficult to explain was the uptake of Co; the Co tissue concentrations tended to consistently increase with an increase in WTR application rate. A decrease in Ni uptake on application of WTR has been reported (Elliott and Singer, 1988) and ascribed to immobilization by the alkaline conditions created by the WTR. On the whole, it can be stated that the field application of this WTR up to rates of 1280 Mg ha<sup>-1</sup> to the Hutton and Westleigh soils grown to perennial ryegrass and tall fescue did not significantly alter the tissue levels of pollutant metals.

**Table 5.6** Selected heavy metals in Dovey tall fescue grown at Ukulinga Farm [means (n = 2) followed by the same letter are not statistically different]

Harvest date	WTR rate (Mg ha <sup>-1</sup> )	Co	Cr	Ni	Pb
			(mg kg <sup>-1</sup> )		
July 2000	0	5.4ab	3.3ab	5.2ab	6.2ab
	320	4.9a	2.4a	5.4ab	5.9a
	1280	8.8c	3.1ab	3.6a	7.3ab
	LSD(0.05)	2.8	2.3	4.5	3.7
November 2001	0	5.1a	8.1ab	7.4ab	4.6ab
	320	7.1ab	6.7a	5.9a	4.3a
	1280	13.1b	11.2b	9.0c	5.8ab
	LSD(0.05)	7.1	4.1	1.5	3.2

The concentrations of these metals in the grass tissue were high compared to those reported by other investigators. For sewage sludge applied to a field, Buttigieg *et al.* (1989) reported highest values, in mg kg<sup>-1</sup>, of 1.3 for Cr, 5.78 for Ni and 1.55 for Pb in perennial ryegrass. In a perennial ryegrass/white clover sward to which had been applied 0.6 kg ha<sup>-1</sup> Co as CoSO<sub>4</sub>·7H<sub>2</sub>O (Paterson, Klessa and MacPherson, 1989) the highest plant Co reported was 0.77 mg kg<sup>-1</sup> DM, higher than the highest of 0.12 mg kg<sup>-1</sup> reported by Hopkins *et al.* (1994) for a field to which no Co had been applied. The highest Co levels reported by Sherrell (1990) for applications up to 3.15 kg ha<sup>-1</sup>, were

2.76 mg kg<sup>-1</sup> of DM. Tiller (1989) indicated that the transfer of metal to plant depends on the kind of plant, the particular metal and the soil chemical environment. The current results, however, do not present a case against application of the WTR since the grass from the control also had high concentrations. Reported tolerable dietary concentrations for long term feeding to ruminants are Cr (III): 3000, Ni: 50 and Pb: 30 mg kg<sup>-1</sup> DM (Webber *et al.*, 1984; cited by Buttigieg *et al.*, 1989). Since the metal concentrations measured at both field experiments are well below these concentrations, and the DM yields showed no signs of decline, it can be reasonably concluded that the concentrations were neither zootoxic nor phytotoxic.

#### 5.4 Conclusions

From an agricultural point of view, land disposal of the water treatment residue might be deemed unproductive since it did not bring about any noticeable improvements in the growth of the grasses at either field trial site. There is an indication, however, that the WTR might increase yields by increasing plant-available N (See Sections 5.3.4 and 6.3.3). This aspect was, however, not the only or the main issue. It is clearly encouraging from the land disposal (and thus economic viewpoint) that no negative effects on either the perennial ryegrass or tall fescue were in evidence.

The main issue is safe disposal of the material onto land, and to that extent it could be said that the investigated option of land application is appealing. Whether the material is spread on the surface (mulched treatment) or incorporated with the soil did not make any difference to the performance of the grass species. Indeed the successful growth of grass in the mulched treatment was indicative of the possible use of the WTR as a soil substitute.

## CHAPTER 6

### WATER TREATMENT RESIDUE AND CHANGES IN SOME SOIL CHEMICAL PROPERTIES: LABORATORY EXPERIMENTS

#### 6.1 Introduction

Two sets of chemical properties of the water treatment residue are likely to have the greatest impact on soil chemical changes. These are the basic pH and free carbonates, and the extractable cations and soluble solutes (Section 3.3). In Chapter 4 it was shown in a pot experiment how this WTR increased pH in all 5 soils used, and decreased the amount of extractable acidity in the Ia-C and Nb-F1 soils. These effects clearly indicate the liming potential of this material.

When the WTR is applied to soil, dissolution of some of its constituents should be one of the first processes to occur. One effect of this would be an increase in the electrical conductivity of the soil solution, followed by cation exchange reactions involving soluble and extractable cations. One of these exchange reactions is that involving Al and Ca that resulted in the liming effect seen in Chapter 4.

Most of the studies that have been carried out on WTR as reviewed (Chapter 2) have concerned alum materials. Also, except for a few investigations, the liming/pH influence of the WTR has not been an issue. From an environmental point of view, liming might be used to reclaim chemically degraded soils (Logan, 1990) and, as a corollary to that, could prevent chemical degradation of soils. A major agricultural benefit of lime is the amelioration of acid soils. Under controlled conditions, WTR has been found to have different influences on soil pH values with a decrease (Wang *et al.*, 1998), no marked change (Rengasamy *et al.*, 1980) and increases (Elliott and Singer, 1988; Heil and Barbarick, 1989; Ahmed *et al.*, 1997) in this soil property having been reported. In the field Geertsema *et al.* (1994) reported that the WTR (and lime) did not have any significant effects on pH 30 months after application.

These differences in results that at first sight appear contradictory can be explained by considering the following. The alum WTRs used by Wang *et al.* (1998) had low pH values of 3.9 and 5.3. Rengasamy *et al.* (1990) used low rates of the alum WTR with the highest being 20 Mg ha<sup>-1</sup>. This, coupled with the relatively low pH (6.5) of the material and thus probable insignificant quantities of free carbonates, meant that no appreciable pH changes could be expected. On the other hand, Elliott and Singer (1988), Heil and Barbarick (1989) and Ahmed *et al.* (1997) used ferric (pH 9.3), ferric (pH 7.3) and alum (pH 7.45) WTRs, respectively. The corresponding effects were to raise the soil pH values from 5.3 to 8.0 at 8% dry mass application, from 4.7 to 7.0 at 20 g kg<sup>-1</sup>, and from 5.7 to 7.5 at 800 Mg ha<sup>-1</sup>, respectively. If the soil bulk density is assumed to be 1340 kg m<sup>-3</sup> and depth of incorporation 0.15 m, the first two rates would be equivalent to 120 Mg ha<sup>-1</sup> and 50 Mg ha<sup>-1</sup>, respectively.

Although applied to ameliorate acid soils, lime has also been demonstrated to sometimes have undesirable side effects, amongst which are to reduce extractable Mg (Grove, Sumner and Syers, 1981) and to decrease K potential (Wooldridge, 1990). Also of concern is how rapidly, and to what extent, the lime reacts with soils. Because of its slow rate of reaction the Fertilizer Advisory Service of the KwaZulu-Natal Department of Agriculture recommends application of lime about a month before planting; this also assumes that the soil is adequately moist in that period.

Cation exchange reactions, which would definitely occur between the WTR and soils, have been the subject of numerous investigations. Some examples involved creating a homoionic soil by saturating the soil with a particular cation, notably Ca (Singh, Pal and Poonia, 1981; Poonia, Mehta and Pal 1986; Poonia and Niederbudde, 1990; Kumar, Mehta, Grewal and Singh, 1997) before effecting the exchanges by introducing another cation. Other cation exchange reactions have been studied in clay material that had been isolated from the bulk soil (Doula, Ioannou and Dimirkou, 1995; Escudey, Diaz, Foerster and Galindo, 1997). Nissinen, Ilvesniemi and Tanskanen (1998) studied cation exchange reactions in podzolic soils under field conditions.

Cation exchange reactions determine the relative affinity of the competing cations for the soil

adsorption sites (Kumar *et al.*, 1997), and can affect chemical transport in soils (Leij and Dane, 1990). Both of these are of considerable interest to the land disposal of WTR. The soluble products of the cation exchange reactions expected after dissolution would indicate which species are likely to be redistributed or leached. Solubility and redistribution of solutes are critical in determining the agronomic acceptability and environmental influence of the land disposal of the WTR.

Although the WTR investigated in this report has a low amount of free carbonates and relatively low electrical conductivity (Chapter 3), at the quantities that may be applied these might end up at excessive levels. Thus over liming and salinization might result which, from an agronomic point of view, would exclude such application rates. However, as pointed out before, the study is of environmental concern as well, so that the quantities of WTR land-treated would not only be limited by agronomic concerns but also by perceived effects on the environment.

The objectives of this chapter are as follows:

- to establish to what extent the WTR increases pH and reduces acidity in acid soils;
- to monitor WTR reaction with respect to some chemical changes over time;
- to determine the effects of WTR on soil water extracts; and
- to establish the effects of the WTR on extractable basic cations.

## 6.2 Materials and methods

### 6.2.1 Incubation experiment: set-up and monitoring

Eleven of the soils described previously (Section 3.2.2) were used, with the strongly acid Av and Ia-W soils of particular interest to test the liming potential of the WTR. The Nb-A and Nb-F samples of the Namib form was used.

Soil samples (2.5 kg), excluding the Av and Ia-W, were incubated at ambient temperature and field

capacity for 3 months after being treated with WTR at rates equivalent to 0, 40, 80, 120, 320 and 1280 Mg ha<sup>-1</sup>. The highest rate of application was equivalent to 723.20, 699.40, 666.64, 853.36, 613.88, 613.88, 729.36, 618.36 and 677.24 mg kg<sup>-1</sup> for the Hu-F, Hu-M, Hu-T, Ia-C, Nb-A, Nb-F, Sd, Va and We soils, respectively. In order to monitor the WTR reaction, sub-samples were taken during the incubation period, with the first being of the initial dry mixture (Day 1). Other samples were taken as indicated in the results. After air-drying, these samples were analysed for pH (duplicate 10 g samples suspended in 25 mL water for 1 hour). Extractable cations were not measured, since the salt solutions used could confound results by extracting potentially reactive, but as yet not reacted, species (Section 3.3). pH was also measured in 1M KCl (1:2.5 soil: solution ratio for 1 hour), as a monitoring exercise rather than to follow trends.

The experiment using the Av and Ia-W soils was set up after the one with the other nine soils was terminated, and ran for two months. The same rates of WTR were applied but with the addition of rates of 20, 60 and 100 Mg ha<sup>-1</sup>, and dolomitic lime at rates equivalent to 7.5 and 15 Mg ha<sup>-1</sup>. Here the equivalent rates for 1280 Mg ha<sup>-1</sup> were 775.76 and 948.20 mg kg<sup>-1</sup> for the Av and Ia-C soils, respectively. The higher lime level was calculated to reduce the acid saturation to 1%. This 15 Mg ha<sup>-1</sup> corresponded to 9.00 and 11.00 mg kg<sup>-1</sup> for the Av and Ia-W soils, respectively. The calcium carbonate equivalent of the dolomitic lime was 80%. The monitoring procedure was the same as for the nine soils. All treatments were based on the density of the soil sample (determined in the laboratory from mass and volume of sample), and an assumed field incorporation of 150 mm.

### 6.2.2 Extractable cations and cation exchange capacity (CEC)

At the termination of the incubation experiment, duplicate air-dry samples of selected treatments were extracted with 0.1M barium chloride (Gillman, 1979; Section 3.2.3) or 1M potassium chloride (Section 3.2.3). Water extracts were obtained by shaking soil with distilled water in a soil to water ratio of 1:2 (Sonnevelt and Van der Ende, 1971; cited by Rhoades, 1996). This ratio was selected as it is relatively close to a saturation extract but easier to work with, and also because relative changes rather than absolute solute concentrations were needed (Rhoades, 1996). Samples were

analysed for electrical conductivity (EC) and pH (Chapter 3), acidity and Al by titration (Thomas, 1982), Ca, Mg and K (by atomic absorption spectrophotometry), bicarbonate and chloride (United States Salinity Laboratory Staff, 1954), nitrate (by RQflex using nitrate strips), phosphate (Murphy and Riley, 1962) and sulphate by precipitation as barium sulphate (Verma *et al.*, 1977).

The CEC was determined in the Av and Ia-W soils for selected treatments by extracting the soil four times with strontium chloride followed by extraction with ammonium acetate (Hughes and Girdlestone, 1994).

### 6.2.3 Relationship between surface and solution cations

The incubated soil samples treated with 0 and 1280 Mg ha<sup>-1</sup> WTR were used. Duplicate 30 g of each sample were extracted with 60 mL of distilled water three times for 1 hour on an end-over-end shaker, with 50% ethanol washes (60 mL, 10 min) between extractions. The three extracts were analysed separately. Successive extractions were done to get an idea of the long term effects of the WTR, on soluble species and exchangeable cations, after a large quantity of water had passed through. These were preferred to elution studies since water-extractable cations could be related to the corresponding barium chloride-extractable cations. Moreover, the field experiment was expected to provide an indication of solute migration.

To establish the amount of extractable cations corresponding to soluble cations at water extracts 2 and 3, fresh samples were used. Duplicate 10 g samples were, successively, extracted with 20 mL water, washed with 20 mL of 50% ethanol and extracted with 50 mL 0.1M BaCl<sub>2</sub>. The procedure was repeated twice with only the 0.1M BaCl<sub>2</sub> extracts retained for analysis for Al by a pyrocatechol violet colorimetric method (South African Sugar Association Experiment Station procedure; Appendix 4.1) using a UV/visible spectrophotometer, and Ca, K and Mg by atomic absorption spectrophotometry.

The equation on which the relationship is based is essentially that proposed by Vanselow (1932) as

cited by Sposito (1981). The equation is



where Ex represents the exchangeable form, and aq the soluble form of the cation.

The selectivity coefficient from this reaction, referred to as the Vanselow selectivity coefficient (Sposito, 1981) or conditional equilibrium constant (Sumner and Miller, 1996) is defined by

$$K_v = [\text{ExCa}](\text{Mg}^{2+})/[\text{ExMg}](\text{Ca}^{2+}) \dots (6.2)$$

where [ ] denotes concentrations and ( ) denotes activities.

Cation activities were calculated using the Visual Minteq programme (Allison, Brown and Novo-Gradac, 1991).

### 6.3 Results and discussion

#### 6.3.1 pH and acidity changes with time

The results of monitoring the reaction of the WTR are given in Figures 6.1 - 6.9 for the nine soils. There was an increase in pH in both water and KCl as the amount of WTR applied increased. The increase was generally observed in the first 14 days, after which the pH tended to remain fairly constant.

There were some soils and treatments that did not fully follow this general trend. These deviations were not, however, caused by the applied material since the control results were similarly affected. In some cases the pH decreased after reaching a maximum i.e., the Hu-M soil (Figures 6.2a and 6.2b) after 35 days; Hu-T (water pH) after 14 days (Figures 6.3a); Ia-C (water pH) at WTR rates up to 120 Mg ha<sup>-1</sup> after about 35 days (Figures 6.4a); Nb-A (water pH) at all levels of the WTR (Figures



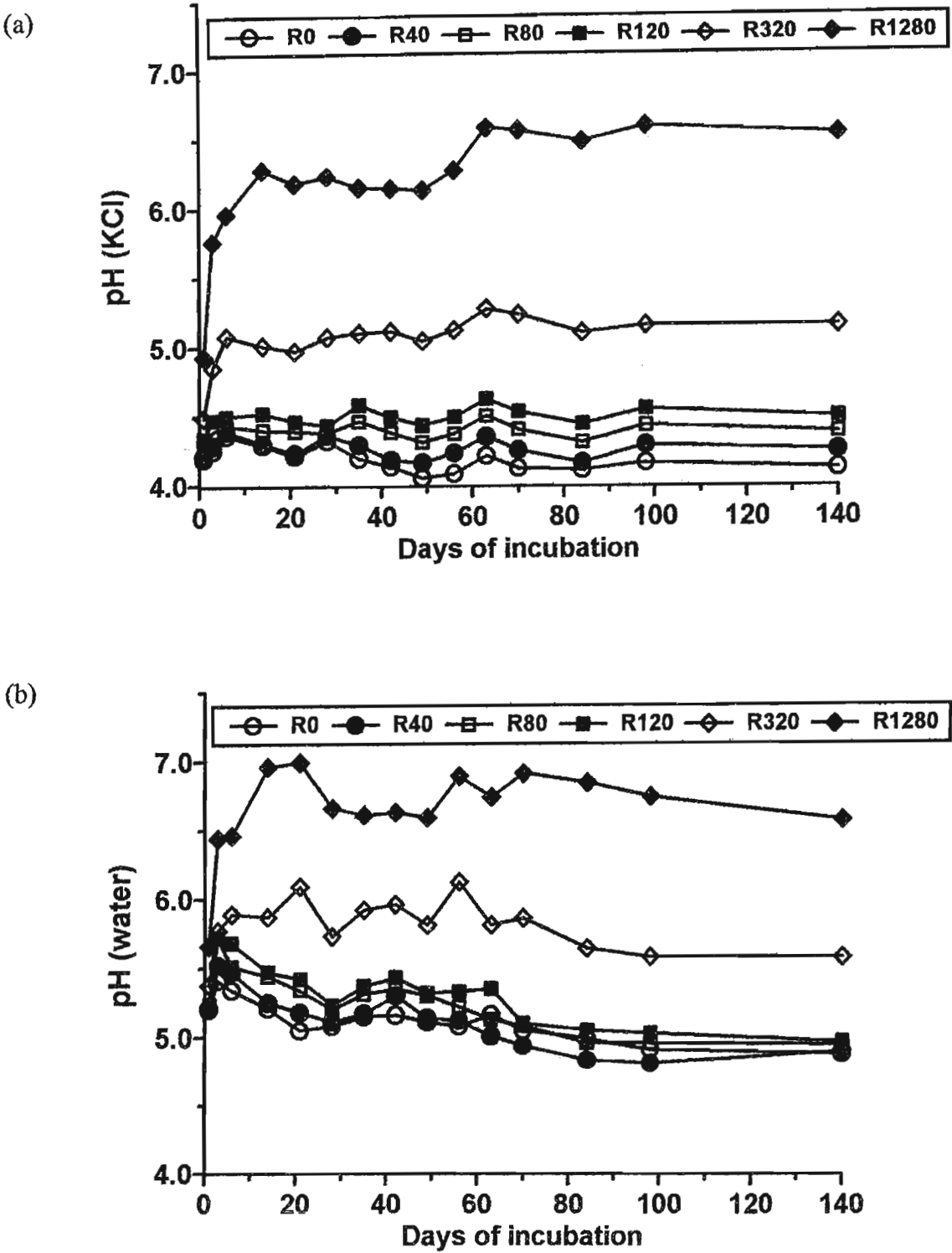
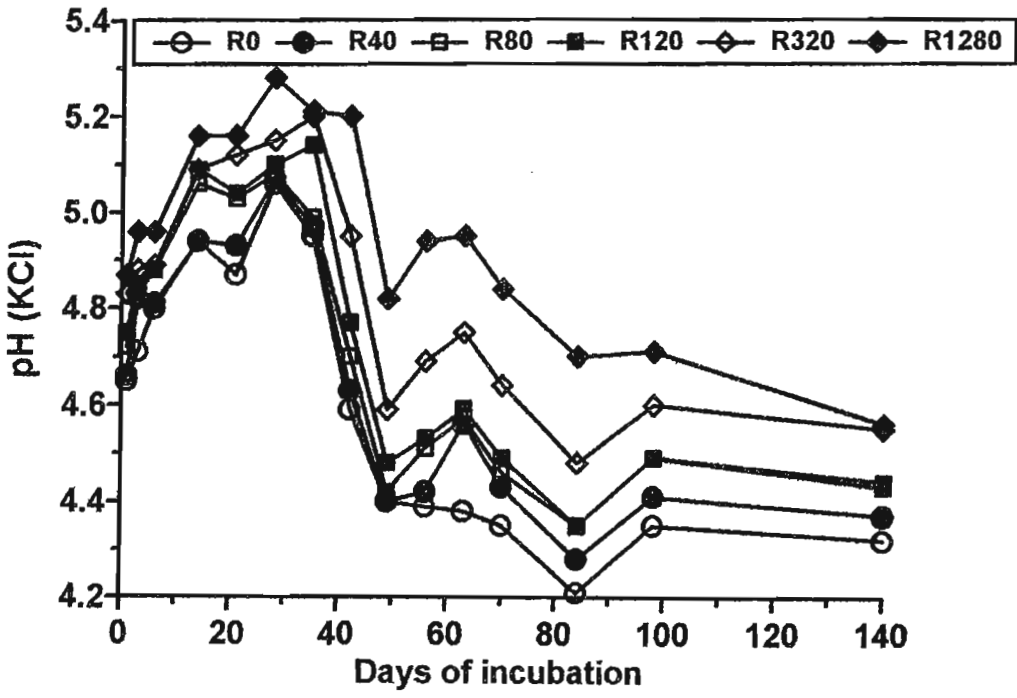


Figure 6.1 Changes in (a) KCl and (b) water pH with time in the Hu-F soil incubated with different rates of water treatment residue (R)

(a)



(b)

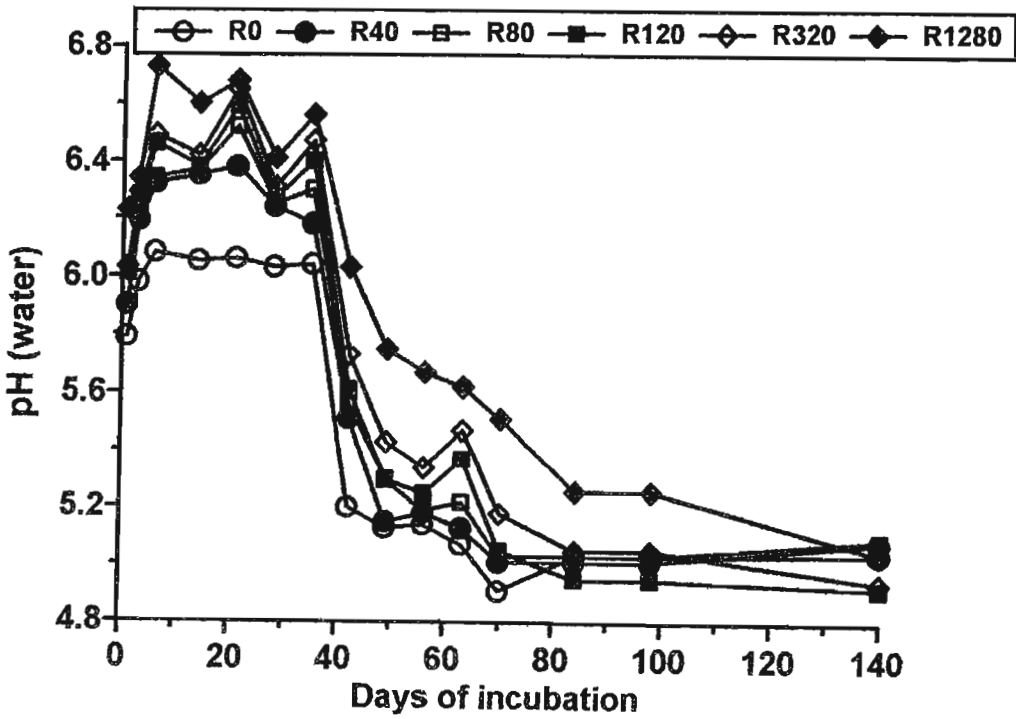


Figure 6.2 Changes in (a) KCl and (b) water pH with time in the Hu-M soil incubated with different rates of water treatment residue (R)

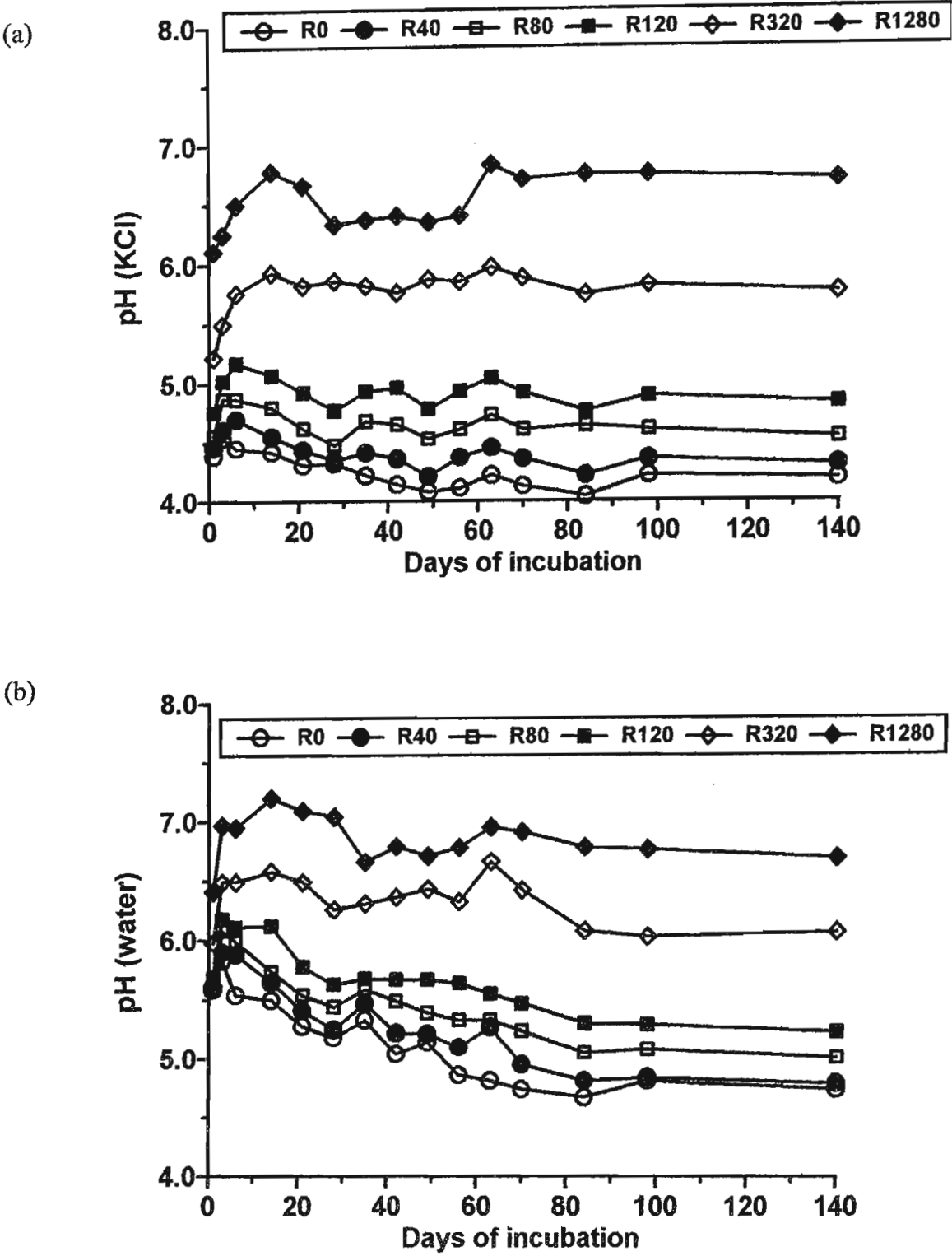


Figure 6.3 Changes in (a) KCl and (b) water pH with time in the Hu-T soil incubated with different rates of water treatment residue (R)

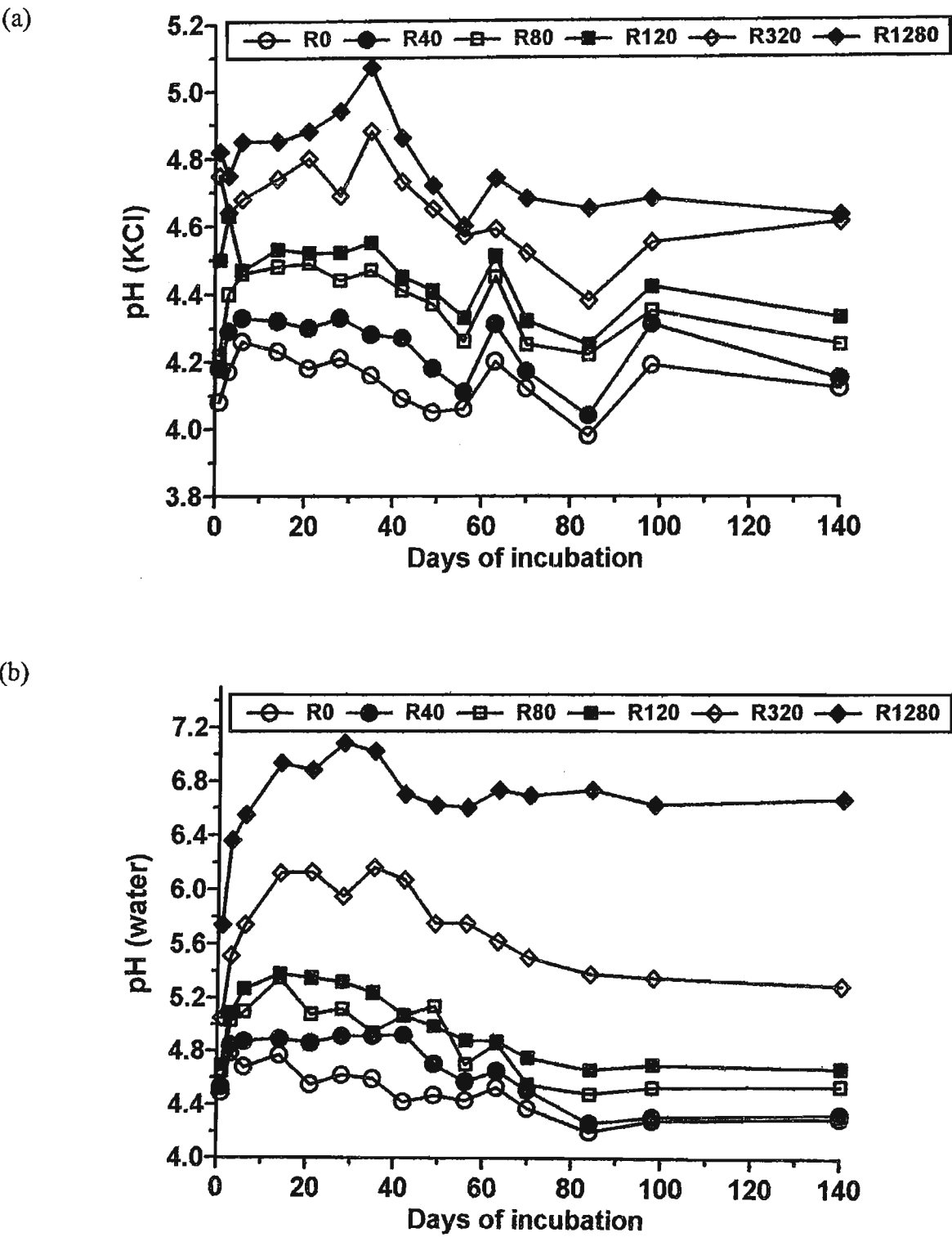


Figure 6.4 Changes in (a) KCl and (b) water pH with time in the Ia-C soil incubated with different rates of water treatment residue (R)

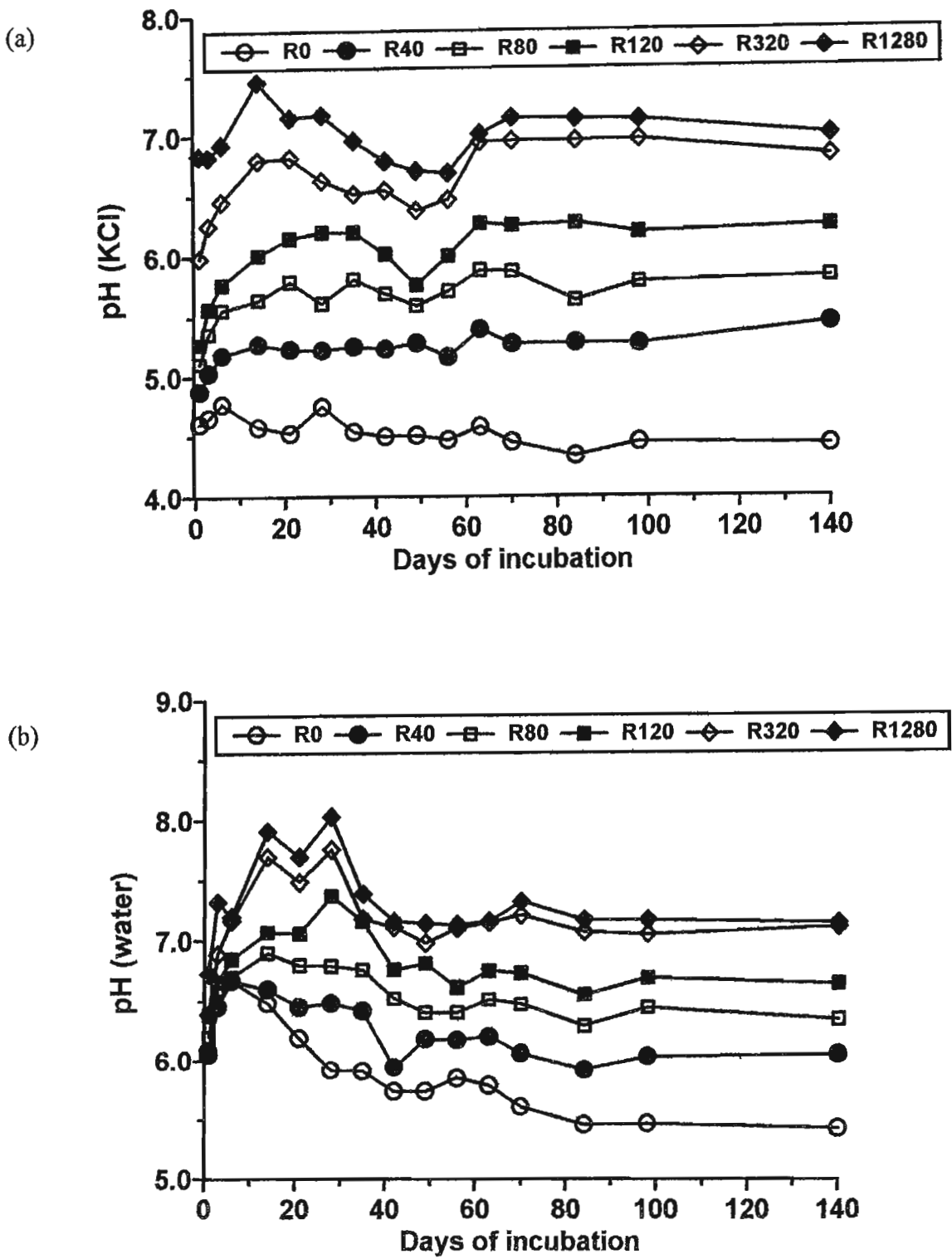


Figure 6.5 Changes in (a) KCl and (b) water pH with time in the Nb-A soil incubated with different rates of water treatment residue (R)

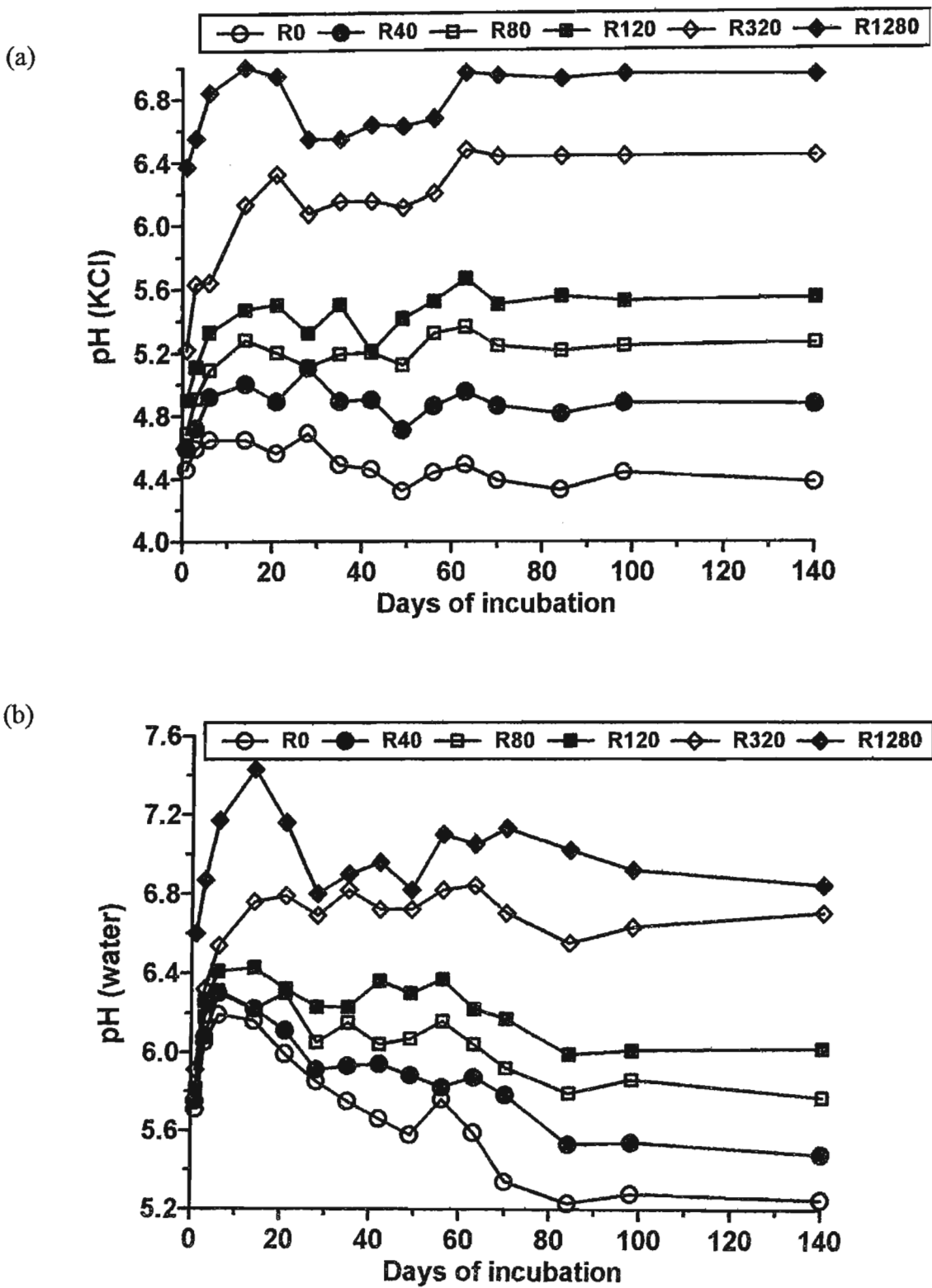


Figure 6.6 Changes in (a) KCl and (b) water pH with time in the Nb-F soil incubated with different rates of water treatment residue (R)

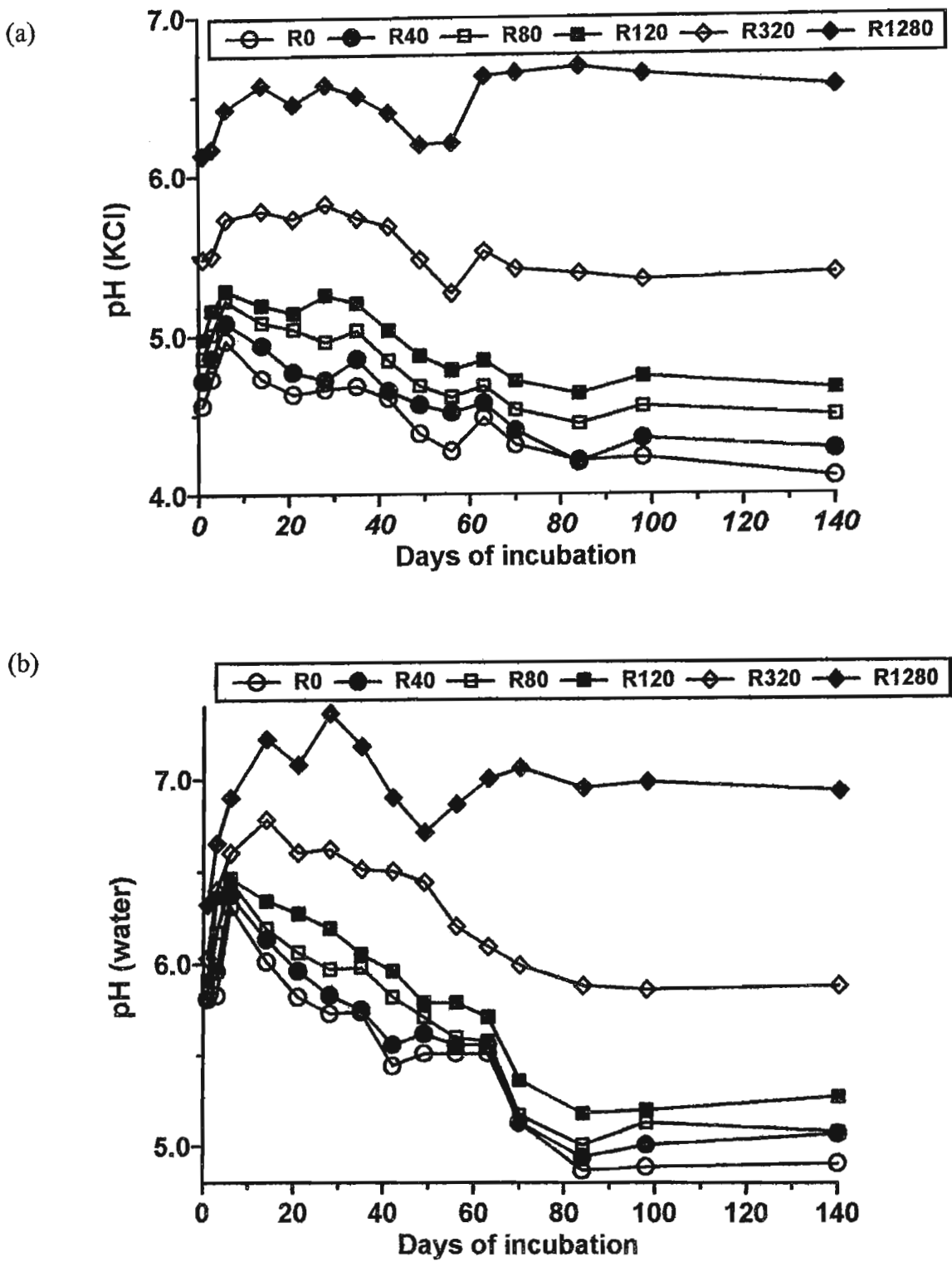


Figure 6.7 Changes in (a) KCl and (b) water pH with time in the Sd soil incubated with different rates of water treatment residue (R)

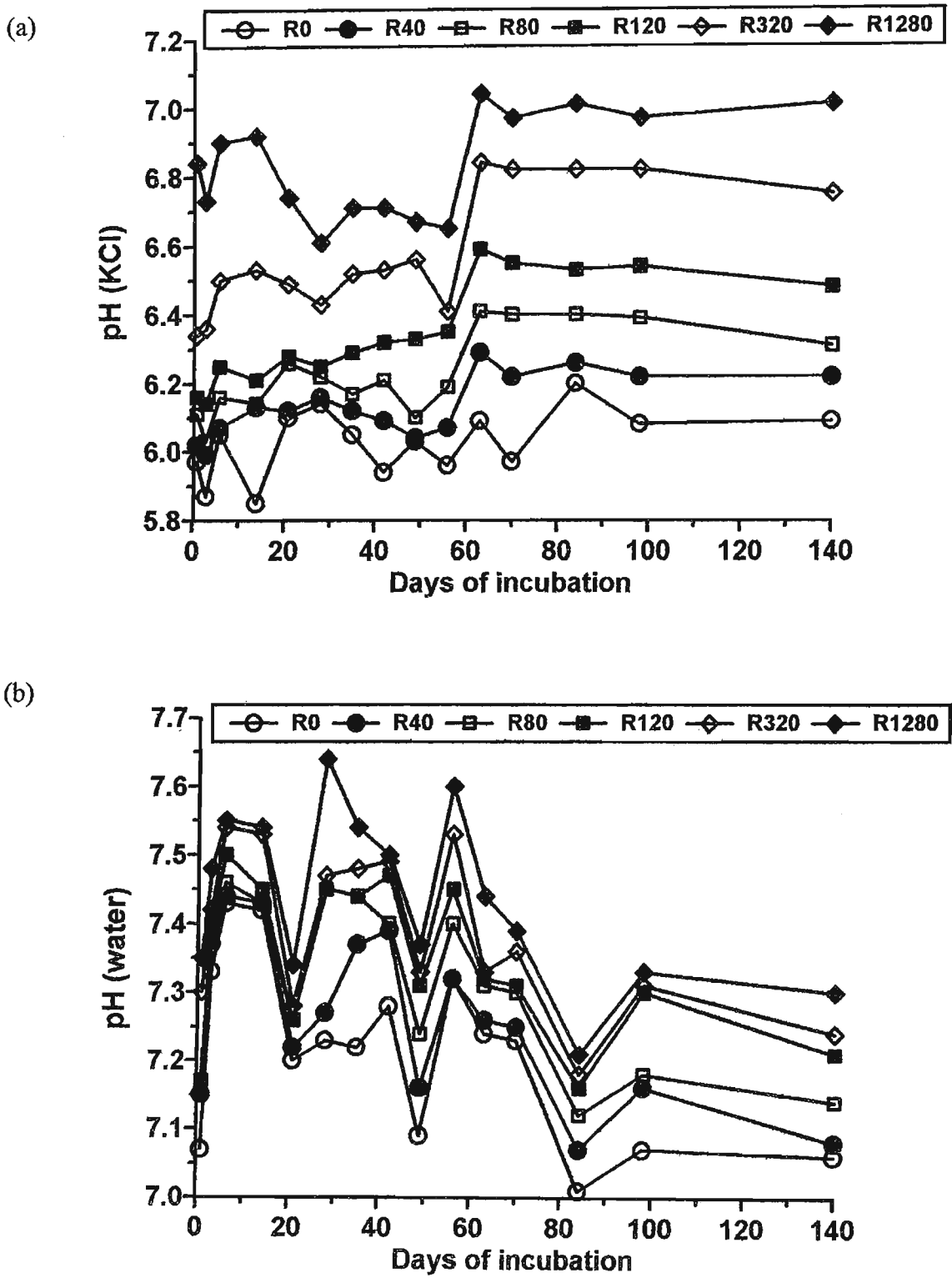


Figure 6.8 Changes in (a) KCl and (b) water pH with time in the Va soil incubated with different rates of water treatment residue (R)



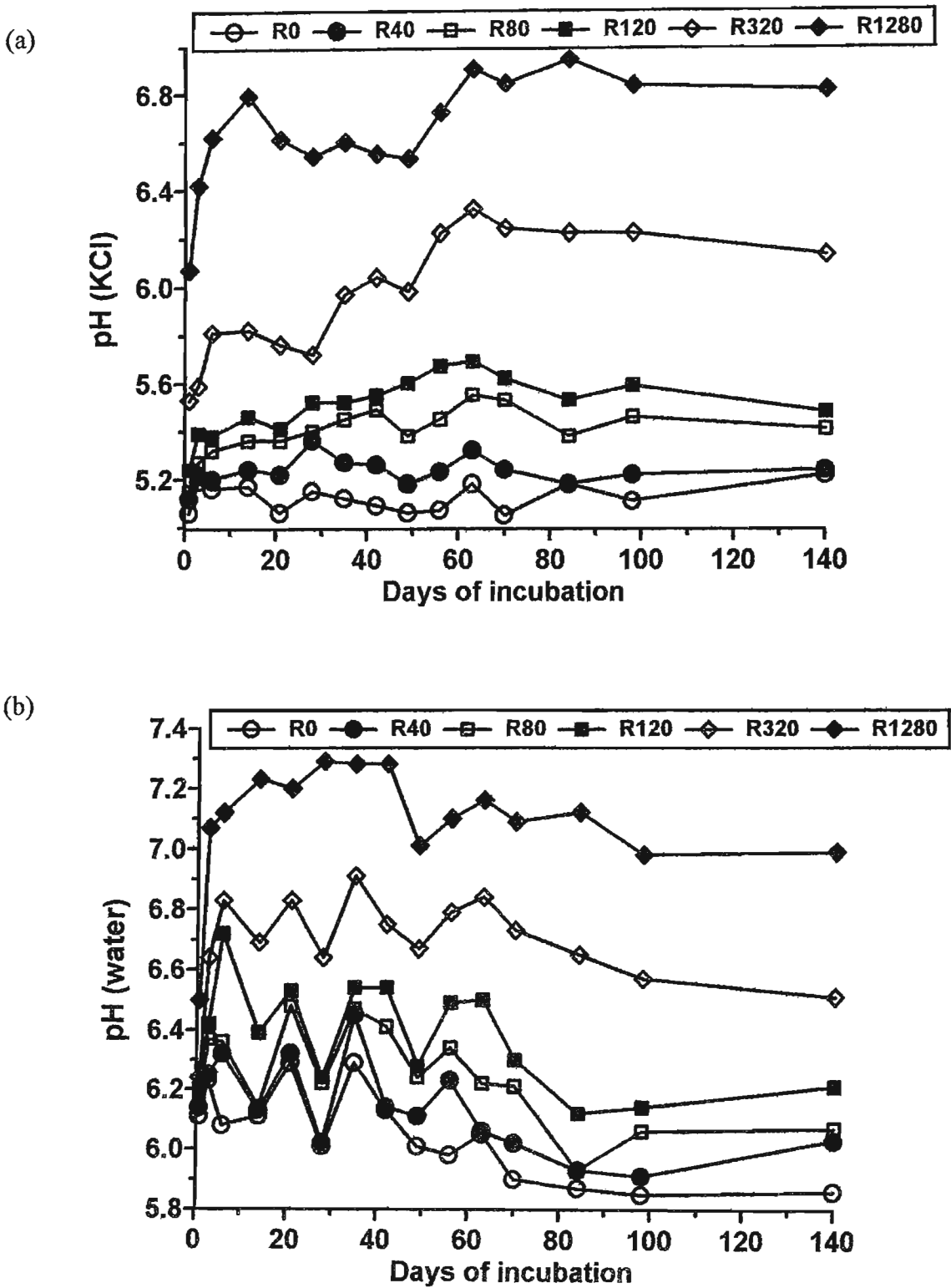


Figure 6.9 Changes in (a) KCl and (b) water pH with time in the We soil incubated with different rates of water treatment residue (R)

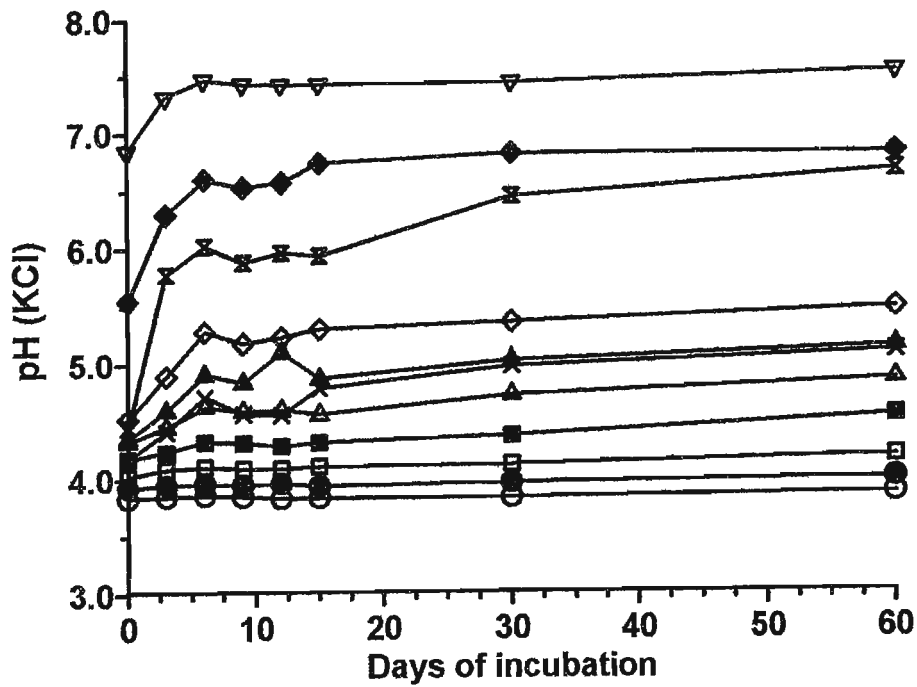
6.5a); Nb-F (water pH) at WTR levels  $< 320 \text{ Mg ha}^{-1}$  (Figures 6.6a); Sd (water pH) at all levels of the WTR (Figures 6.7a); Sd (KCl pH) at WTR levels  $< 320 \text{ Mg ha}^{-1}$ ; and We (pH water) where the WTR was applied at rates  $< 320 \text{ Mg ha}^{-1}$ . In the Va soil the pH did not show any clear response to the WTR over time (Figures 6.9a and 6.9b) although the pH measured in both water and KCl did increase with increase in the application rate of the WTR.

These somewhat aberrant results occurred in samples where pH was measured in water. It is possible therefore that the poorly buffered water suspensions were subject to a decrease in pH on absorbing atmospheric carbon dioxide. Also at the relatively low rates of application where the decrease in pH was mostly observed, the WTR probably did not supply enough soluble salts to resist the carbon dioxide influence.

In the Av (Figures 6.10a and 6.10b) and Ia-W (Figures 6.11a and 6.11b) soils, the maximum pH was reached after 6 days for both the lime and the WTR treatments. Comparing these results with those of the other nine soils, it appears that liming materials react faster where pH is initially lower, although a direct comparison is not possible as the experiments were conducted at different times and therefore at possibly different ambient temperatures.

Potassium chloride extractable acidity was also fairly constant in both soils after Day 6 for rates up to  $100 \text{ Mg ha}^{-1}$  in the Av soil (Table 6.1) and  $120 \text{ Mg ha}^{-1}$  in the Ia-W soil (Table 6.2). The lime (L1 rate) also behaved similarly. For the WTR rates higher than those mentioned above for the respective soils, and for the L2 rate of lime, the reaction was completed in an even shorter time. These results are comparable to those of Osei (1995) where, studying the effects of analytical grade calcium carbonate in acid soils under laboratory conditions, the highest pH was reached in 10 days and exchangeable Al was eliminated in 7 days.

(a)



(b)

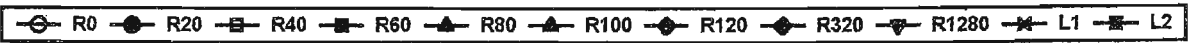
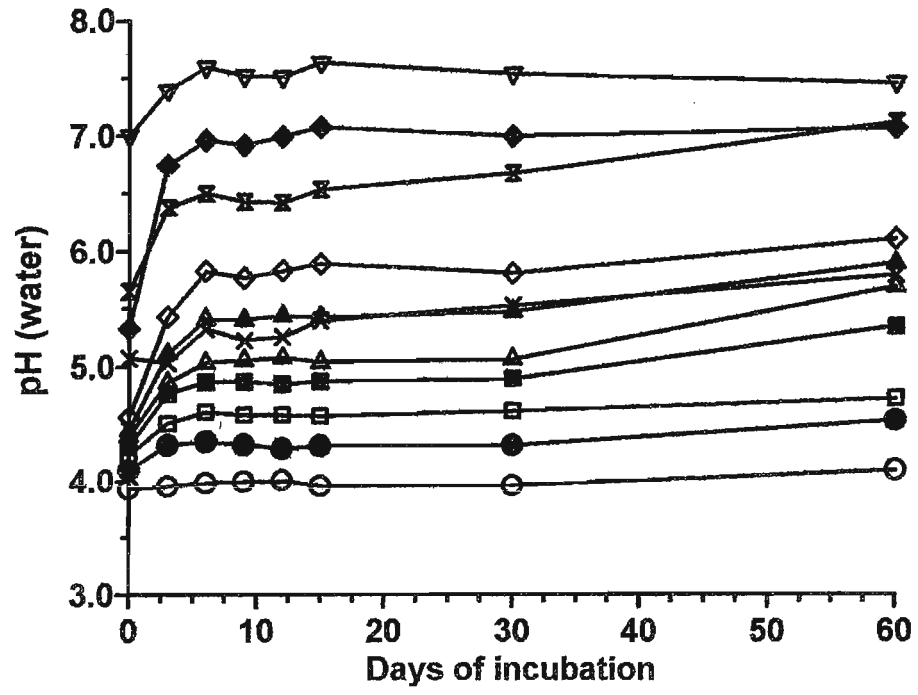


Figure 6.10 Changes in (a) KCl and (b) water pH with time in the Av soil incubated with different rates of water treatment residue (R) and lime (L)

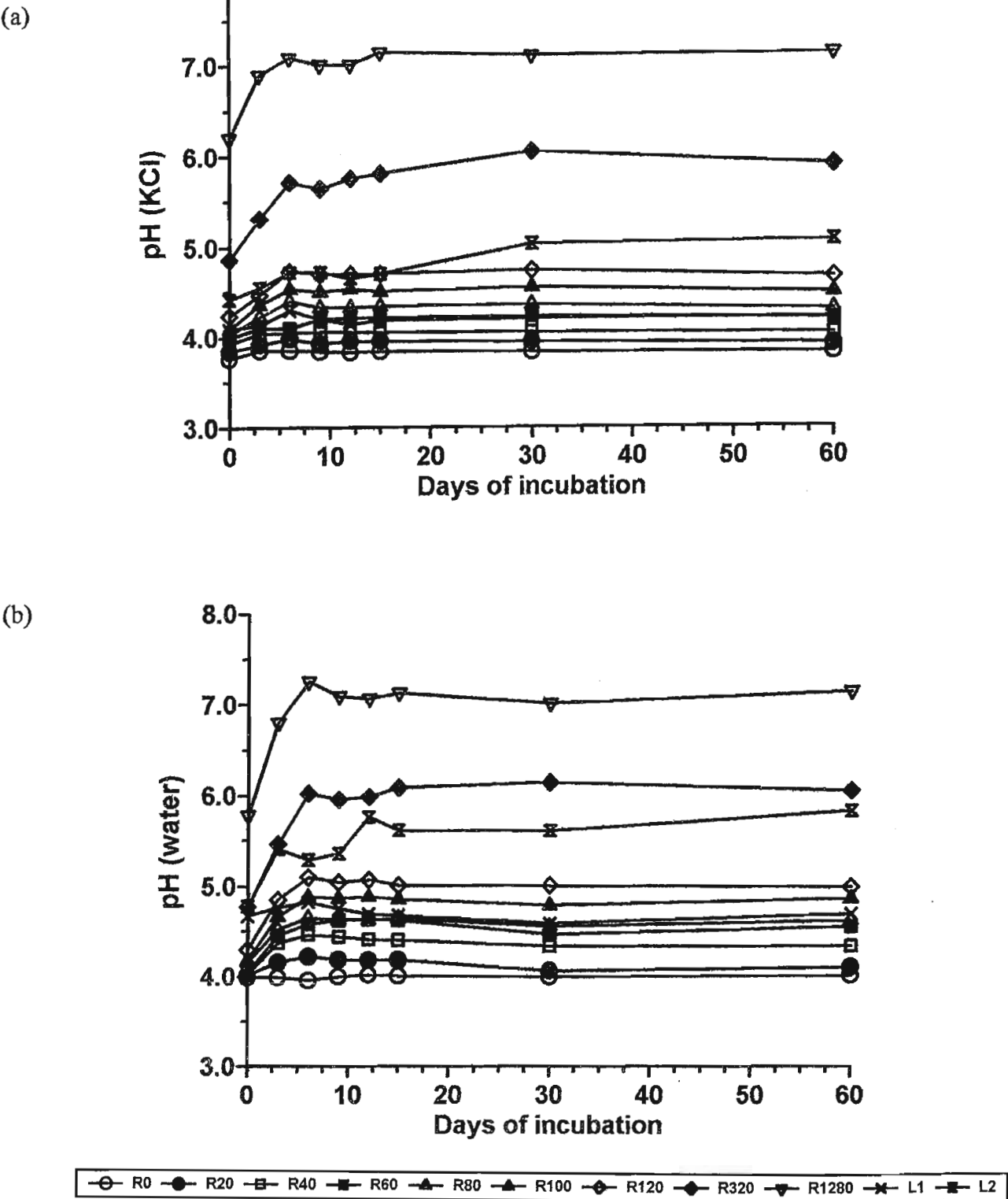


Figure 6.11 Changes in (a) KCl and (b) water pH with time in the Ia-W soil incubated with different rates of water treatment residue (R) and lime (L)

**Table 6.1** Changes in extractable acidity ( $\text{cmol}_c \text{kg}^{-1}$ ) with time in the Av soil incubated with water treatment residue or lime over 60 days

Day	Water treatment residue (Mg ha <sup>-1</sup> )								Lime (Mg ha <sup>-1</sup> )		
	0	20	40	60	80	100	120	320	1280	7.5	15
1	3.80	2.96	2.04	1.53	0.87	0.78	0.44	0.05	1.92	1.92	0.94
3	3.65	2.35	1.40	0.74	0.31	0.19	0.09	0.03	0.54	0.54	0.40
6	3.74	2.18	1.00	0.42	0.12	0.07	0.05	0.04	0.16	0.16	0.02
9	3.52	2.25	1.10	0.48	0.15	0.07	0.06	0.04	0.24	0.24	0.03
12	3.42	2.14	1.14	0.52	0.16	0.08	0.05	0.04	0.26	0.26	0.03
15	3.63	2.23	1.10	0.46	0.17	0.08	0.04	0.03	0.12	0.12	0.02
30	3.72	2.09	1.11	0.38	0.11	0.06	0.05	0.03	0.09	0.09	0.02
60	3.64	2.00	0.89	0.18	0.07	0.06	0.04	0.03	0.03	0.03	0.02

**Table 6.2** Changes in extractable acidity ( $\text{cmol}_c \text{kg}^{-1}$ ) with time in the Ia-W soil incubated with water treatment residue or lime over 60 days

Day	Water treatment residue (Mg ha <sup>-1</sup> )								Lime (Mg ha <sup>-1</sup> )		
	0	20	40	60	80	100	120	320	1280	7.5	15
1	3.80	3.18	2.58	2.14	1.94	1.54	0.91	0.12	0.04	2.11	0.94
3	3.66	2.58	1.70	1.21	0.81	0.46	0.35	0.09	0.00	1.50	0.38
6	3.66	2.31	1.45	0.83	0.46	0.26	0.18	0.09	0.00	1.10	0.24
9	3.86	2.66	1.46	1.02	0.62	0.36	0.22	0.09	0.00	1.16	0.24
12	4.00	2.23	1.44	0.74	0.50	0.25	0.22	0.06	0.00	1.14	0.21
15	3.47	2.22	1.36	0.70	0.45	0.27	0.17	0.08	0.00	1.03	0.18
30	3.63	2.44	1.46	0.74	0.47	0.23	0.14	0.08	0.00	0.82	0.04
60	3.96	2.70	1.42	0.88	0.52	0.27	0.17	0.06	0.00	0.82	0.06

### 6.3.2 Extractable cations and cation exchange capacity

As expected, since the WTR contains a high amount of extractable Ca and appreciable contents of Mg (Section 3.3), the salt extractable forms of these cations in the nine soils increased with increasing application rate (Table 6.3a). Results for the Av and Ia-W soils are given in Table 6.3b. Potassium and Na (results not shown) were both unaffected and were in low concentrations throughout ( $< 0.5 \text{ cmol}_c \text{kg}^{-1}$ ).

Just like lime, the WTR increased extractable Ca and Mg whilst reducing acidity and Al (Table

6.3b). The observed decrease in acid saturation was thus due to both an increase in the basic cations and a decrease in acidic cations.

In the Av soil an acid saturation of about 20% (21.5%) was achieved at about 40 Mg ha<sup>-1</sup> of applied WTR and at pH values of 4.83 (H<sub>2</sub>O) and 4.27 (KCl) (Table 6.3b. The comparable values for Ia-W soil were 60 Mg ha<sup>-1</sup> of WTR and pH values 4.60 (H<sub>2</sub>O) and 4.24 (KCl). Thus the Ia-W soil, with appreciably higher organic matter content that contributes to buffering, needed a higher rate of WTR to reach similar pH values and acid saturation. The lower lime level in the Ia-W soil gave an acid saturation of 16% at a pH of 5.33 (H<sub>2</sub>O) and 4.33 (KCl), the water value being notably higher than that of the comparative WTR application rates. If lime and the WTR are compared with respect to pH (H<sub>2</sub>O), then in the Av soil the lower lime level gave the values of a WTR rate between 120 and

**Table 6.3a** Calcium and magnesium extracted with barium chloride from nine incubated soils at selected rates of water treatment residue (Mg ha<sup>-1</sup>)

Soil	Calcium (cmol <sub>c</sub> kg <sup>-1</sup> )				Magnesium (cmol <sub>c</sub> kg <sup>-1</sup> )			
	0	80	320	1280	0	80	320	1280
Hu-F	5.04	6.48	7.03	8.77	1.94	2.19	2.41	2.77
Hu-M	4.97	5.27	5.46	5.91	3.29	3.41	4.09	4.71
Hu-T	2.36	2.68	5.65	10.60	1.48	1.63	1.79	3.41
Ia-C	1.99	2.22	6.46	11.76	0.91	1.57	1.65	3.33
Nb-A	0.81	1.43	2.55	5.13	0.58	0.63	0.72	1.75
Nb-F	1.65	2.16	4.55	8.46	0.56	0.60	0.77	3.24
Sd	4.78	6.74	8.24	8.34	4.76	5.04	5.90	6.78
Va	4.69	5.35	7.21	8.80	2.53	2.80	3.43	3.54
We	4.91	7.11	8.09	8.90	2.82	3.02	3.25	3.38

320 Mg ha<sup>-1</sup> and between 100 and 120 Mg ha<sup>-1</sup> for the pH (KCl). In the Ia-W soil the corresponding values were again between 120 and 320 Mg ha<sup>-1</sup> for pH (H<sub>2</sub>O) and about 80 Mg ha<sup>-1</sup> for pH (KCl). So different results are obtained by using acid saturation or pH to compare the liming potential of the WTR with that of the lime in terms of equivalent application rates of WTR.

pH values for lime (Table 6.3b) were interpolated in a pH vs WTR application rate graph (results

not shown) to get amount of WTR equivalent to a respective level of lime. The following results were obtained, incorporating also the 80% effectiveness of the lime and the 3.8% active calcium carbonate in the WTR:-

In the Av soil the water pH values of 6.26 for L7.5 (6.0 Mg ha<sup>-1</sup> at 80% effectiveness) and L15 (12.0 Mg ha<sup>-1</sup> at 80% effectiveness) give WTR rates of 162.5 and 655 Mg ha<sup>-1</sup>, respectively. The corresponding amounts of calcium carbonate contained by these rates at 3.8% are 6.2 and 24.9 Mg ha<sup>-1</sup>. The corresponding rates of WTR in the Ia-W for soil pH values of 5.33 and 5.90 are 170 and 305 Mg ha<sup>-1</sup>. The active calcium carbonate content in 170 and 305 Mg ha<sup>-1</sup> of WTR is 6.5 and 11.6 Mg ha<sup>-1</sup>, respectively. Except for the higher level of lime in the Av soil, where some error might have occurred in the pH measurement, the calcium carbonate equivalents between the WTR and lime are in reasonable agreement. It can also be reported here that the potassium chloride pH values did not show this calcium carbonate relationship.

Cation exchange capacity in the Av and Ia-W soils increased with increase in amount of WTR or lime applied (Table 6.3b). This is testimony to the significant presence of constituents with variable charge surfaces in these two soils, although the WTR could have contributed its own CEC (see Table 3.1b).

### 6.3.3 Water extracts

Results of water extractable ions (Tables 6.4a and b) showed a similar trend to that of salt extractable cations for Ca and Mg. For the lime treatment, the concentrations are very low, with Ca and Mg amounts being equivalent to those of between 0 and 80 Mg ha<sup>-1</sup> of applied WTR. This was expected since in these variable charge soils the increase in pH will have created negative charges that attracted Ca and Mg to the surfaces of soil colloids thus reducing their solubility. The data from Tables 6.4a and b also show that there is an increase in chloride and nitrate with addition of the WTR. The chloride results could be expected since the WTR contains significant quantities of this element (Section 3.3). Nitrate, however, was not expected to increase since both Kjeldahl and soluble forms were low (Section 3.3). If the nitrate originated from the soil, then the increase could

have been through supply of moisture, or pH amelioration that increased the activity of mineralizing microorganisms. If this was the case, then the Nb-A and Nb-F soils, with low contents of organic matter, should have shown little response. Results in Table 6.4a, however, show that the nitrate levels increased by between seven and ten times at the highest rate of WTR in these soils. If an increase in pH was the cause, then the higher nitrate levels would have been observed only in the Av and Ia-W soils which had low initial pH values; again, this was not the case. Also against the role of pH was the fact that lime did not increase the nitrate levels compared to the control.

**Table 6.3b** Some selected chemical properties in the Av and Ia-W soils incubated with different rates of water treatment residue (R) and lime (L)

Soil	Treatment	pH (H <sub>2</sub> O)	pH (KCl)	Acidity	Al	Ca	Mg	CEC	Acid saturation
	(Mg ha <sup>-1</sup> )					(cmol <sub>c</sub> kg <sup>-1</sup> )			(%)
Av	R0	4.13	3.95	3.45	2.93	0.49	0.13	1.1	84.7
	R20	4.51	4.02	1.91	1.58	1.94	0.33	nd	45.7
	R40	4.83	4.27	0.86	0.59	2.68	0.47	nd	21.3
	R60	5.32	4.67	0.14	0.14	3.43	0.63	nd	3.3
	R80	5.66	4.94	0.06	0.13	3.93	0.77	1.1	1.3
	R100	5.86	5.22	0.05	0.06	5.06	0.89	nd	0.8
	R120	6.07	5.55	0.04	0.03	5.34	0.93	nd	0.6
	R320	6.80	6.87	0.03	0.01	8.26	1.23	1.9	0.3
	R1280	7.36	7.48	0.00	0.00	10.34	2.89	4.0	0.0
	L7.5	6.26	5.43	0.02	0.00	2.40	2.50	1.4	0.4
	L15	7.07	6.77	0.01	0.00	3.46	3.31	1.7	0.2
Ia-W	R0	3.83	3.84	3.89	3.35	0.41	0.18	1.5	86.8
	R20	4.16	3.97	2.63	1.85	1.71	0.41	nd	55.4
	R40	4.41	4.13	1.57	0.77	2.67	0.71	nd	31.7
	R60	4.60	4.24	0.86	0.42	2.93	0.85	nd	18.5
	R80	4.73	4.35	0.55	0.27	4.77	0.94	1.4	8.8
	R100	4.91	4.58	0.25	0.12	5.49	1.15	nd	3.6
	R120	5.01	4.67	0.17	0.07	6.43	1.33	nd	2.1
	R320	5.94	5.90	0.05	0.02	10.39	2.06	2.1	0.4
	R1280	6.91	7.16	0.00	0.00	13.13	3.00	5.4	0.0
	L7.5	5.33	4.33	0.84	0.49	2.27	2.27	1.7	16.0
	L15	5.90	5.39	0.05	0.0	3.41	3.41	1.9	0.7

nd=not determined



**Table 6.4a** Some water extractable solutes in nine incubated soils at selected rates of water treatment residue (R)

Soil	Treatment (Mg ha <sup>-1</sup> )	Ca	Mg (cmol <sub>c</sub> L <sup>-1</sup> )	Cl	NO <sub>3</sub>
Hu-F	R0	0.24	0.14	0.06	0.40
	R80	1.27	0.17	0.08	0.44
	R320	1.53	0.20	0.13	0.53
	R1280	2.51	0.36	0.35	1.08
Hu-M	R0	0.27	0.42	0.04	0.11
	R80	0.30	0.47	0.04	0.97
	R320	0.33	0.45	0.04	0.97
	R1280	0.39	0.42	0.07	0.97
Hu-T	R0	0.15	0.16	0.04	0.35
	R80	0.20	0.18	0.06	0.59
	R320	0.33	0.22	0.15	0.62
	R1280	1.16	0.47	0.48	1.03
Ia-C	R0	0.27	0.27	0.07	0.91
	R80	0.54	0.30	0.09	1.25
	R320	0.71	0.40	0.15	1.37
	R1280	1.38	0.43	0.48	1.71
Nb-A	R0	0.02	0.03	0.08	0.09
	R80	0.07	0.08	0.10	0.15
	R320	0.22	0.12	0.12	0.35
	R1280	0.99	0.28	0.26	1.06
Nb-F	R0	0.04	0.03	0.06	0.09
	R80	0.14	0.08	0.10	0.12
	R320	0.27	0.12	0.14	0.28
	R1280	1.01	0.28	0.31	0.63
Sd	R0	0.27	0.20	0.00	0.05
	R80	0.44	0.32	0.12	0.72
	R320	0.68	0.37	0.22	0.73
	R1280	0.85	0.45	0.23	0.76
Va	R0	0.05	0.05	0.08	0.08
	R80	0.17	0.39	0.11	0.22
	R320	0.31	0.58	0.15	0.47
	R1280	0.97	0.78	0.34	0.70
We	R0	0.02	0.02	0.09	0.01
	R80	0.58	0.12	0.15	0.31
	R320	1.33	0.19	0.20	0.48
	R1280	1.50	0.37	0.30	0.66

**Table 6.4b** Some water extractable solutes in Av and Ia-W soils incubated with different rates of water treatment residue (R) and lime (L)

Soil	Treatment (Mg ha <sup>-1</sup> )	Ca	Mg (cmol <sub>c</sub> L <sup>-1</sup> )	Cl	NO <sub>3</sub>
Av	R0	0.17	0.05	0.06	0.15
	R80	0.39	0.09	0.13	0.21
	R320	1.09	0.20	0.35	0.44
	R1280	1.54	0.45	0.64	0.67
	L7.5	0.18	0.32	0.07	0.17
	L15	0.25	0.44	0.11	0.19
Ia-W	R0	0.09	0.08	0.05	0.35
	R80	0.43	0.15	0.20	0.44
	R320	1.30	0.36	0.55	0.75
	R1280	2.49	0.61	0.74	1.16
	L7.5	0.14	0.40	0.03	0.04
	L15	0.16	0.50	0.06	0.05

To clarify whether the increase in nitrate levels with applied WTR was a function of time, non-incubated soil-WTR and soil-lime mixtures of all eleven soils were compared with the incubated soils. These results (Table 6.5) show that incubation increased water extractable nitrate, and that untreated soils also released nitrate with time. Some of the water extractable nitrate came from the soil, but the majority came from the WTR. The incubated Nb-A soil, for example, released only 0.03 cmol<sub>c</sub> L<sup>-1</sup> of nitrate, but when mixed with the lowest rate of the WTR (80 Mg ha<sup>-1</sup>) four times as much nitrate was released. From all this, it can be deduced that on incubation with soil, the WTR releases nitrate with time. This is probably through mineralization of its own organic constituent(s), followed by nitrification. The possibility of initial soil inorganic ammonium being a nitrate source is rejected because it is only the WTR-treated soils which experienced these nitrate increases; the control and lime-treated soils did not, the latter thus ruling out pH as a major factor in the results (as suggested above). The possibility of the highly mobile nitrate moving with percolating soil water raises concern on the possibility of ground water pollution by this species. This issue is addressed in Chapter 7.

Bicarbonate, phosphate and sulphate could not be detected by the analytical methods used. Similarly, amounts of K and Na were either very low or undetectable. Calcium, Mg, Cl and  $\text{NO}_3$  were thus the dominant and thus most significant ions in the water extracts.

It is noted that for some soils and treatments (Tables 6.4a and b), the sum of cations and anions are not the same as should be expected. A possible reason is the inadequacy of the analytical methods used, especially for bicarbonate and sulphate.

#### 6.3.4 Successive barium chloride and water extracts

Except for pH, all other properties of water extracts, i.e., electrical conductivity, Ca, Mg, Cl and  $\text{NO}_3$  decreased with increase in number of extractions as expected (Table 6.6). These observations are true for all soils and the two application rates of the WTR considered, i.e., 0 and  $1280 \text{ Mg ha}^{-1}$ . Since it is observed in the control as well, the increase in pH with increasing number of extractions is not solely caused by the introduction of the basic WTR. This increase was observed in the strongly acid Av and Ia-W soils as well, where the water extractions would be expected to favour removal of Ca and Mg whilst facilitating the adsorption of Al, which would then reduce pH. Water-extractable Al was indeed analytically detectable only in the first extraction at the 0 rate of WTR in both soils, being  $0.14$  and  $0.38 \text{ cmol}_e \text{ kg}^{-1}$  ( $0.07$  and  $0.19 \text{ cmol}_e \text{ L}^{-1}$ ) in the Av and Ia-W soils, respectively.

Breakthrough pH curves of acid soils treated with Ca-saturated coal-derived organic products showed a progressive decrease in pH which passed through a minimum before steadily increasing (Noble, Randall and James, 1995). This pH behaviour was reportedly caused by the ionic strength, which had an inverse relationship to the pH. In the column-leaching work of Smith, Goh, Bond and Freney (1995), calcium chloride and phosphogypsum as eluents produced curves where pH showed a decline with increase in volume of leachate. On the other hand, where calcium citrate and calcium fulvate were eluents, pH increased with increase in the leachate volume (Smith *et al.*, 1995). The explanation for the pH increase was a ligand exchange reaction between citrate or fulvate anions and

**Table 6.5** Water extractable nitrate (cmol<sub>c</sub>L<sup>-1</sup>) in incubated and non-incubated soils mixed with water treatment residue (R) or lime (L) at different rates (Mg ha<sup>-1</sup>)

Soil	Non-incubated						Incubated					
	R0	R80	R320	R1280	L7.5	L15	R0	R80	R320	R1280	L7.5	L15
Av	0.11	0.11	0.09	0.07	0.10	0.11	0.19	0.24	0.45	0.92	0.11	0.12
Hu-F	0.09	0.11	0.12	0.11	na	na	0.07	0.37	0.69	0.98	na	na
Hu-M	0.03	0.03	0.03	0.03	na	na	0.24	0.43	0.67	0.73	na	na
Hu-T	0.00	0.00	0.00	0.00	na	na	0.40	0.70	0.95	1.57	na	na
Ia-C	0.30	0.58	0.69	0.74	na	na	0.96	1.09	1.17	1.40	na	na
Ia-W	0.07	0.07	0.06	0.05	0.06	0.06	0.32	0.40	0.79	1.29	0.29	0.32
Nb-A	0.00	0.00	0.00	0.00	na	na	0.03	0.14	0.32	0.71	na	na
Nb-F	0.00	0.00	0.01	0.02	na	na	0.01	0.61	0.73	0.76	na	na
Sd	0.00	0.00	0.00	0.00	na	na	0.03	0.60	0.67	0.83	na	na
Va	0.00	0.00	0.00	0.00	na	na	0.12	0.15	0.28	0.72	na	na
We	0.04	0.04	0.06	0.12	na	na	0.01	0.17	0.26	0.38	na	na

na=treatment not applied

hydroxyl ions to release these basic anions into solution. In the work of both Noble *et al.* (1995) and Smith *et al.* (1995) there was no report on the control treatments. Gillman, Burkett and Coventry (2001) also reported an increase in leachate pH of eluted soils after incubation with basalt dust. Small increases in soil pH after leaching were also observed in control experiments (Gillman *et al.*, 2001), as happened in the subsequent water extracts in the current study. Thomas (1996) presented evidence that the pH of a particular soil increases with increase in the water to soil ratio. In other words, as the soil solution becomes more dilute (more water compared to soil), the pH increases. As the repeated extractions used here dilute the soil solution, the pH results in the current study seem to subscribe in part to this principle of soil: solution ratio. As is reported above, an increase in ionic strength reduces pH (Noble *et al.*, 1997), then apparently a decrease in ionic strength by dilution has the effect of increasing the pH. The re-adsorption of Al because of dilution probably reduces its extent of hydrolysis, with consequently less hydrogen ions released.

Amounts of Ca and Mg extracted with BaCl<sub>2</sub> also decrease with each successive extraction, the

**Table 6.6** Some chemical properties of successive barium chloride and water extracts of the soils treated with water treatment residue (WTR) at rates of 0 and 1280 Mg ha<sup>-1</sup>

Soil	WTR (Mg ha <sup>-1</sup> )	Extr. no.	H <sub>2</sub> O extracts						BaCl <sub>2</sub> extracts	
			EC	pH	Ca	Mg	Cl	NO <sub>3</sub>	Ca	Mg
			(dS m <sup>-1</sup> )			(cmol <sub>c</sub> kg <sup>-1</sup> )			(cmol <sub>c</sub> kg <sup>-1</sup> )	
Av	0	1	0.29	4.44	0.10	0.01	0.02	0.04	0.42	0.03
		2	0.07	4.58	0.02	0.00	0.00	0.00	0.34	0.02
		3	0.03	4.82	0.02	0.00	0.00	0.00	0.22	0.02
	1280	1	1.39	7.37	3.67	0.90	1.23	1.34	14.41	3.37
		2	0.22	7.44	0.32	0.14	0.10	0.16	10.68	2.00
		3	0.08	8.00	0.14	0.06	0.00	0.02	10.48	1.75
Hu-F	0	1	0.44	4.52	0.29	0.29	0.12	0.86	5.04	2.18
		2	0.05	4.99	0.05	0.06	0.06	0.18	4.50	1.66
		3	0.03	5.15	0.04	0.04	0.00	0.04	4.34	1.31
	1280	1	1.35	6.63	0.95	0.72	0.60	2.16	7.03	2.76
		2	0.23	6.88	0.45	0.16	0.14	0.46	5.96	2.11
		3	0.10	7.02	0.04	0.07	0.08	0.28	5.34	1.82
Hu-M	0	1	0.91	5.50	0.64	0.84	0.08	1.76	4.97	4.71
		2	0.13	5.80	0.06	0.09	0.04	0.24	4.28	4.02
		3	0.06	5.97	0.04	0.07	0.00	0.04	4.03	3.20
	1280	1	1.90	7.20	0.78	0.85	0.12	2.04	5.46	4.10
		2	0.25	7.20	0.08	0.11	0.04	0.30	4.79	3.42
		3	0.09	7.55	0.04	0.06	0.00	0.14	4.60	2.92
Hu-T	0	1	0.40	4.87	0.29	0.31	0.08	0.70	2.36	1.79
		2	0.12	5.30	0.05	0.04	0.00	0.08	1.85	1.33
		3	0.02	5.33	0.04	0.02	0.00	0.02	1.63	1.09
	1280	1	0.88	5.21	2.32	0.93	0.96	2.06	10.60	3.41
		2	0.08	5.60	0.46	0.30	0.12	0.50	8.50	1.78
		3	0.03	5.62	0.33	0.12	0.00	0.18	7.63	1.57
Ia-C	0	1	0.56	4.65	0.55	0.60	0.14	1.84	1.99	1.65
		2	0.06	4.93	0.06	0.09	0.00	0.26	1.44	0.78
		3	0.02	5.31	0.02	0.02	0.00	0.06	1.40	0.58
	1280	1	2.12	6.90	2.76	0.53	0.84	3.42	11.76	3.33
		2	0.42	6.97	0.64	0.18	0.24	0.72	9.45	2.004
		3	0.21	7.04	0.23	0.08	0.10	0.34	8.96	1.55

EC=electrical conductivity

**Table 6.6 cont.**Some chemical properties of successive barium chloride and water extracts of the soils treated with water treatment residue (WTR) at rates of 0 and 1280 Mg ha<sup>-1</sup>

Soil	WTR (Mg ha <sup>-1</sup> )	Extr. no.	H <sub>2</sub> O extraction						BaCl <sub>2</sub> extraction	
			EC	pH	Ca	Mg	Cl	NO <sub>3</sub>	Ca	Mg
			(dS m <sup>-1</sup> )			(cmol <sub>c</sub> kg <sup>-1</sup> )			(cmol <sub>c</sub> kg <sup>-1</sup> )	
Ia-W	0	1	0.22	3.67	0.15	0.12	0.10	0.70	0.39	0.20
		2	0.03	3.85	0.05	0.03	0.08	0.12	0.24	0.07
		3	0.02	4.31	0.04	0.02	0.02	0.02	0.12	0.04
	1280	1	1.87	6.48	3.75	0.90	1.48	2.32	17.99	3.37
		2	0.32	6.59	0.45	0.14	0.10	0.28	14.50	2.09
		3	0.17	6.62	0.19	0.06	0.06	0.04	13.62	1.72
Nb-A	0	1	0.07	5.45	0.04	0.06	0.16	0.20	0.81	0.72
		2	0.01	5.72	0.02	0.04	0.12	0.16	0.53	0.54
		3	0.00	5.99	0.02	0.02	0.04	0.00	0.45	0.42
	1280	1	1.07	7.18	1.98	0.56	0.50	2.14	5.13	1.75
		2	0.18	7.27	0.44	0.12	0.06	0.46	3.21	1.34
		3	0.08	7.52	0.14	0.06	0.00	0.18	2.75	1.02
Nb-F	0	1	0.11	5.00	0.08	0.06	0.10	0.18	1.80	0.56
		2	0.01	5.50	0.04	0.03	0.04	0.02	1.74	0.40
		3	0.01	5.77	0.02	0.02	0.02	0.00	1.65	0.18
	1280	1	1.08	7.08	2.03	0.56	0.78	1.26	8.46	3.24
		2	0.18	7.29	0.33	0.12	0.10	0.28	7.84	2.53
		3	0.08	7.45	0.14	0.06	0.02	0.04	6.97	1.83
Sd	0	1	0.67	4.79	0.60	0.94	0.00	0.30	6.05	7.49
		2	0.06	5.01	0.06	0.09	0.00	0.04	5.32	6.24
		3	0.03	5.42	0.04	0.06	0.00	0.02	4.34	5.60
	1280	1	0.54	6.46	1.36	0.98	0.46	1.20	11.07	6.41
		2	0.14	6.61	0.23	0.19	0.04	0.14	9.07	4.83
		3	0.10	7.00	0.08	0.08	0.02	0.02	8.54	4.58
Va	0	1	0.16	6.91	0.10	0.10	0.16	0.16	4.69	3.43
		2	0.03	7.00	0.10	0.10	0.02	0.02	4.30	2.67
		3	0.02	7.19	0.06	0.06	0.00	0.00	3.26	1.78
	1280	1	1.11	7.11	1.94	0.77	0.70	1.40	8.80	3.54
		2	0.25	7.32	0.33	0.16	0.18	0.30	6.76	2.28
		3	0.11	7.53	0.14	0.08	0.04	0.08	5.97	1.78
We	0	1	0.09	5.80	0.06	0.04	0.18	0.02	4.65	3.25
		2	0.03	6.30	0.02	0.04	0.08	0.00	4.26	3.09
		3	0.02	6.42	0.00	0.04	0.04	0.00	3.46	2.19
	1280	1	1.05	6.68	0.54	0.75	0.62	1.32	9.55	3.38
		2	0.17	7.11	0.16	0.16	0.12	0.20	8.03	2.48
		3	0.08	7.18	0.06	0.08	0.04	0.06	7.21	1.97

EC=electrical conductivity

differences between consecutive ( $\text{BaCl}_2$ ) extractions generally reflecting “losses” by the water extractions in-between. In trying to relate the “exchangeable” ( $\text{BaCl}_2$ -extractable) and soluble ( $\text{H}_2\text{O}$ ) cations, a binary system of cations is needed to suit the relevant equation (Sposito, 1981; Sumner and Miller, 1996). Soils chosen for relating exchangeable and soluble cations were thus the Hu-M, Hu-T, Nb-A, Sd, Va and We. Since each of these soils contained more than 95% of Ca and Mg in “exchangeable” form, it was assumed that they represented a binary system.

Application of Equation 6.2 yielded the data in Table 6.7. The Vanselow selectivity coefficient (Eq. 6.2) shows the nature of the distribution of cations between the solid soil fraction and the soil solution (Orlov, 1992). This distribution in the current investigation changes with increase in number of extractions, and with introduction of the WTR in all six soils. These changes were expected since this selectivity coefficient varies with the composition of the exchange phase (Sumner and Miller, 1996), which surely changes with the introduction of the WTR, and the sequential extractions.

**Table 6.7** Selectivity coefficients ( $K_v$ ) of a Ca-Mg exchange reaction in six soils treated with 0 and 1280  $\text{Mg ha}^{-1}$  of water treatment residue (R) under successive extractions

Extr. no.	Hu-M		Hu-T		Nb-A		Sd		Va		We	
	R0	R1280	R0	R1280	R0	R1280	R0	R1280	R0	R1280	R0	R1280
1	1.40	1.46	1.39	1.26	1.63	0.84	1.26	1.24	1.37	2.49	0.99	3.91
2	1.60	1.84	1.11	3.09	1.37	0.65	1.31	1.56	1.61	2.97	2.48	3.24
3	2.10	2.28	0.83	1.75	1.07	1.17	0.09	1.87	1.97	3.24	nd	4.79

nd means not calculable because Ca not detectable in solution

In the data of Kerr (1929), cited in Sposito (1981), the values of a Ca-Mg reaction coefficient in a silt loam, which differs from the Vanselow selectivity coefficient by using concentrations instead of activities, ranged between 2.84 and 3.07, with a mean of 2.08.

In four of the six soils, namely Hu-M, Sd, Va and We, the changes generally give evidence of

Equation 6.1 shifting to the right, thus favouring adsorption of Ca and solubility of Mg. This was deduced from the  $K_v$  values generally increasing with the introduction of the WTR, and also with increase in number of extractions (Table 6.7). In other words there is a selectivity of Ca over Mg by the exchange complex for these soils under the imposed conditions. Not only would Ca be preferentially surface-adsorbed compared to Mg because of its higher ionic potential (Bohn, McNeal and O'Connor, 2001), but mass action effects of Ca because of the introduced WTR would enhance this selectivity. Leaching of Mg would thus be expected to be accelerated by application of the WTR in these four soils. In the Nb-A soil the trend appeared to be a shift of Equation 6.1 to the left with both the application of the WTR and increase in number of extractions. Since this soil has a very low cation exchange capacity (Table 3.1b), the exchange reaction is somewhat insignificant, such that virtually all Ca introduced with the WTR remains in solution.

#### 6.4 Conclusions

The WTR applied to a range of soils increased pH, extractable Ca and Mg, soluble salt content, chloride, nitrate and cation exchange capacity whilst decreasing acidity. From an agronomic point of view, these are favourable changes. The increase in nitrate content could in part explain the increase in yields observed in the pot experiment (Section 4.3.1) and Ukulinga field experiment (Section 5.3.3). From an environmental point of view there might be some concern with respect to increased solubility of chloride and nitrate. These two anions are highly mobile and might cause relatively high amounts of Ca and Mg, the other dominant ions, to be leached to the groundwater. Of greater concern, however, would be if heavy metals were amongst such companion cations. This matter is addressed in Chapter 9.



## CHAPTER 7

### WATER TREATMENT RESIDUE AND SOLUTE DYNAMICS IN FIELD EXPERIMENTS

#### 7.1 Introduction

The soil is an open system, being in contact with the atmosphere and the groundwater with which it exchanges materials. Such exchanges are causes of ongoing disturbances to any equilibrium the soil strives to achieve.

With man's activities, an *in situ* soil system at equilibrium becomes even less likely. Inputs are forever being made to soils - ranging from applications of, *inter alia*, manures, fertilizers, limes, irrigation water and pesticides, to disposal of waste materials.

Geertsema *et al.* (1994) considered that WTR disposed of on land can affect the environment through plant quality, soil quality, soil water and groundwater. These investigators proceeded to monitor and analyse relevant materials to establish whether 30 months after application to a field on which pine trees were growing this material would have any effect(s) on any of these environmental aspects. No such effects were observed. Some factors associated with plant quality under field conditions were addressed in Chapter 5. The interest here is on the influence of the WTR on certain soil chemical properties and soil water.

The objectives of this chapter are to establish whether the WTR applied to the field would have any influence on the following:-

- depth distribution of pH;
- migration of major solutes (excluding P); and
- changes in soil solution composition.

## 7.2 Materials and methods

Soils were sampled from fallow plots of the two experimental sites (Section 5.2.3) at dates and depths indicated (Tables 7.1 to 7.6). Analysis was done on soil samples collected from 1998 to 2001. The samples used were collected mainly from the control and 1280 Mg ha<sup>-1</sup> treatments which is where any drastic differences were likely to occur. Plots with the 1280 Mg ha<sup>-1</sup> mulched treatments were sampled from the surface of the actual soil, in other words below the mulch.

The pH was measured in water and/or 1M KCl solution in a 1:2.5 soil: solution ratio. Calcium and Mg were extracted with 1M KCl solution and analysed using an atomic absorption spectrophotometer.

To determine the soluble species, the soil solution was separated from a saturated paste by vacuum following overnight equilibration. Electrical conductivity (EC) of the saturation extract was determined with a conductivity meter, Ca and Mg were analysed as indicated above, bicarbonate and chloride by titration (United States Salinity Laboratory Staff, 1954) and nitrate by an RQflex (Chapter 3).

## 7.3 Results and discussion

### 7.3.1 Depth distribution of pH in soils from Brookdale and Ukulinga Farms

The pH values of the Brookdale samples increased with the passing of years in the incorporated 1280 Mg ha<sup>-1</sup> in all studied depths (Table 7.1a). In the mulched treatment, essentially the same observation was made except for the 200-400 mm depth in 2000 with a higher value and the 0-200 mm depth in 2001 with a lower value. In the first year of the experiment (1998), the pH of the samples where the WTR was applied was less than that of the control. In the following three years the pH values of the WTR-treated soils became greater than those of the control samples at the 0-200 mm depth. For all three treatments in 1998 the pH increased with depth, an unexpected situation

especially considering that the land had been under cropping, and so would have been limed. For the control and the incorporated treatment, except for the 0-200 mm depth in 2000, this situation persisted until 2001. In the mulched treatment the expected decrease of pH with depth was observed in 1999 and 2000, with the situation reverting to that of 1998 in 2001. What can be read from these results is that the water treatment residue increases pH, although these effects apparently do not last for long.

In the 2001 samples from Brookdale, the trend of pH increasing with depth is still evident in all treatments, including lime (Table 7.1b). The pH generally increased in the order:- control, mulched and incorporated WTR treatments at almost all depths. The greater effectiveness of the incorporated treatment is attributed to a higher rate of reaction between the WTR and soil which is facilitated by the mixing. The higher lime treatments also increased pH compared to the control and the lower lime level. The pH increases resulting from the WTR and lime extend to essentially the 1000-1200 mm depth, defying the understood fact of lime effects being confined to the area of application.

**Table 7.1a:** Potassium chloride pH values of selected depth samples from Brookdale Farm at selected rates of water treatment residue from 1998 to 2001

Sampling date	Sampling depth (mm)	WTR applied		
		0	1280i	1280m
		(Mg ha <sup>-1</sup> )		
September 1998	0-200	4.52	4.41	4.30
	200-400	4.48	4.48	4.35
	400-600	4.86	4.82	4.73
February 1999	0-200	4.49	4.57	5.40
	200-400	4.88	4.70	4.88
	400-600	4.96	4.94	4.97
February 2000	0-200	4.47	5.33	5.79
	200-400	4.97	5.00	4.84
	400-600	5.22	5.07	5.04
February 2001	0-200	4.34	5.12	4.49
	200-400	4.87	4.86	4.96
	400-600	5.01	5.37	5.17

i = incorporated treatment; m = mulched treatment

**Table 7.1b** Potassium chloride and water pH values of depth samples from Brookdale Farm at selected rates ( $\text{Mg ha}^{-1}$ ) of water treatment residue (R) and lime (L) in February 2001

Sampling depth (mm)	pH(KCl)					pH( $\text{H}_2\text{O}$ )				
	R0	R1280i	R1280m	L2	L10	R0	R1280i	R1280m	L2	L10
0-200	4.34	5.12	4.49	4.49	5.18	5.30	5.77	5.16	4.95	5.73
200-400	4.87	4.86	4.96	4.83	5.10	5.43	5.41	5.52	5.34	5.68
400-600	5.01	5.37	5.17	5.00	5.21	5.68	5.81	5.67	5.41	5.67
600-800	5.18	5.82	5.44	5.38	5.64	5.61	6.28	5.66	5.35	5.95
800-1000	5.20	6.04	5.65	5.35	5.73	5.37	6.35	5.62	5.28	5.98
1000-1200	5.26	6.12	5.56	5.29	5.65	5.70	6.23	5.66	5.34	5.81

i = incorporated treatment; m = mulched treatment

This pH trend, however, is also observed in the control plots (Table 7.1b), implying that the WTR and lime treatments enhanced rather than caused it.

In the We soil (Table 7.2), the ability of the WTR and the lime to increase pH (KCl and  $\text{H}_2\text{O}$ ) over the control is mostly clear in the 0-100 and 100-200 mm depths. The effects of the WTR are throughout the whole profile, i.e., to the 400-500 mm depth for pH(KCl). As in the Brookdale depth samples, it is not understood by what mechanism this increase in pH with depth could have occurred. In Chapter 6 it was shown that the abundant anions in a WTR-treated soil were chloride and nitrate, which are potential acids. Bicarbonate, the likely ion for increasing pH with depth, was determined to be low and so would be expected to have insignificant effects.

### 7.3.2 Depth distribution of Ca and Mg in soils from Brookdale and Ukulinga Farms

Introduction of the WTR reduces the concentrations of both Ca and Mg (Table 7.3a). These results contradict those from the incubation experiment where application of the WTR increased the concentrations of these two cations (Table 6.3a). The possibility of the dilution effect caused by the relatively inert large aggregates of the WTR is disputed by the fact that the mulched treatment also

**Table 7.2** Potassium chloride and water pH values of depth samples from Ukulinga Farm at selected rates ( $\text{Mg ha}^{-1}$ ) of water treatment residue (R) and lime (L) in February 2001

Sampling depth (mm)	pH(KCl)			pH( $\text{H}_2\text{O}$ )		
	R0	R1280	L10	R0	R1280	L10
0-100	5.00	7.24	6.25	6.15	7.54	6.85
100-200	4.97	6.64	5.54	6.08	6.87	6.25
200-300	4.93	5.64	4.85	6.06	6.08	5.71
300-400	5.07	5.58	5.21	6.27	5.98	6.25
400-500	5.22	5.92	5.28	6.50	6.32	6.47

**Table 7.3a** Depth distribution of Ca and Mg from 1998 to 2001 in soil samples from Brookdale Farm at selected intervals and rates ( $\text{Mg ha}^{-1}$ ) of water treatment residue (R)

Sampling date	Sampling depth (mm)	Ca ( $\text{cmol}_e \text{kg}^{-1}$ )			Mg ( $\text{cmol}_e \text{kg}^{-1}$ )		
		R0	R1280i	R1280m	R0	R1280i	R1280m
September 1998	0-200	4.28	2.55	2.22	3.01	2.41	2.17
	200-400	3.29	2.53	2.14	2.97	2.70	2.21
	400-600	2.37	1.15	1.45	3.45	3.08	2.59
February 1999	0-200	4.08	2.45	3.31	3.04	2.36	2.68
	200-400	4.47	2.29	2.68	3.75	2.68	2.61
	400-600	2.80	1.38	1.62	3.99	3.18	3.03
February 2000	0-200	2.90	2.78	3.56	2.46	2.25	1.78
	200-400	2.87	3.80	2.17	3.32	2.31	2.13
	400-600	1.96	1.48	1.57	3.51	2.45	2.49
February 2001	0-200	2.53	2.73	3.01	2.41	2.09	1.66
	200-400	2.53	2.26	2.72	2.93	2.21	2.00
	400-600	1.94	1.52	2.25	3.86	2.02	2.48

i = incorporated treatment; m = mulched treatment

decreased extractable Ca compared to the control in 1998. After 1998 the concentrations of Ca increased in both incorporated and mulched treatments, probably because the WTR released more of this cation as its aggregates continued to break to smaller sizes. On the other hand, Ca in the

control plots tended to decline with time, as did Mg for all treatments and depths. This behaviour of the two cations in the control treatment shows that their redistribution in the profile is not caused solely by the application of the WTR.

Both lime treatments resulted in higher concentrations of both Ca and Mg than the control treatment (Table 7.3b). Both the WTR and the lime have resulted in an increase in levels of these two cations to the lowest depth of 1000-1200 mm. By this time (2001) the Ca concentrations where the WTR was applied are greater than in the control, and the mulched treatment has higher concentrations of Ca than the incorporated treatment over all depths considered. The higher concentrations in the WTR-treated samples over the control shows continued release of Ca from the WTR, whilst the depletion in the control plots is not replenished.

**Table 7.3 b** Depth distribution of Ca and Mg in February 2001 soil samples from Brookdale Farm at selected rates ( $\text{Mg ha}^{-1}$ ) of water treatment residue (R) and lime (L)

Sampling depth (mm)	Ca ( $\text{cmol}_e \text{kg}^{-1}$ )					Mg ( $\text{cmol}_e \text{kg}^{-1}$ )				
	R0	R1280i	R1280m	L2	L10	R0	R1280i	R1280m	L2	L10
0-200	2.53	2.73	3.01	4.47	6.80	2.41	2.09	1.66	2.90	3.80
200-400	2.53	2.26	2.72	3.22	4.35	2.93	2.21	2.00	3.10	3.84
400-600	1.94	1.52	2.25	3.04	3.36	3.86	2.02	2.48	3.20	4.50
600-800	1.25	1.83	1.47	3.04	2.35	2.02	1.94	1.88	3.30	4.37
800-1000	1.00	1.16	1.36	1.94	1.89	1.41	1.64	2.02	3.04	4.37
1000-1200	0.77	1.21	1.53	1.33	1.87	0.97	1.92	2.04	2.62	4.74

i = incorporated treatment; m = mulched treatment

In the Ukulinga Farm depth samples both the WTR and lime had increased Ca concentrations to 400-500 mm by 2001 (Table 7.4). Concerning Mg, its concentrations are lower in the WTR-treated samples than in the control, and highest in the lime-treated plots. These results are similar to those of the Brookdale samples, implying that the behaviour of the WTR is essentially similar in both soils.

**Table 7.4** Depth distribution of Ca and Mg in February 2001 soil samples from Ukulinga Farm at selected rates (Mg ha<sup>-1</sup>) of water treatment residue (R) and lime (L)

Sampling depth (mm)	Ca (cmol <sub>c</sub> kg <sup>-1</sup> )			Mg (cmol <sub>c</sub> kg <sup>-1</sup> )		
	R0	R1280	L10	R0	R1280	L10
0-100	3.13	4.98	4.43	1.80	1.12	3.97
100-200	3.16	4.85	4.35	1.61	1.55	3.61
200-300	2.93	3.95	4.18	1.52	1.45	3.36
300-400	2.84	3.82	4.10	1.84	1.62	3.77
400-500	2.67	3.72	4.27	2.02	1.57	4.48

### 7.3.3 Analysis of saturation extracts

The WTR applied as mulch at the rate of 1280 Mg ha<sup>-1</sup> substantially and consistently increased the electrical conductivity of the saturation extract with respect to the control in the Brookdale Farm samples (Table 7.5) in all six depths considered. On the other hand, the incorporated similar treatment registered both slight increases and decreases. This electrical conductivity trend is also followed by the concentrations of Ca, Mg, Cl and NO<sub>3</sub>. This agrees with results from the incubation experiment (Section 6.3.3) that these four ions are the species likely to leach. At the 0-200 and 200-400 mm depths the concentration of Ca is higher than that of Mg for all three treatments, whereas the reverse holds for the lower depths. This points to more ready leaching, or redistribution, of Mg compared to Ca - an expected occurrence.

It would have been expected that the incorporated treatment, where the WTR was in intimate contact with the soil, would produce greater effects than the mulched treatment. The question is what causes this seeming anomaly? Is it because the mulched treatment is more effective, or is it that the effects of the incorporated treatment are already past the stage of the mulched treatment? A look at the pH (H<sub>2</sub>O) values (Table 7.5) shows that, except for the 200-400 mm depth, the incorporated treatment has resulted in higher pH values than the mulched treatment. This is evidence for the effects of the incorporated treatment extending to 1200 mm as well. This is also shown for

**Table 7.5** Depth distribution of some chemical properties in saturation extracts of February 2001 soil samples with selected rates of water treatment residue at Brookdale Farm

Depth	WTR	EC	pH	Ca	Mg	HCO <sub>3</sub>	Cl	NO <sub>3</sub>
(mm)	(Mg ha <sup>-1</sup> )	(dS m <sup>-1</sup> )	(H <sub>2</sub> O)			(mmol <sub>c</sub> L <sup>-1</sup> )		
0-200	0	0.58	5.37	1.9	1.6	0.7	1.1	3.6
	1280i	0.49	5.65	2.0	1.4	1.0	1.4	2.5
	1280m	0.92	5.37	3.7	2.4	0.7	1.4	5.8
200-400	0	0.46	5.60	1.4	1.3	nd	nd	nd
	1280i	0.51	5.44	1.9	1.5	nd	nd	nd
	1280m	0.83	5.60	3.0	2.7	nd	nd	nd
400-600	0	0.40	5.70	1.0	1.5	0.7	1.0	2.4
	1280i	0.44	5.75	1.3	1.4	0.7	1.6	2.1
	1280m	0.89	5.69	2.3	3.4	0.5	1.6	6.0
600-800	0	0.39	5.53	0.8	1.6	0.4	1.1	2.1
	1280i	0.37	5.90	0.9	1.3	0.6	1.5	1.9
	1280m	1.12	5.64	2.6	5.1	0.8	4.5	6.2
800-1000	0	0.31	5.45	0.5	1.2	0.5	1.8	1.6
	1280i	0.33	6.54	0.7	1.3	0.6	1.4	1.4
	1280m	1.24	5.56	2.6	5.4	nd	nd	nd
1000-1200	0	0.24	5.50	0.4	0.5	0.4	1.1	1.0
	1280i	0.33	6.14	0.7	1.3	1.4	2.3	2.0
	1280m	1.05	5.59	2.3	4.7	0.7	3.5	6.4

EC = electrical conductivity; nd = not analysed

extractable Ca and Mg (Table 7.3b). It can thus be deduced that what has indeed happened is that leaching has occurred more readily in the incorporated treatment to the extent that the soil has returned to its initial soluble salt status. Besides incorporation being expected to accelerate the WTR-soil reaction, the migration of salts from the incorporated treatment also starts 200 mm ahead of those for the mulched treatment, thus encouraging quicker downward migration.

In the Ukulinga experiment (Table 7.6), all the properties measured, namely electrical conductivity, pH, soluble Ca, Mg, Cl, HCO<sub>3</sub> and NO<sub>3</sub> increased with the introduction of the WTR at 1280 Mg ha<sup>-1</sup>. Again, even in this soil the effects are throughout the whole profile, i.e., down to 500 mm. In this soil, however, the concentration of Ca is higher than that of Mg throughout the entire profile where the WTR is applied, which is expected since this material contains more Ca than Mg, and Mg should leach more readily than Ca.



**Table 7.6** Depth distribution of some chemical properties in saturation extracts of February 2001 soil samples with selected rates of water treatment residue at Ukulinga Farm

Depth (mm)	WTR (Mg ha <sup>-1</sup> )	EC (dS m <sup>-1</sup> )	pH (H <sub>2</sub> O)	Ca	Mg	HCO <sub>3</sub> (mmol <sub>c</sub> L <sup>-1</sup> )	Cl	NO <sub>3</sub>
0-100	0 1280	0.40 0.88	6.05 6.97	0.9 5.0	0.8 1.9	1.0 5.6	1.0 1.8	2.1 5.0
100-200	0 1280	0.47 1.04	5.90 6.68	1.0 3.0	0.9 2.5	nd nd	nd nd	nd nd
200-300	0 1280	0.46 0.98	5.93 6.19	1.1 5.0	1.0 2.9	0.9 4.0	1.8 1.5	2.3 5.4
300-400	0 1280	0.41 0.89	6.00 6.12	1.0 3.7	0.9 2.5	0.9 1.8	1.1 1.0	2.2 5.7
400-500	0 1280	0.40 0.90	6.11 6.33	0.7 2.6	0.6 2.0	nd nd	nd nd	nd nd

EC = electrical conductivity; nd = not determined

In this soil, as in that at Brookdale Farm, it would be expected that the groundwater would be enriched by these ions. Data supplied by Umgeni Water (Table 7.7) suggests this indeed might be the case in the experiment at Brookdale Farm. There is a suggestion that there might be slight increases in Ca and Mg concentrations in the borehole water after 1997, before these seem to revert to initial levels for Ca from 2000. For Cl and N there are no clear trends as to their concentrations. Geertsema *et al.* (1994) reported “one-time flux” increases in groundwater nitrogen following application of alum sludge to soil, but attributed these to the initial tillage disturbance rather than a long-term mineralization and leaching effect. In the current study, however, it is the mineralization that is speculated to have released the nitrogen, based on the control treatments releasing less nitrogen in the incubation experiment (Section 6.3.3). The analysis of the dam water (Table 7.7) suggests there is no transport of any of the mentioned elements with runoff water. In both water sources none of the concentrations come close to those that might be considered harmful to humans and livestock according to the data of Lal and Edwards (1994; cited by Havlin, Beaton, Tisdale and Nelson, 1999). The permissible concentrations given by these authors are < 200 mg L<sup>-1</sup> for Ca, < 400 mg L<sup>-1</sup> for Cl and < 10 mg L<sup>-1</sup> for N with respect to human consumption. The concentrations given for livestock consumption are < 1000, < 1000 and < 50 mg L<sup>-1</sup> for Ca, Cl and N, respectively.

**Table 7.7** Calcium, chloride, magnesium and nitrate in borehole<sup>1</sup> (B) and dam<sup>1</sup> (D) water at Brookdale Farm from 1997 to 2002 (data supplied by Umgeni Water)

Date	EC		Ca		Mg		NO <sub>3</sub> -N		Cl	
	B	D	B	D	B	D	B	D	B	D
	(mS m <sup>-1</sup> )						(mg L <sup>-1</sup> )			
11.12.1997	13.0	12.6	10.1	9.8	5.6	6.6	<0.05	nd	9.3	nd
26.03.1998	20.9	nd	21.0	9.6	7.2	6.0	<0.05	<0.05	7.0	8.4
04.06.1998	27.5	13.0	21.0	8.8	10.0	6.2	1.78	<0.05	12.4	8.3
10.09.1998	22.8	16.0	23.0	10.4	7.4	8.1	0.05	<0.05	5.7	9.6
03.12.1998	22.1	10.9	20.0	7.2	7.1	4.3	0.19	<0.05	5.1	8.4
06.05.1999	21.7	14.8	20.3	10.2	8.0	7.3	<0.05	0.08	6.5	11.1
03.06.1999	22.4	18.3	22.0	13.4	8.1	9.1	0.06	<0.05	6.1	12.6
02.09.1999	nd	15.7	nd	10.1	nd	6.6	nd	nd	nd	nd
02.12.1999	22.6	13.2	22.0	6.4	7.6	3.6	<0.05	<0.05	6.9	9.0
30.03.2000	13.2	11.2	9.3	7.1	6.2	4.5	<0.05	<0.05	9.0	8.9
08.06.2000	16.4	10.5	16.0	8.3	7.6	5.4	<0.05	<0.05	8.9	9.6
07.09.2000	18.2	12.0	17.0	9.6	6.8	5.7	<0.05	<0.05	7.5	6.7
10.04.2001	12.1	13.0	6.2	8.3	6.5	5.7	<0.05	<0.05	8.1	8.9
07.06.2001	13.4	13.7	8.2	10.1	7.8	7.1	<0.05	<0.05	8.0	7.4
07.09.2001	nd	14.9	nd	11.6	nd	7.5	nd	<0.05	nd	8.2
04.04.2002	19.0	13.6	19.0	nd	7.4	nd	<0.05	nd	6.4	nd
13.06.2002	15.1	13.4	11.5	10.6	10.2	6.7	<0.05	<0.05	8.7	8.2
12.09.2002	17.7	14.1	15.9	10.9	12.2	6.9	<0.05	<0.05	7.7	8.8

EC=electrical conductivity; nd=not determined

With enrichment of the groundwater with nutrients likely to lead to environmentally harmful eutrophication of some water bodies, then to what extent would that restrict the practice of land disposal of the WTR? Hughes *et al.* (2005) report that the solute concentrations in the soils of the grassed plots were much lower than those in the fallow plots at both sites. Owens, Edwards and Van Keuren (1994) similarly reported reduced leaching from soils grown to a grass-legume mixture. To reduce migration of solutes to the groundwater, it would thus be advisable for land disposal of WTR to be accompanied by growing plants on the treated soils to absorb some of the solutes. Not only would this reduce the amount of solutes reaching the groundwater, it would also provides spin-offs of agricultural advantage (animal feed) and soil conservation (especially where grass is the chosen

<sup>1</sup> The dam and the adjacent borehole are about 400 m downslope from the field experiment

vegetation). Another suggestion (Owens and Bonta, 2004) is minimal N fertilization. With excreta from grazing animals a likely source of N in runoff water (Mundy, Nexhip, Austin and Collins, 2003), then hay production would probably be a better option to reduce  $\text{NO}_3$  in transit water than direct grazing.

Analysing the data in Tables 7.5 and 7.6 by the Vanselow selectivity coefficient (Equation 6.2) yielded results with a different trend to those of the incubation experiment (Table 6.7). In these field results (Table 7.8) the Vanselow coefficients decreased with application of the WTR. This decrease in the Vanselow coefficients with the introduction of the WTR implies a shift of Equation 6.1 to the left, meaning possible preferential adsorption of Mg over Ca, or induced abundance of soluble Ca compared to soluble Mg. Whilst no evidence of preferential adsorption of Mg is forthcoming (Tables 7.3b and 7.4), there does seem to be more soluble Ca in the We soil compared to Mg (Table 7.6). The reverse, however, essentially holds in the Hu-F soil (Table 7.5) from 400-600 mm depth downwards. Differences between laboratory and field experiments are expected, since other ions present in a natural system may affect the equilibrium (Pleysier, Juo and Herbillon, 1979; Rhue and Mansell, 1988; Chung, Zasoski and Burau, 1994; Nissinen *et al.*, 1998). The field samples were fertilized as compared to the incubation samples to which were just added the WTR. These field samples should thus not be treated as binary systems. Using a Vanselow-type reaction to analyse field samples at different depths of various soils for a Ca-Mg relationship, Nissinen *et al.* (1998) found selectivity coefficients with values around 0.5 for different soils. Whilst these values are generally comparable to those of the Ukulinga's We soil and also the 0-200mm of Brookdale's Hu-F soil, they are very different from the 200-400 mm depth downwards for all three treatments considered (except for the 400-600 mm depth of the incorporated treatment). The explanation for this lies partly with the observation that from the 400-600 mm depth the concentration of Mg is higher than that of Ca in the Brookdale soil (Table 7.5). This has the effect of increasing the Vanselow selectivity coefficients as calculated from Equation 6.2. It is probable that this Mg was transitory and not directly under the influence of, or related to, the exchangeable form of the element; in other words this solution Mg was not in equilibrium with exchangeable Mg.

**Table 7.8** Selectivity coefficients of a Ca-Mg system in soil depth samples from Brookdale and Ukulinga Farms at selected rates of water treatment residue

Experimental site	Depth (mm)	WTR rate (Mg ha <sup>-1</sup> )		
		0	1280i	1280m
Brookdale	0-200	0.37	0.23	0.28
	400-600	1.33	0.71	1.31
	600-800	3.23	1.54	2.51
	800-1000	3.34	2.61	nd
	1000-2000	1.50	2.93	2.73
Ukulinga	0-100	0.51	0.09	na
	200-300	0.48	0.21	na
	300-400	0.59	0.28	na

na=treatment not applied; nd=not calculated because anions not analysed

## 7.4 Conclusions

Land treatment of the WTR caused slight and somewhat temporary increases in pH throughout the profile at both field experimental sites. There was also an enhancement of the downward migration of Ca and Mg, although evidence from borehole water is that this should not cause any alarm. Evidence from the dam suggests that there is no increased transport of any solutes by runoff water. There is evidence of slow reactivity of the WTR with the soil, such that its solutes tend to merge and be diluted with the soil as a whole. This probably accounts for the rather neutral response observed for grass (Chapter 5). Combining disposal with growth of vegetation such as grass (as investigated here) would make the practice safer and maybe even less expensive since the vegetation might be commercially used.

## CHAPTER 8

### WATER TREATMENT RESIDUE AND PHOSPHORUS BEHAVIOUR IN SOILS

#### 8.1 Introduction

Investigations involving application of WTR to soils by different workers have highlighted that this material can sorb P. Amongst workers who have demonstrated this property in WTR are Lucas *et al.* (1994), Peters and Basta (1996), Ahmed *et al.* (1997), Haustein *et al.* (2000) and Dayton, Basta and Jakober (2001).

The determination of sorption isotherms is probably the most common technique for studying P behaviour in soils. These studies take into account both the capacity and intensity factors, and can thus be used to predict the amount of fertilizer P needed to adjust the soil solution P to a level optimum for crop growth (McGee, 1972; Bhuiyan and Sedberry, 1995). Two of the most commonly used relationships to describe sorption are the Freundlich and Langmuir isotherms.

Although not as commonly investigated as sorption, desorption is nonetheless important since it essentially governs absorption by plants, leaching and transportation of P in runoff water. Different sorption/desorption models tested by Garcia-Rodeja and Gil-Sotres (1995) established that the concentration of initially desorbable P decreased exponentially with contact time between P and soil, indicating that sorption is continuous but increasingly slow. These results tend to confirm that sorption and desorption give complementary information as proposed by Quang and Dufey (1997). Furthermore, their results also suggested a need to examine the form of transformation that the sorption takes.

The lack of attainment of equilibrium between the solution and solid phases (Grant and Heaney, 1997; Quang and Dufey, 1997; Papadopoulos, Dimirkou and Ioannou, 1998) is an indication that either there is an infinite number of sorption sites in a given amount of soil, or that more sorption

sites are created as transformation reactions occur in the soil, or both. Of these, the creation of sorption sites is the most likely. Sorption of applied P in soil is a form of transformation since P is converted from a highly mobile form to a less mobile or an immobile one. Whereas in sorption experiments the interest has been mainly on the loss of the element from solution, transformation studies are concerned with the soil constituents with which P has become associated .

It has been demonstrated that sorption can be correlated with soil constituents such as “active” calcium carbonate (Lopez-Pineiro and Navarro, 1997), clay content (Singh and Gilkes, 1991; Quang, Thai, Linh and Dufey, 1996; Lopez-Pineiro and Navarro, 1997) and various Al and Fe species (Singh and Gilkes, 1991; Quang *et al.*, 1996; Lopez-Pineiro and Navarro, 1997; Owusu-Bennoah, Szilas, Hansen and Borggaard, 1997). Fractionation of P has been carried out on WTRs and WTR-treated soils (Jonasson, 1996; Cox *et al.*, 1997). Results obtained, although by using different fractionation methods, indicated transformation to Al and Ca forms.

In addition to the agronomic aspects of P behaviour in soils there is also a need to consider the environmental impacts of P should it leach from the soil. Although loss of P is in general not expected to be significant, in coarse-textured soils it can be a problem because of their low number of sorption sites. High concentrations of P in soils are mostly as a result of application of fertilizers, and if lost by leaching it may pollute water bodies either via runoff or groundwater (e.g. McPharlin, Jeffrey, Toussaint and Cooper, 1994; Siemens *et al.*, 2004).

The objectives of this chapter are as follows:-

- to determine the influence of WTR on P sorption by soils;
- to establish the transformation of P in WTR-treated soils; and
- to study the extractability of P in WTR-treated soils.

## 8.2 Materials and methods

### 8.2.1 Soil samples

Both incubated and non-incubated samples of 11 soils (Chapter 6) were used for this study, although not necessarily in all aspects simultaneously.

### 8.2.2 Determination of optimum sorption time

Five grams of untreated soil or WTR were allowed to sorb P from 50 mL of 0.005 M calcium chloride solution containing an equivalent of 500  $\mu\text{g P g}^{-1}$  soil (250  $\mu\text{g g}^{-1}$  in the Hu-T, Nb-A and Nb-F soils) as potassium dihydrogen phosphate in a 100 mL centrifuge tube. The suspensions were equilibrated for 0, 1, 8, 24 and 48 hours. At the end of each incubation time, the suspensions were centrifuged until clear and then filtered through Whatman No. 42 filter paper before analysis by the molybdenum blue method (Murphy and Riley, 1962) using a UV/visible spectrophotometer. From the results it was established that the amount of P sorbed in the 8 hour period was almost the same as for the longer times. As a result, it was decided to equilibrate the suspensions for 0, 0.5, 1, 2, 4, 6 and 8 hours, to investigate sorption within this shorter time period.

### 8.2.3 Determination of P sorption pattern

The P levels used here were very high and were intended to test to what extent the WTR could be used as an environmental “cleansing agent” by reducing excessive levels of this element in waste materials, soils or water bodies. In this study, to 5 g samples in centrifuge tubes were added concentrations of P as potassium dihydrogen phosphate in 50 mL of solution which was 0.005M with respect to calcium chloride. For the Av and Ia-W soils, the soil:solution ratio was 1:50. The P concentrations were 0, 200, 400, 600, 800, 1000, 1400 and 1800  $\mu\text{g g}^{-1}$  for all soils except the Hu-T, Nb-A, Nb-F, Va and We soils where they were 0, 40, 160, 320, 400, 600, 800 and 1000  $\mu\text{g g}^{-1}$ . Suspensions were shaken for 6 hours before analysis as indicated above (Section 8.2.2).

#### 8.2.4 Fractionation of P

Soil samples from the pot (Chapter 4) and incubation (Chapter 6) experiments with 0 and the highest rate of WTR, i.e., 120 Mg ha<sup>-1</sup> for samples from the pot experiment and 1280 Mg ha<sup>-1</sup> for the incubated samples, were subjected to the fractionation procedure of Hedley, Stewart and Chauhan (1982) as modified by Zhang and MacKenzie (1997). This fractionation sequentially extracts readily available, plant-available, Al and Fe components, Ca-associated P and residual P using calcium chloride, sodium bicarbonate, sodium hydroxide, hydrochloric acid, and a sulphuric acid-hydrogen peroxide mixture, respectively. The calcium chloride and sodium bicarbonate fractions are considered biologically available, the hydroxide fraction moderately resistant and the rest unavailable to plants. The sulphuric acid-hydrogen peroxide extraction was not done in the current study.

#### 8.2.5 Extraction of P from field samples

Surface soil samples (0-200 mm depth) where the WTR had been applied at rates of 0 and 1280 Mg ha<sup>-1</sup> from both field trials were extracted with Ambic (Section 3.2.3) and 0.05M calcium chloride solutions at soil:solution ratio of 1:5 and 1:2, respectively, and P analysed as before (Section 3.2.3). Soil samples analysed were for September 1998, February 1999, 2000 and 2001 at the Brookdale Farm, and February 1999 and 2001 at the Ukulinga Farm. The Ambic extractant was used to give an indication of available P as practised by the Fertilizer Advisory Service in the KwaZulu-Natal Province. The calcium chloride extractant was used to give an indication of P desorption (Doula *et al.*, 1997).

#### 8.2.6 Extraction of aluminium and iron

Free Al and Fe in the WTR and “original” soil samples were extracted by the dithionite-citrate-bicarbonate (DCB) procedure (Mehra and Jackson, 1960). Poorly crystalline forms of these elements were determined by the acid ammonium oxalate method (Jackson, Lim and Zelazny, 1986). The



metals were analysed by atomic absorption spectrophotometry. This analysis was to assist in the understanding of P behaviour in the different soils and WTR-treated soils, since these soil constituents can play a significant role in the sorption of P (e.g. Carreira and Lajtha, 1997).

### 8.3 Results and discussion

#### 8.3.1 Time-dependence and kinetics of P sorption

Sorbed P was taken to be the difference between that added and that remaining in solution at the end of the shaking period. Since it was deemed important to cater for previously sorbed P (Tolner and Füleky, 1995), corrections were made for “native” P extracted with 0.005M CaCl<sub>2</sub> solution.

There was a marked increase in the amount of P sorbed with time up to about 8 hours, after which the curve tended to level off (Figure 8.1a). These results appear to be consistent with those of other workers including Rajan and Fox (1975), and Papadopoulos *et al.* (1998), who concluded that the reaction between phosphate and soils is rapid at first, then becomes slower and continues for a long time without reaching any true equilibrium. More than 90% of the P sorbed in 48 hours was sorbed within the first 8 hours. In the other sorption-time curve (Figure 8.1b) it can be seen that at 6 hours the extent of sorption approximately equalled that at 8 hours. Thus for the later experiments 6 hours was adopted as the standard equilibration time.

It can also be seen that the WTR was comparable in terms of the amount of P sorbed with the highly weathered Hu-F and Ia-C soils that are known to be high sorbing soils. This implies that the WTR might be expected to severely reduce the mobility and perhaps plant-availability of P when applied to soils less highly sorbing than itself. The solution concentration-time relationship was subjected to a first order kinetic equation (Bhuiyan and Sedberry, 1997; Papadopoulos *et al.*, 1998), which in integrated form is represented as

$$\ln C = -kt + \ln C_0 \quad \dots (8.1)$$

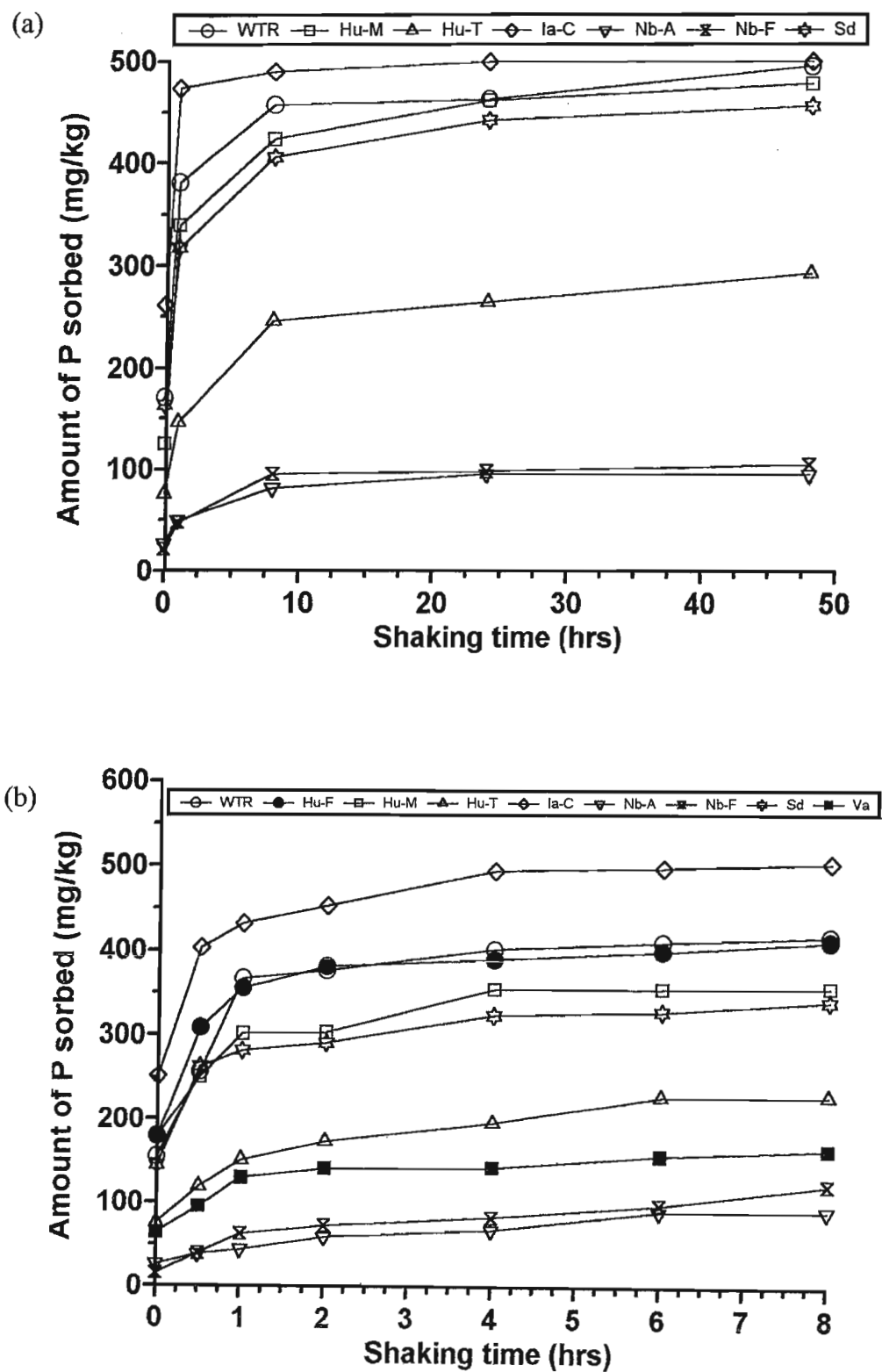


Figure 8.1 Sorption of phosphorus by WTR and soils at different shaking times up to (a) 48 hours and (b) 8 hours

where  $C$  is the P solution concentration at time  $t$ ,  $k$  is the rate coefficient and  $C_0$  is the initial solution concentration of P.

The relationship of  $\ln C$  against  $t$  (Figure 8.2) is not a straight line as expected from the first order equation. Basically, a first order reaction implies that only one reactant is involved, a possible situation in pure systems. In soil such an occurrence would be expected if the sorbent (soil) is taken to have unit activity, although Papadopoulos *et al.* (1998) did establish that a kaolinite-goethite system could be described by the first order kinetics. These workers deduced that either the reaction was simple, or that all reactions involved had similar reaction rates. Quang *et al.* (1996) considered that a fast reaction at early times was due to adsorption, and that a later one that could last for a long time was related to secondary precipitation, etc. This “early” reaction, which could also be the mechanism at low P concentrations, would probably be the simple one mentioned by Papadopoulos *et al.* (1998). Although there are not enough points to make an accurate decision (Figure 8.2), it may be that 2 hours is about the transition time between the simple and complex processes. Since in the current study the reaction failed to comply with first order kinetics, the implication is that more than one reactant overall was involved in the sorption of P. Sorption of P under the conditions considered was thus higher than first order, and from that it is proposed that other mechanisms in addition to simple adsorption occurred.

### 8.3.2 Sorption of P in incubated and non-incubated soils

The P isotherm is given as the relationship between the sorbed P and that remaining in solution at the end of the equilibration (shaking) period. Sorbed P is taken as the difference between the initial P concentration in solution and that remaining after shaking. In Figure 8.3 the P remaining in solution at the end of the shaking period is designated the equilibrium concentration. In general, the points tend to follow the isotherm trend of a smooth curve. The exception is the Nb-A soil (Figure 8.3g) at WTR rates of 320 and 1280 Mg ha<sup>-1</sup>, both incubated and non-incubated. Introducing a high amount of the WTR apparently changes the general sorption pattern. After about 15 mg L<sup>-1</sup> solution P the curves corresponding to these rates suddenly change direction to become steeper. It might be

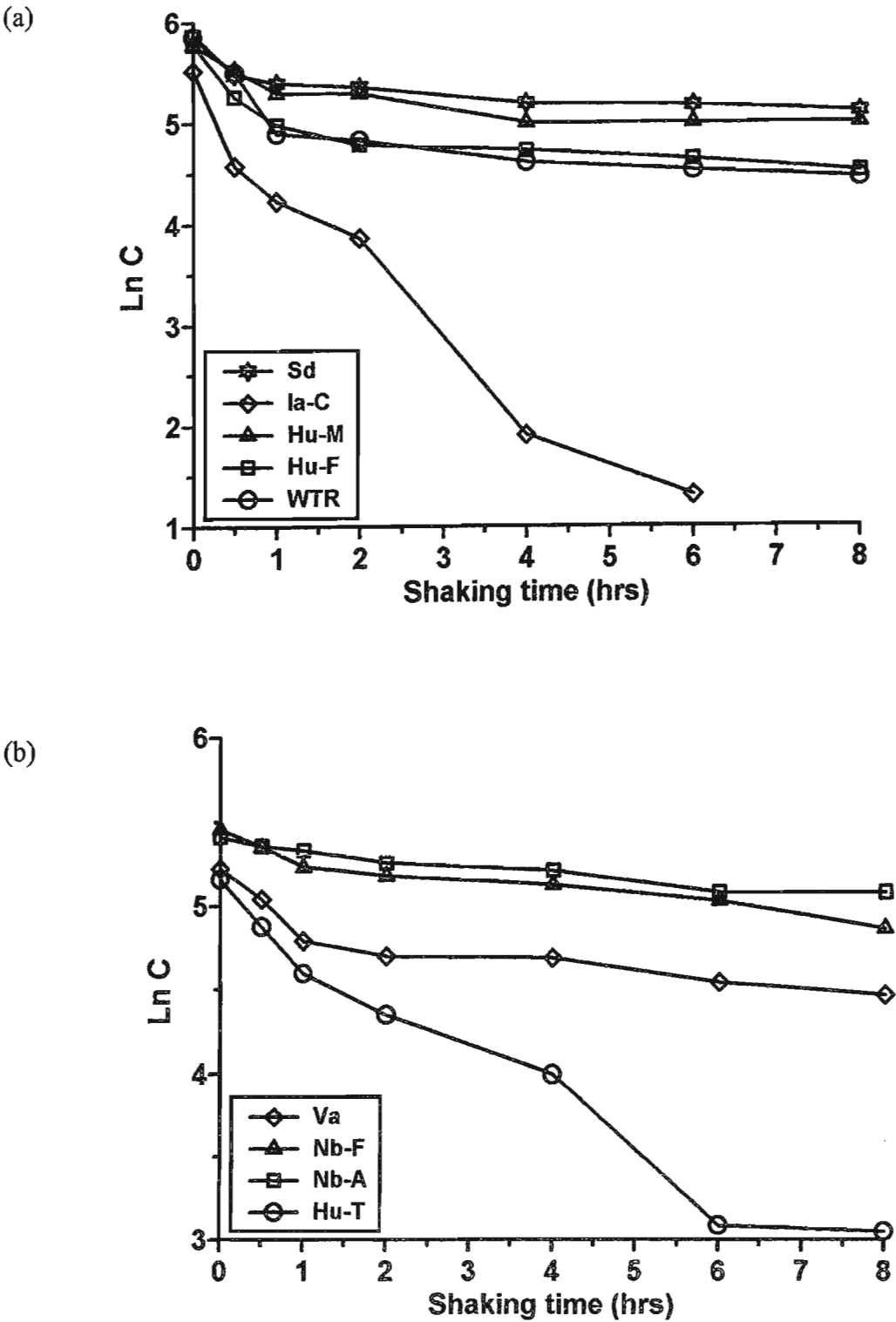


Figure 8.2 First order kinetic relationship of phosphorus reaction in (a) WTR and soils at 500 mg kg<sup>-1</sup> and (b) soils at 250 mg kg<sup>-1</sup>

that in this poorly buffered, coarse-textured soil the high number of sorption sites added by the WTR have this profound effect.

In the Av soil (Figure 8.3a), the highest sorption was for the non-incubated samples at WTR rates of 320 and 1280 Mg ha<sup>-1</sup>. Where samples were incubated, sorption at these rates was the same as that of the 80 Mg ha<sup>-1</sup> rate in the non-incubated samples. These observations suggest that some constituent of the WTR might be changing with incubation and reducing its P sorption capacity. Such results have been identified before. From the results of their work on an alum WTR, Ahmed *et al.* (1997) concluded that its high sorption capacity experienced under laboratory conditions might be reduced with ageing, leading to release of this nutrient for plant use. Butkus *et al.* (1998) also suggested application of P to the WTR before soil application, so that the P would then be supplied to plants as a “slow-release” fertilizer (Ahmed *et al.* 1997). In the current situation, part of the answer is perhaps linked to the lime in the WTR. It has been reported that carbonates, and the WTR contains 3.8% lime (Section 3.3.1), can act as sorbents for P (Lopez-Pineiro and Navarro, 1997; Zhou and Li, 2001). So as the carbonate reacts and diminishes in the soils following incubation, then more P is released into solution compared to the non-incubated soil. In general, the extent of sorption tended to increase with increasing WTR applied.

Other soils in which the sorption capacity increased with application of the WTR, especially at 1280 Mg ha<sup>-1</sup>, were the Hu-F, Hu-T, Nb-A, Nb-F, Sd, Va and We (Figure 8.3 b, d, g, h, i, j and k, respectively). Although no common properties between these soils could be readily identified as the cause of this similar response, there was general agreement with the results of Bainbridge, Miles, Praan and Johnston (1995). Studying sorption of P in some Natal (now KwaZulu-Natal) soils, they found that soils with the lowest sorption were sandy (texture of the Hu-T, Nb-A and Nb-F soils). The correlation of P sorption in South African soils with clay content has also been reported by McGee (1972) and Henry and Smith (2002). The Va soils, dominated by 2:1 clay minerals and with relatively few sorption sites, were classified by Bainbridge *et al.* (1995) into the group of intermediate sorption.

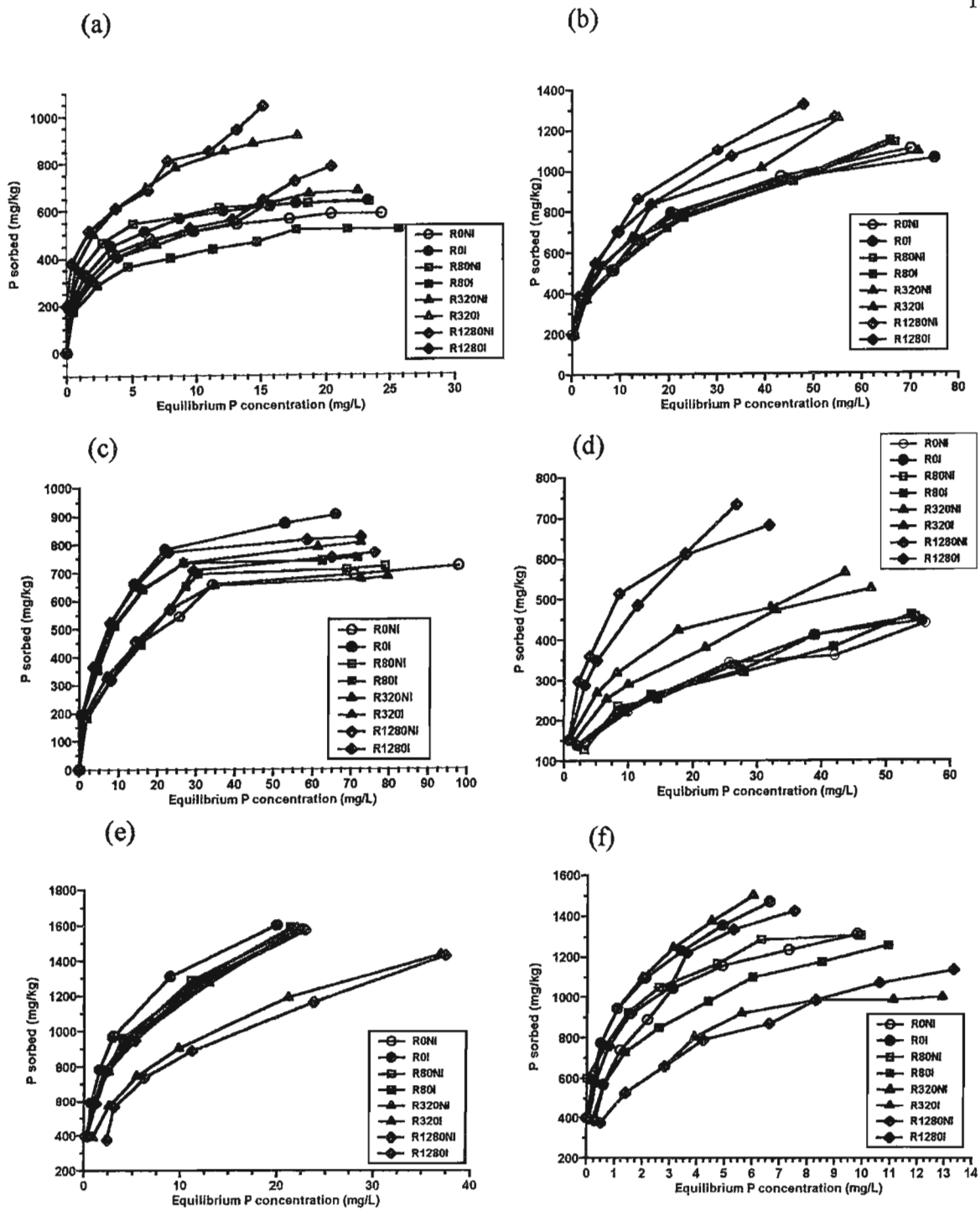


Figure 8.3 Relationship between equilibrium and sorbed phosphorus for incubated (I) and non-incubated (NI) soils (a) Av, (b) Hu-F, (c) Hu-M, (d) Hu-T, (e) Ia-C and (f) Ia-W at different rates of the water treatment residue (R)

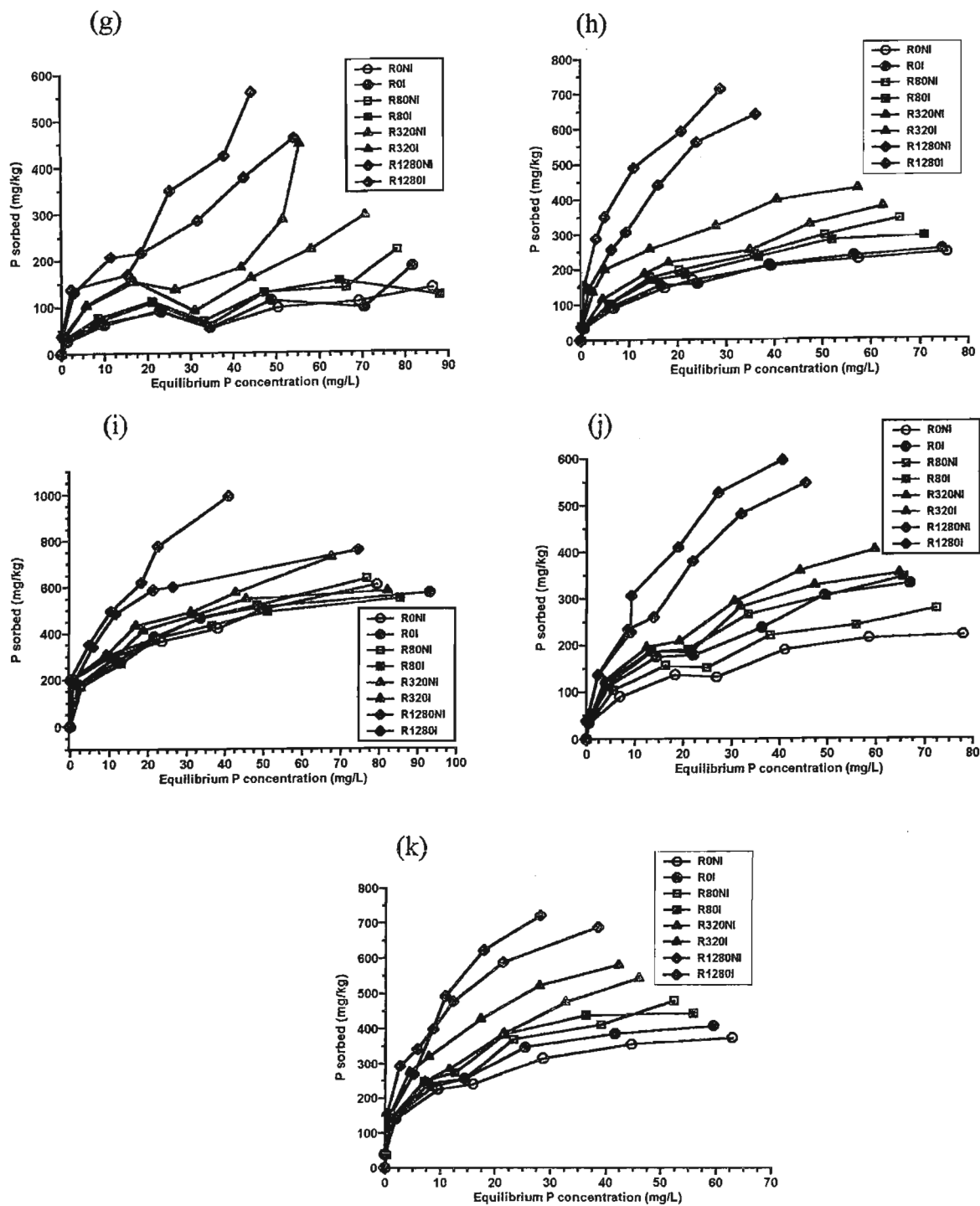


Figure 8.3 cont. Relationship between equilibrium and sorbed phosphorus for incubated (I) and non-incubated soils (g) Nb-A, (h) Nb-F, (i) Sd, (j) Va and (k) We at different rates of the water treatment residue (R)

According to the classification, the Hu-F, a weathered soil, is amongst the highest sorbing soils (Figure 8.3b). It, however, experienced an increase in sorption on application of the WTR, unlike in the other highly weathered Av (Figure 8.3a), Hu-M (Figure 8.3c), Ia-C (Figure 8.3e) and Ia-W (Figure 8.3f) soils. Part of the explanation for the seemingly contradictory result lies in the fact that the Hu-F soil has been used for cropping purposes for almost 40 years (Mr N. Houston, pers. comm., 1998; cited in Moodley, 2001), and thus has been previously fertilized with P. The cumulative effect of P application over these years would result in occupation of some sorption sites. Such initially retained P can reduce the sorption of added P (Bainbridge *et al.*, 1995; Duffera and Robarge, 1999) to some extent. The creation of new sorption sites by addition of the WTR thus increased this soil's sorption behaviour.

Differences in sorption capacities also seem to be associated with oxalate-extractable Al (Table 8.1), which increases sorption as was reported also by Bainbridge *et al.* (1995) for KwaZulu-Natal soils. In all the soils where sorption was increased by the introduction of the WTR, except for the Hu-F soil, this form of Al was lower than in the WTR. In all these soils it can be expected that the WTR would reduce labile P and so perhaps induce deficiency in plants, and decrease runoff and leaching losses.

Application of the WTR increased the pH in all soils (Figures 6.1 to 6.11), but had mixed effects on the extent of P sorption. Sorption of P was notably increased where the soil had an initially relatively high pH e.g. Va, and clearly decreased where the pH was initially low as in the Ia-W soil. Thus on its own pH would not seem to be a significant factor.

In addition to the Av soil, other soils in which the sorption capacity was higher in non-incubated samples at similar rates of WTR were the Hu-T, Nb-A, Nb-F and Sd. This observation applies also to the Hu-F soil except for the 1280 Mg ha<sup>-1</sup> treatment where the incubated sample had the higher sorption capacity. The isotherms of incubated samples coincided where no WTR was applied, suggesting that this behaviour was due more to the WTR than the soil. Again, there was no common feature between these soils that could explain their similar behaviour. They are, however, generally



the soils identified as having relatively low sorption capacities.

In the Va and We soils (Figure 8.3 j and k, respectively), incubated samples sorbed more than the corresponding non-incubated samples. It was only in the Ia-C and Ia-W soils (Figure 8.3 e and f, respectively) that the WTR decreased sorption. These soils thus had a greater sorption capacity than the WTR, and so application of this material would be likely to improve P availability.

**Table 8.1** Aluminium and iron extracted with dithionite-citrate-bicarbonate (DCB) and acid ammonium oxalate in water treatment residue and soils

Sample	DCB		Oxalate	
	Al	Fe	Al	Fe
	(g 100g <sup>-1</sup> )			
WTR	0.38	7.74	0.19	2.96
Av	0.60	2.03	0.19	0.36
Hu-F	0.92	3.38	0.24	1.46
Hu-M	1.54	8.20	0.24	0.63
Hu-T	0.60	6.58	0.13	0.21
Ia-C	3.37	9.22	0.41	0.45
Ia-W	2.36	1.91	0.52	1.84
Nb-A	0.04	1.01	0.06	0.17
Nb-F	0.18	0.77	0.11	0.26
Sd	0.44	5.41	0.16	0.34
Va	0.13	1.21	0.10	1.08
We	0.23	1.75	0.07	0.71

### 8.3.3 Application of sorption isotherms

Agbenin and Tiessen (1994) identified three parameters as important criteria for determining a soil's capacity to immobilize added P, namely the adsorption maximum, P affinity and buffer index. To determine sorption maxima, P affinity and P requirement in the current study, use was made of the linear forms of the Freundlich and Langmuir equations. Only data from the incubated samples were considered.

### 8.3.3.1 Freundlich isotherm

The Freundlich equation is presented as:-

$$\log Q = n \log C + \log K_F \dots (8.2)$$

where  $Q$  is the amount of solute sorbed,  $n$  is a correction factor,  $C$  is the equilibrium solution concentration and  $K_F$  is the distribution coefficient. A plot of  $\log Q$  against  $\log C$  should yield a straight line with slope  $n$  and intercept  $\log K_F$ .

In the plot of the Freundlich relationship (Figure 8.4), the points do not always follow a straight line for all soils although the coefficients of determination  $\{R^2(F), \text{Table 8.2}\}$  are high, ranging between 0.887 and 1.000. From the Freundlich linear relationship, the amount of sorbed  $P$  required to provide a solution concentration of  $0.2 \text{ mg L}^{-1}$  was calculated (Table 8.2, column FPR). This concentration has been suggested to be the standard  $P$  requirement (herewith the Freundlich  $P$  requirement, FPR) of soils that will satisfy the requirements of many crops (Fox and Kamprath, 1970). Of interest here was to have a reference value to test whether the WTR would cause any differences to the requirement rather than an interest in absolute quantities. The effects of the application of the WTR on the amount of  $P$  required to achieve this solution concentration (Table 8.2) were to decrease, virtually not change, or to increase it. Associated clearly with the first effect were the Av, Ia-C and Ia-W soils, which are the highly weathered soils with a  $P$  sorption capacity higher than that of the WTR. These results agree with the observations made in Section 8.3.2, based on Figure 8.3, that the WTR was likely to increase availability of  $P$  in the Ia-C and Ia-W soils. In the Hu-F, Hu-M, Sd and Va, application of the WTR had virtually no effect on the  $P$  requirement of the soils. The soils where there was an increase in the  $P$  requirement with application of the WTR were the Hu-T, Nb-A, Nb-F and We soils. These soils have a relatively low  $P$  sorption capacity (Table 8.2, Column b). Also supporting this observation, the Freundlich distribution coefficient (Table 8.2, Column  $K_F$ ) increased with application of the WTR to these four soils. Since this coefficient indicates partitioning of  $P$  between the solid and solution phases, then its increase

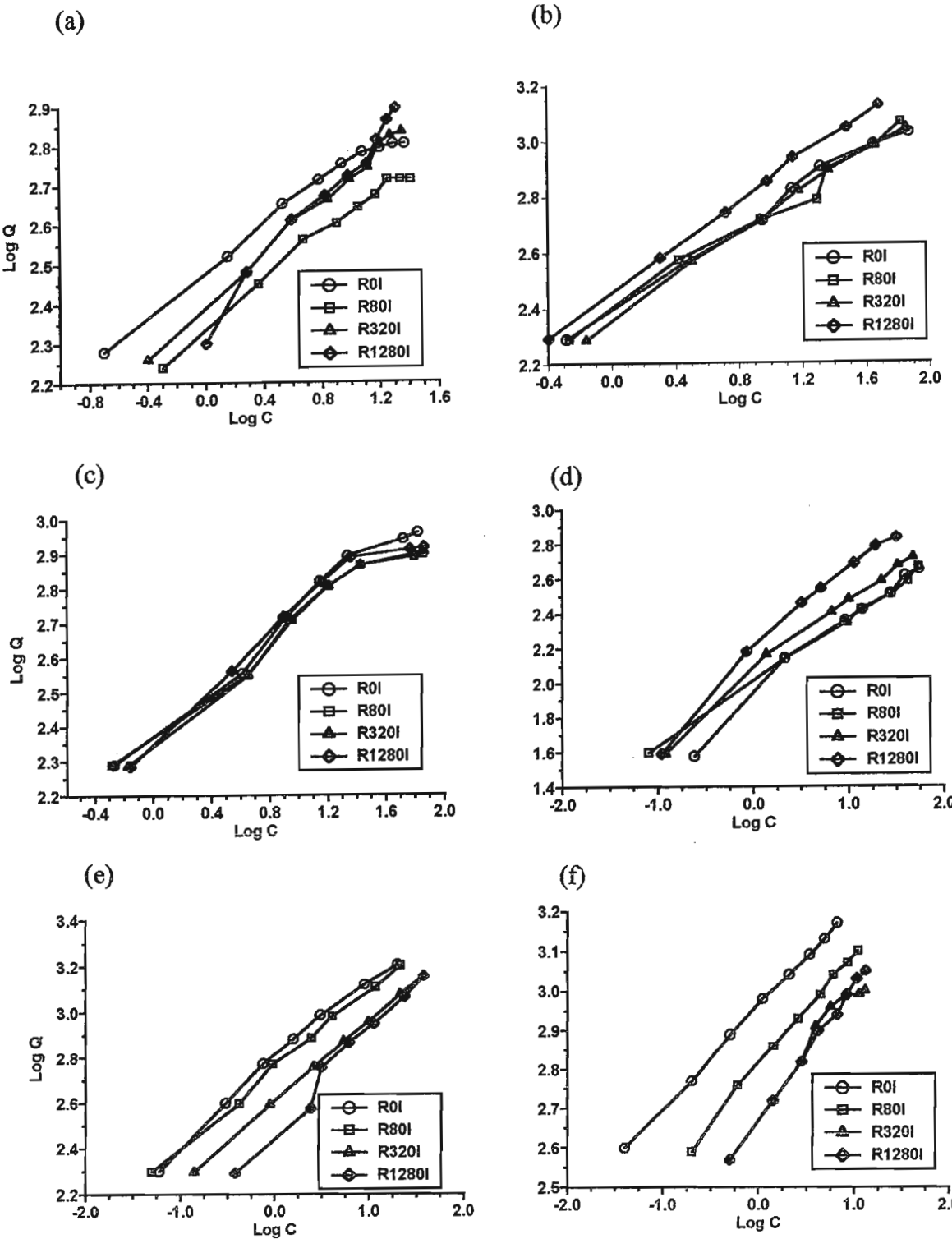


Figure 8.4 Sorption of phosphorus in the (a) Av, (b) Hu-F, (c) Hu-M, (d) Hu-T, (e) Ia-C and (f) Ia-W incubated soils at different rates of water treatment residue (R) as described by linear Freundlich relationship

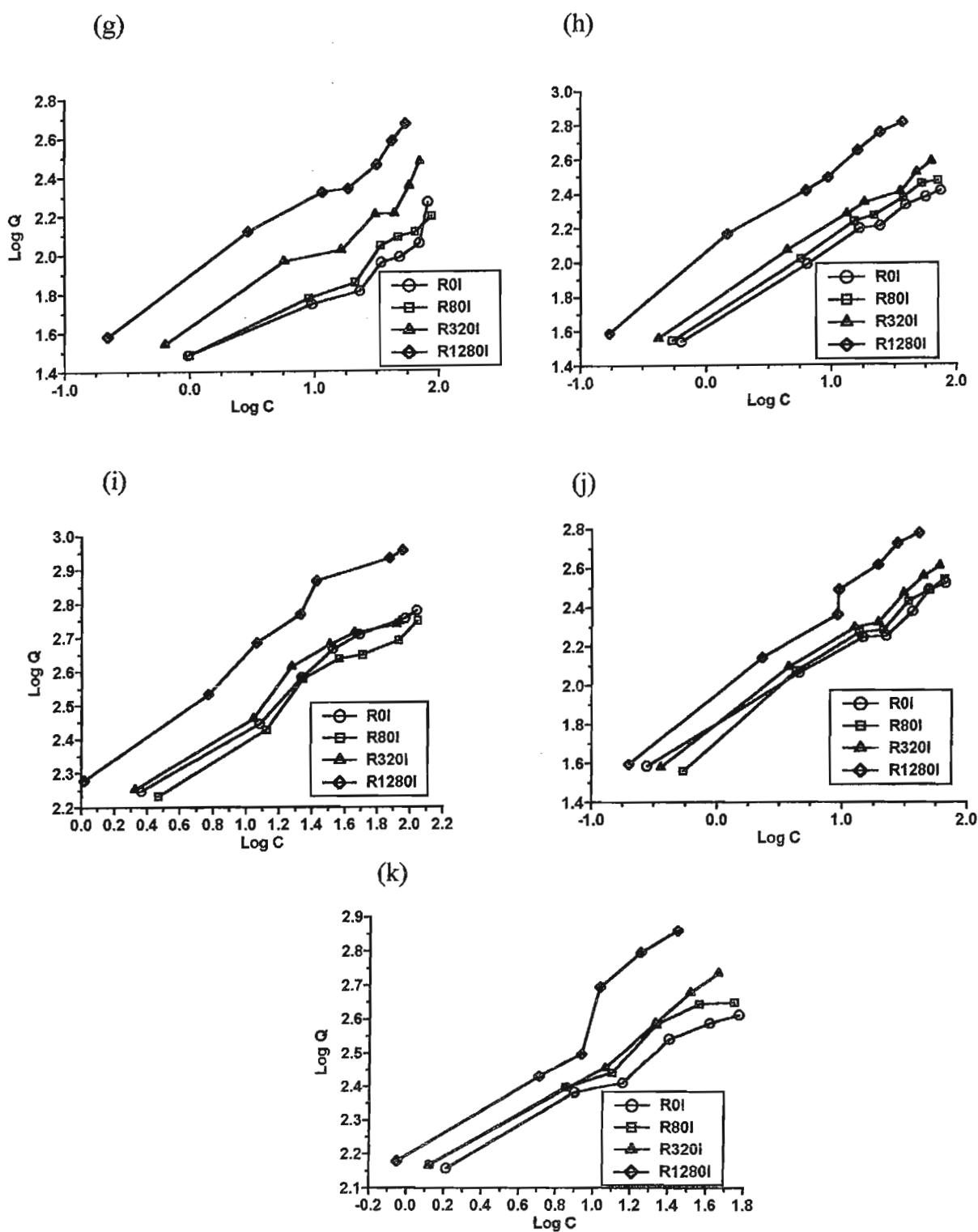


Figure 8.4 cont.

Sorption of phosphorus in the (g) Nb-A; (h) Nb-F2; (i) Sd; (j) Va and (k) We incubated soils at different rates of water treatment residue (R) as described by linear Freundlich relationship

implies an increase in sorbed P at the expense of solution P. The introduction of the WTR to these soils thus reduced the availability and mobility of P. The improved retention would reduce leaching to groundwater in these mostly coarse-textured soils.

The question of the reliability of these FPR values then arises. To address this, use is made of instances where it is possible to compare the amount of P sorbed calculated directly from the experimental data with that calculated from the linear form of the equation at  $0.2 \text{ mg L}^{-1}$  P solution concentration. In the experimental data of the Av soil at  $0 \text{ Mg ha}^{-1}$  WTR,  $190.0 \text{ mg kg}^{-1}$  compares with  $200.6 \text{ mg kg}^{-1}$  from the Freundlich isotherm. For the Ia-W soil at WTR rates of 0 and  $80 \text{ Mg ha}^{-1}$  respectively,  $595.0$  and  $390 \text{ mg kg}^{-1}$  from experimental calculations corresponded with  $602.3$  and  $404.4 \text{ mg kg}^{-1}$  from the Freundlich isotherm. At  $1280 \text{ Mg ha}^{-1}$  of the WTR in the We soil,  $39.8 \text{ mg kg}^{-1}$  from the experimental results corresponds with  $36.4 \text{ mg kg}^{-1}$  from the isotherm. It can thus be concluded that for the soils and conditions of the experiment, the linear form of the Freundlich isotherm can be useful in determining P requirements of soils.

#### 8.3.3.2 Langmuir isotherm

The Langmuir equation is expressed as:-

$$C/Q = C/b + 1/K_L \quad (8.3)$$

where Q is the amount of solute sorbed,  $K_L$  is a constant related to binding energy (P affinity), C is the final solution concentration and b is the maximum amount of solute that can be sorbed (adsorption maximum). If C/Q is plotted against C, and the data obey the Langmuir equation, a linear relationship with slope  $1/b$  and intercept  $1/K_L b$  will result. As judged by  $R^2$  values (Table 8.2, column  $R^2(L)$ ) which ranged between 0.789 and 0.998, the linear plot of the Langmuir isotherm (Figure 8.5), conforms to this type of curve.

The equilibrium concentrations plotted here ranged from 0.2 to 25.7, 0.3 to 74.96, 0.52 to 72.60, 0.8

**Table 8.2** Freundlich and Langmuir parameters for water treatment residue-treated incubated soils

Soil	WTR rate (Mg ha <sup>-1</sup> )	K <sub>F</sub> (L kg <sup>-1</sup> )	FPR (mg kg <sup>-1</sup> )	R <sup>2</sup> (F)	K <sub>L</sub> * 10 <sup>-1</sup> (L kg <sup>-1</sup> )	b (mg kg <sup>-1</sup> )	LPR (mg kg <sup>-1</sup> )	R <sup>2</sup> (L)
Av	0	304.7	200.6	0.981	7.34	667.8	85.6	0.998
	80	220.3	140.3	0.988	4.33	559.0	57.8	0.993
	320	247.3	135.7	0.994	3.24	741.0	58.2	0.977
	1280	215.4	111.2	0.980	1.79	912.9	31.6	0.943
Hu-F	0	111.8	63.5	0.990	0.14	1132.0	29.2	0.989
	80	108.8	61.6	0.984	0.10	1210.9	24.0	0.948
	320	98.4	53.9	0.997	0.11	1172.6	25.8	0.983
	1280	113.9	59.6	0.998	0.14	1441.0	41.2	0.973
Hu-M	0	105.3	59.1	0.982	0.19	952.8	36.1	0.991
	80	112.6	66.5	0.968	0.24	827.4	38.9	0.995
	320	102.4	58.7	0.973	0.22	845.5	36.3	0.996
	1280	106.7	60.9	0.967	0.25	870.9	43.4	0.997
Hu-T	0	29.6	14.6	0.983	0.13	481.9	12.6	0.964
	80	43.6	24.3	0.998	0.14	471.4	13.3	0.947
	320	40.9	20.7	0.987	0.17	557.8	18.9	0.969
	1280	44.3	19.7	0.982	0.23	754.0	34.7	0.983
Ia-C	0	264.5	148.2	0.988	0.69	1670.4	202.7	0.990
	80	256.2	147.1	0.997	0.53	1649.4	158.5	0.980
	320	178.2	100.4	1.000	0.26	1508.0	73.4	0.976
	1280	111.4	55.2	0.979	0.16	1584.4	48.3	0.972
Ia-W	0	909.4	602.3	0.999	17.22	1534.6	556.4	0.989
	80	643.2	404.4	0.996	9.35	1327.9	302.5	0.948
	320	480.8	287.9	0.966	7.45	1109.4	223.0	0.983
	1280	469.6	270.7	0.997	4.77	1264.5	110.0	0.973
Nb-A	0	12.1	6.9	0.887	0.09	121.4	2.2	0.946
	80	12.5	7.0	0.968	0.06	169.9	2.0	0.937
	320	15.9	8.3	0.952	0.05	298.8	2.8	0.789
	1280	27.9	14.2	0.980	0.08	480.3	7.6	0.856
Nb-F	0	16.0	8.1	0.995	0.08	285.4	4.7	0.974
	80	17.4	8.5	0.997	0.08	333.0	5.8	0.972
	320	19.7	9.4	0.994	0.08	411.2	6.7	0.936
	1280	31.2	13.6	0.995	0.12	745.4	17.2	0.925
Sd	0	60.4	35.0	0.981	0.09	633.5	10.0	0.990
	80	56.5	33.1	0.961	0.10	541.5	11.1	0.994
	320	66.2	38.9	0.960	0.12	600.3	14.8	0.994
	1280	78.9	43.8	0.974	0.10	982.5	19.6	0.992
Va	0	25.1	13.4	0.989	0.08	365.3	5.8	0.917
	80	18.0	8.7	0.988	0.08	385.8	6.1	0.952
	320	21.6	10.4	0.993	0.08	456.5	6.6	0.922
	1280	26.8	11.7	0.991	0.09	716.9	12.8	0.894
We	0	39.2	21.0	0.972	0.20	429.9	16.5	0.986
	80	33.3	16.4	0.939	0.19	482.7	17.5	0.987
	320	74.3	45.6	0.987	0.16	571.0	18.3	0.939
	1280	68.7	36.4	0.974	0.16	818.2	25.3	0.829

K<sub>F</sub> = Freundlich distribution coefficient; FPR = P requirement based on Freundlich relationship; K<sub>L</sub> = Langmuir affinity coefficient; b = Langmuir sorption maxima; LPR = P requirement based on Langmuir relationship; F and L refer to Freundlich and Langmuir respectively.

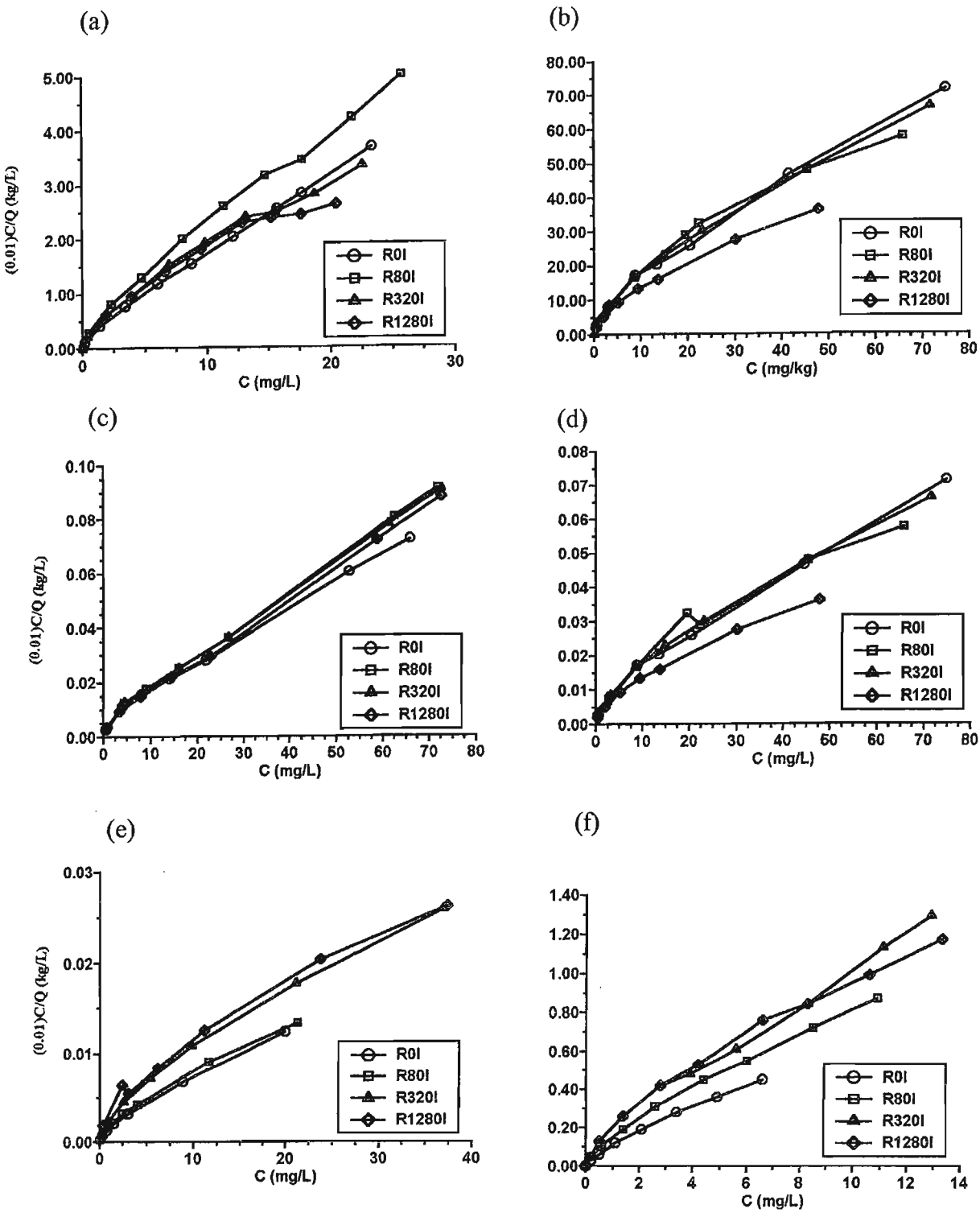


Figure 8.5 Sorption of phosphorus in the (a) Av, (b) Hu-F, (c) Hu-M, (d) Hu-T, (e) Ia-C and (f) Ia-W incubated soils at different rates of water treatment residue (R) as described by linear Langmuir relationship

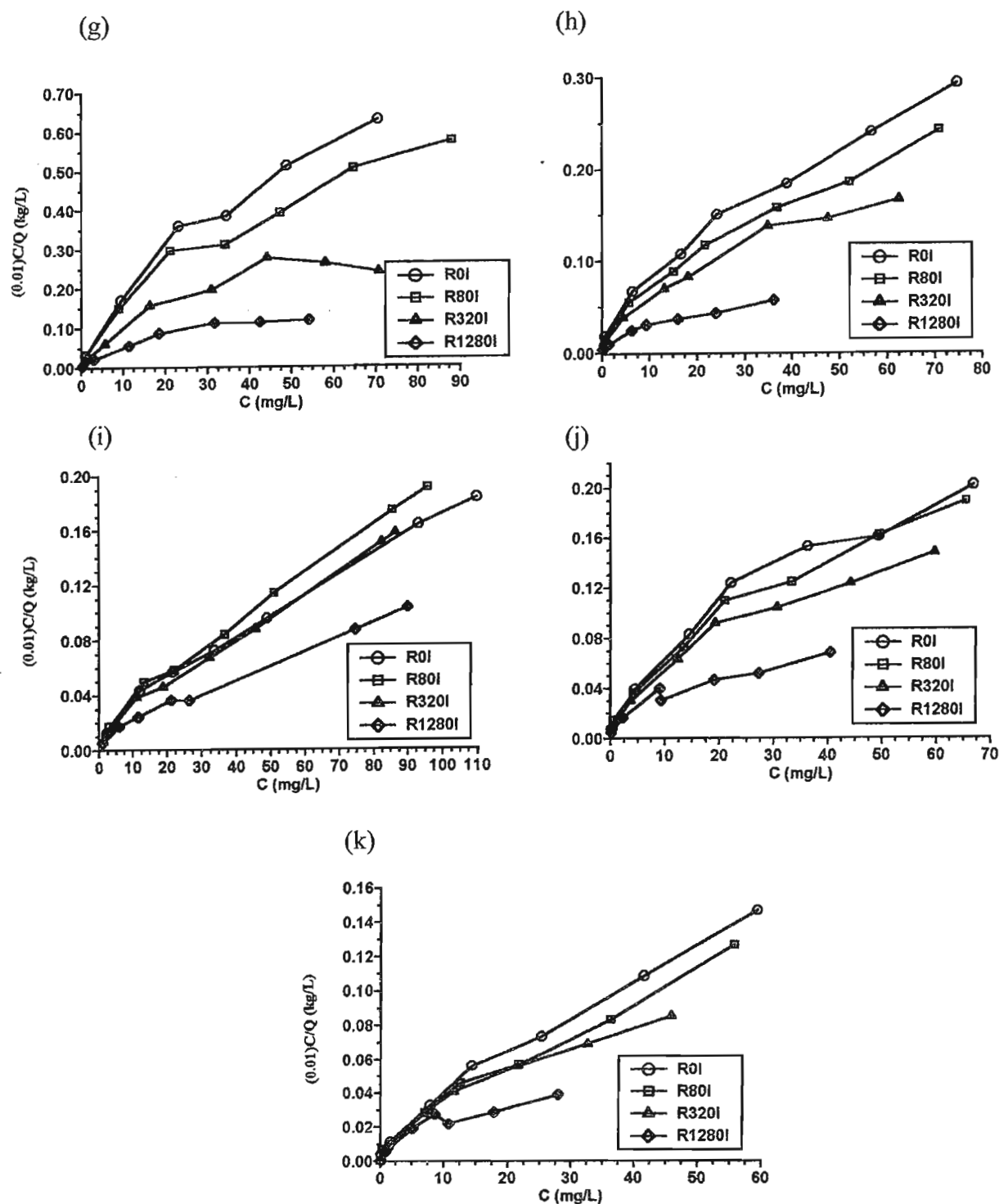


Figure 8.5 cont.

Sorption of phosphorus in the (g) Nb-A, (h) Nb-F, (i) Sd, (j) Va and (k) We incubated soils as described by linear Langmuir relationship



to 55.48, 0.1 to 37.4, 0.2 to 13.3, 2.2 to 88.0, 1.7 to 74.56, 1.04 to 110.6, 2.0 to 66.92 and 0.1 to 62.36 mg L<sup>-1</sup> in the Av, Hu-F, Hu-M, Hu-T, Ia-C, Ia-W, Nb-A, Nb-F, Sd, Va and We soils, respectively. For Eastern Transvaal (now Mpumalanga Province of South Africa) sesquioxenic soils, McGee (1972) established that deviation from linearity in the Langmuir isotherm occurred when P solution concentrations were above 0.3 mg L<sup>-1</sup>. On the other hand, for selected tobacco-growing soils of South Africa, Henry and Smith (2002) reported compliance with the Langmuir isotherm for P concentrations from 0.025 to 2.00 mg L<sup>-1</sup>. In the present study, the relationship seems to hold up to much higher concentrations according to the R<sup>2</sup> values. However, irrespective of the high R<sup>2</sup> values, in Figure 8.5 it can be seen that the relationship could be best described by two lines, similar to the results of Lopez-Pineiro and Navarro (1997). In the Hu-M soil (Figure 8.5c) for example, each of the four curves is essentially two straight lines meeting at an equilibrium P concentration of 3.75 mg L<sup>-1</sup>. Another example is the We soil (Figure 8.5k) where there seems to be deviations from linearity at equilibrium P concentration of 2.5 and 10 mg L<sup>-1</sup>. Singh and Gilkes (1991) referred to a non-linear distribution of their Langmuir data to form a curve. It can be seen, for example, that Figures 8.5b, 8.5 e and 8.5f for the Hu-F, Ia-C and Ia-W soils, respectively, better represent smooth curves rather than straight lines or a series of straight lines. In general though, the points in Figure 8.5 do not follow true straight lines.

The introduction of the WTR reduces the affinity of P (Table 8.2, column K<sub>L</sub>) in the Av, Ia-C and Ia-W soils whereas it remains virtually unchanged in the other soils. Whilst for the three soils the results agree with the observations made in Sections 8.3.2 and 8.3.3.1, the results for the others are at variance. For especially the coarse-textured Nb-A, Nb-F and Hu-T soils, it was expected that the P affinity should increase. More consistent with earlier observations are the results of the sorption capacities. Increases are notable for the Av, Hu-F, Hu-T, Nb-A, Nb-F, Sd, Va and We soils (Table 8.2, column b). In the Hu-M, Ia-C and Ia-W soils application of the WTR is accompanied by a decrease in the sorption maximum. It would thus seem that the sorption maximum is a better parameter for describing P sorption than the affinity term. Comparing the P requirement based on the Langmuir isotherm (Table 8.2, column LPR) with the FPR, it can be seen that the two are different, with the LPR being consistently much lower. As the appropriateness of the Freundlich

isotherm has been demonstrated, it is thus the Langmuir isotherm which is incorrect. A reason for the apparent deficiencies concerning P affinity and P requirement based on the Langmuir isotherm is now proposed.

The Langmuir isotherm has received some criticism for its inappropriate usage in soil systems (e.g. Veith and Sposito, 1977; Harter and Smith, 1981), one of the reasons being its assumption of similar energy sites. As observed by the points of the linear form of the Langmuir isotherm deviating from straight lines (Figure 8.5), sorption sites are of different energies. The kinetic results (Section 8.3.1) also support this since they give evidence of different mechanisms of sorption. Any calculations or conclusions based on treating all points as equal is bound to lead to misleading results. This understanding has prompted some workers (e.g. Veith and Sposito, 1977) to propose the so-called binary or “two-surface” Langmuir equation to cater for the perceived deficiency. The improved equation has worked on occasions, giving better, higher results of sorption maxima than the basic one (Quang *et al.*, 1996; Lopez-Pineiro and Navarro, 1997). From the literature surveyed the affinity term has actually not been an issue, probably because it does not have any direct practical implications.

Subjecting the current data to the two-surface Langmuir isotherm did not improve the LPR values in all soils. At 0 Mg ha<sup>-1</sup> of WTR, the Av for example, had LPR values of 85.6 mg kg<sup>-1</sup>. The two-surface Langmuir isotherm changed this value from 85.6 to 95.8 mg kg<sup>-1</sup>. Comparing these to the proven FPR values (Section 8.3.3.1) of 200.6 mg kg<sup>-1</sup>, it can be seen that it is not worthwhile to use the binary Langmuir isotherm for these data.

#### 8.3.4 Phosphorus fractionation

##### 8.3.4.1 Pot experiment soils

Calcium chloride extractions did not exhibit any consistent changes with application of either the WTR or the lime, indicating that the amount of solution P was not affected by these treatments

(Table 8.3). This was somewhat in contrast to the work of Jonasson (1996) who reported a reduction in Cl resin-extractable P on application of an alum WTR to soils. Application of the WTR did not change the amount of P extracted with the Ambic solution in the Hu-M, Hu-T and Ia-C soils. In the Nb-F1 soil this fraction decreased whereas in the Sd soil it increased. The sodium bicarbonate fraction remained almost the same in the Hu-M and Hu-T soils, decreased in the Ia-C and Nb-F1 soils, and increased in the Sd soil with application of the WTR. In the Ia-C and Nb-F1 soils application of lime did likewise, which indicated that this reduction could be associated with an increase in pH. Because both of these extractants measure available P, a similar behaviour is expected and this is confirmed here, including in samples where lime was added. The sodium hydroxide extractable fraction increased drastically in the Hu-M soil, only slightly in the Nb-F1 and Sd soils, and decreased slightly in the Hu-T and Ia-C soils. Where the Ia-C soil was limed, no clear pattern was evident whereas in the limed Nb-F1 soil there was a slight decrease in this fraction. The Ia-C soil was the only one in which the HCl fraction did not drastically increase with application of the WTR. Thus in almost all soils the application of the WTR converted P to the highly reaction-resistant calcium phosphate fraction, confirming results obtained by Jonasson (1996). This seemingly occurs in part at the expense of P associated with Al and Fe components. This might happen because the increase in pH brought about by the WTR favoured this redistribution.

#### 8.3.4.2 Incubation experiment soils

Some changes were found (Table 8.4) compared to samples from the pot experiment. For example, in the Hu-M soil the sodium bicarbonate fraction decreased slightly as compared to a large decrease in the sample from the pot experiment. The Ambic fraction on the other hand increased as compared to showing virtually no change in the pot experiment samples. In the Hu-T soil also, these two fractions increased in the incubation samples but were virtually unchanged in the pot samples. It could be that the behaviour of applied P (as in the pot experiment) differed from that of native P (as in the incubation experiment). That a WTR might interact with applied P but not native P was reported by Elliott and Singer (1988) for Fe WTR-treated soils. There was an increase in P in the sodium hydroxide fraction of the Hu-M and Nb-A soils, a decrease in the Hu-F, Ia-C, Nb-F, Va and

**Table 8.3** Fractionation of P in soil samples from the pot experiment

Soil	Treatment	Calcium chloride	Ambic	Sodium bicarbonate	Sodium hydroxide	Hydrochloric acid
	(Mg ha <sup>-1</sup> )			(mg kg <sup>-1</sup> )		
Hu-M	R0	0.4	8.9	13.0	38.0	4.9
	R120	0.4	7.3	3.4	153.5	12.9
Hu-T	R0	0.4	13.8	3.6	135.8	4.4
	R120	0.4	11.2	4.9	113.8	9.7
Ia-C	L0R0	0.2	8.0	16.9	195.2	2.4
	L0R120	0.3	8.1	5.8	185.4	4.0
	L1R0	1.9	5.9	7.7	218.0	3.1
	L1R120	0.5	6.7	7.7	186.0	4.6
Nb-F1	L0R0	0.5	105.4	70.2	121.5	12.2
	L0R120	0.8	48.4	52.1	131.1	57.8
	L1R0	1.9	82.2	60.8	113.9	19.9
	L1R120	0.5	45.0	44.6	123.7	55.1
Sd	R0	0.9	6.0	0.9	161.9	5.7
	R120	1.0	9.2	2.0	189.8	14.1

R=water treatment residue; L=lime

We soils, and an unchanged situation in the Hu-T and Sd soils. The calcium chloride and HCl fractions gave similar results for all soils, the former with no change and the latter with increases when the WTR was applied.

Even within the same soil, certain factors have been found to result in different behaviour of P e.g. P concentration and concentration of background electrolyte (Eze and Loganathan, 1990), and pH (Chen and Barber, 1990; Eze and Loganathan, 1990; Naidu, Syers, Tillman and Kirkman, 1990). The different chemical and mineralogical environments between, and different chemical environments within, similar soils (pot vs incubation experiments), would thus be expected to cause different reactions of P. Application of the WTR with its own properties could cause further differences in both the manner and extent of P behaviour in the soils. No reason can be forwarded for the current situation.

### 8.3.5 Phosphorus extracted from field samples

The September 1998 samples from Brookdale Farm are from untreated plots, whilst the other samples follow application of fertilizers (including P) as from April 1999 (Section 5.2.4). The untreated samples from Ukulinga Farm are in February 2000. In this experiment fertilizer applications were commenced in April 2000. These sampling and fertilizer application practices thus account for the differences in Ambic extractable P at 0 Mg ha<sup>-1</sup> rate of WTR. To explain the lower P observed in the soil samples from the incorporated treatment compared to the control, it is proposed that there could have been some sorption of this element by the WTR (Section 8.3.2). This argument might also hold for the mulched treatment (except for February 2001), considering that some form of Ca might move from the mulch into the soil. As has been indicated (Section 8.3.4), some relatively insoluble calcium phosphates seem to be connected with application of the WTR. The consistently lower P extracted from the incorporated treatment indicates higher induced sorption since the WTR is more effective when mixed with the soil.

The P extracted by calcium chloride did not exhibit any difference with respect to either time or rate of WTR application. The results of Chen and Barber (1990) showed different changes between soil solution and resin-extractable P on liming, with the former decreasing and the latter increasing. The dissimilar trends observed between the Ambic- and calcium chloride-extractable P are thus not necessarily spurious. In the Brookdale soil the calcium chloride-extractable P concentrations range between 0.8 and 1.5 mg kg<sup>-1</sup> which are equivalent to 0.40 and 0.75 mg L<sup>-1</sup>, respectively. For the Ukulinga soil the P solution concentration is on average 0.7 mg L<sup>-1</sup>. For an element of low solubility such as P, these concentrations are high, and a possibility of transportation in runoff water needs to be considered. Concentration of P in the dam water at Brookdale (Appendix 7.1) does not seem to reflect the observations in Table 8.5. Also, the dates where high concentrations of P in the dam water were recorded do not seem to match high water turbidity (results not shown) as might be expected. There thus does not seem to be any inducement of external P transportation by the introduction of the WTR. The problem is whether any of the extractants can be used to predict P release, whether over land or vertically in soils.

**Table 8.4** Fractionation of P in soil samples from the incubation experiment

Soil	Treatment	Calcium chloride	Ambic	Sodium bicarbonate	Sodium hydroxide	Hydrochloric acid
	(Mg ha <sup>-1</sup> )			(mg kg <sup>-1</sup> )		
Hu-F	LOR0	1.0	4.8	4.2	323.3	5.7
	LOR120	1.0	3.3	4.9	187.6	41.0
	L1R0	0.5	6.3	12.8	419.2	6.2
	L1R1280	0.6	1.7	9.2	218.7	23.2
Hu-M	R0	0.6	0.2	6.6	139.2	3.8
	R1280	0.5	12.1	5.0	218.8	5.1
Hu-T	R0	3.3	4.9	2.1	109.9	2.2
	R1280	2.4	54.6	4.2	111.4	43.7
Ia-C	LOR0	0.1	3.2	11.3	146.8	2.9
	LOR120	0.2	1.6	1.0	109.2	17.7
	L1R0	0.0	2.5	12.2	141.1	5.5
	L1R1280	0.2	2.1	2.0	116.9	12.9
Nb-A	R0	1.0	0.3	0.5	27.1	2.5
	R1280	0.3	5.4	6.8	67.2	74.6
Nb-F	R0	0.7	18.4	37.4	264.0	39.5
	R1280	0.8	8.2	13.6	114.1	92.0
Sd	R0	0.1	0.2	0.6	117.8	5.7
	R1280	0.2	1.6	1.4	118.6	43.4
Va	R0	0.7	10.3	10.9	249.8	53.3
	R1280	1.0	9.4	9.1	127.9	89.3
We	R0	1.1	4.0	1.5	192.7	14.8
	R1280	1.1	5.9	5.1	129.6	54.7

R=water treatment residue; L=lime

Since balancing the intensity (solution) and capacity (sorbed) factors is important, depending on just the soluble P to make predictions of mobility might not be enough. The Ambic extractant, on the other hand, measures some sorbed but relatively easily mobilized P. It thus should be a better indicator of P behaviour than the calcium chloride extract. Even this would be somewhat empirical (Agbenin and Tiessen, 1994; Dodor and Oya, 2000) as not all the pool of P controlling the solution conditions might be catered for. As some support to this view, Börling, Otabbong and Barberis

(2004) established that sodium bicarbonate-extractable P (which behaves similarly to Ambic) could not be used alone to predict potential release of P by soils.

**Table 8.5** Calcium chloride and Ambic extractable phosphorus in selected soil samples from the Brookdale and Ukulinga Farms

Field site	Sample date	WTR rate	Calcium chloride	Ambic
		(Mg ha <sup>-1</sup> )	(mg kg <sup>-1</sup> )	
Brookdale	September 1998	0	0.8	5.8
	February 1999	0	1.3	13.0
		1280i	1.3	12.0
		1280m	1.3	17.5
	February 2000	0	1.0	13.0
		1280i	1.0	6.5
		1280m	1.0	8.3
	February 2001	0	1.0	10.5
		1280i	1.3	7.0
		1280m	1.3	13.8
Ukulinga	February 1999	0	1.3	5.0
			1.3	
	February 2001	0	1.5	10.5
		1280	1.5	7.3

i = incorporated treatment; m = mulched treatment

#### 8.4 Conclusions

The determination of P sorption isotherms for a range of soils has revealed differences between them after addition of the WTR. Fractionation of P has yielded results that do not seem to follow any particular pattern. This approach to the study of P is not recommended for future investigations,

as it is laborious and does not yield any useful results. Soils with different properties appear to behave similarly suggesting that the mechanisms at work are different between them. Changes in P sorption as a result of incubation likewise reveal differences between the soils although no conclusive reasons are obvious from the results obtained in this study. Such results are not unusual since the literature contains many conflicting accounts as regards the soil properties that affect P behaviour in soils. In perhaps the largest study undertaken on P dissolution (Sale, *et al.*, 1997) it was found that no single soil factor could adequately predict the dissolution of phosphate rock fertilizer or the subsequent behaviour of the released P at 26 long-term field sites across Australia.

Although it is clear that the WTR is responsible for P sorption the differences in the field between the control plots and those amended with the highest amount of WTR are not great. Further, despite the evidence of both the laboratory experiments and the P extraction data from the field trial soils, at both sites there was no analytical or visual evidence of this sorption causing deficiencies of P that affected the growth of either the perennial ryegrass or the tall fescue (Chapter 5). This evidence is in agreement with the studies discussed in Chapter 2 that have observed that P deficiency due to WTR application is restricted to pot experiments. The few field studies that have been conducted have not indicated any substantial problems with P deficiency and have given rise to the possibility that WTRs may act as slow release fertilizers. In addition, from an environmental perspective, the P sorbing capacity of WTRs may be of potential benefit in situations where leaching of P is a problem such as on coarse-textured soils or where over-fertilization with P on finer-textured soils has exceeded the sorption capacity of the soil.



## CHAPTER 9

### WATER TREATMENT RESIDUE AND BEHAVIOUR OF SOME HEAVY METALS

#### 9.1 Introduction

The concentrations of heavy metals in soils raise concern for three possible reasons, i.e., deficiency of those which are nutrients, toxicity to animals or plants and migration to water bodies.

The fate of metals, whether native or anthropogenic in the soil, is determined by the extent of their retention by soil constituents. Retention is, in turn, governed *inter alia* by the chemical and physical properties of the soil which determine the form of the metal. The form of the metal, e.g. soluble, exchangeable, etc., controls the extent of mobility which decides whether the cation migrates or not and, if so, at what rate and to what extent. Amongst chemical properties affecting sorption are pH (Ma and Liu, 1997; Filius, Streck and Richter, 1998), other cations (Bibak, 1997; Hanafi and Sjaiaola, 1998) and electrolyte or soil solution concentration (Pardo and Guadalix, 1996; Escrig and Morell, 1998).

An investigation by Li, Hue and Hussain (1997) showed a change of Mn and Zn from organic to carbonate forms in a neutral Mollisol but to exchangeable forms in an acid Ultisol, the diminishing form being explained by the decomposition of organic matter. Pre-treatment of Andosols with phosphate before adding Zn resulted in an increase in the exchangeable and Fe-Mn bound forms of Zn (Ahumada, Bustamante and Schalscha, 1997), the former ascribed to phosphate sorption having increased the surface negative charge. Ma and Uren (1997), studying the fate of Zn in soils, concluded that when newly applied this metal was present as soluble and exchangeable forms but transformed into unreactive forms associated with Al, Fe and Mn oxides with time.

Contamination of soils by heavy metals is of importance for ecological and health reasons (Lehoczky, Szabados and Marth, 1996), the former presumably associated with metal migration to

the groundwater and hence water bodies, whilst the latter could be linked to direct uptake by plants or animals. Whilst it is generally considered that most heavy metals are virtually immobile in soils (Karathanasis, 1999), there are nevertheless conditions under which this appears to be incorrect. This deviation from the usual is reflected in increases in plant uptake and/or redistribution in soil profiles.

Downward movement of metals in profiles has been particularly associated with sewage sludge (Section 2.3). Studying metal concentrations of surface and subsurface soils, Moalla and Pulford (1995) concluded that flooding could lead to lowering of redox potential that could mobilize and encourage redistribution of iron. Arnesen and Singh (1998) reported increases in plant-available Cu and Zn following application of some organic materials. Organic anions derived from these materials presumably formed relatively soluble complexes with these cations. Subsurface migration of Cu and Zn has been shown to be enhanced by colloids in a laboratory study with undisturbed columns (Karathanasis, 1999). Application of urea was found to increase Cd concentrations in durum wheat grain grown in a pot experiment (Mitchell, Grant and Racz, 2000). The effects were attributed to increase in ionic strength and cation exchange involving Cd and ammonium, a product of urea hydrolysis.

Disposal of the WTR to land, by virtue of it containing some heavy metals, would constitute anthropogenic addition of these species. These metals in the WTR would add to those already in the soils from weathering of minerals. The view of Naidu, Kookana, Sumner, Harter and Tiller (1997) is that anthropogenic additions pose a greater threat to the environment because of access to animal and plant uptake at the surface, and also because metal forms from such sources are more bioavailable and soluble since they are environmentally unstable.

Forms of metals in WTR have been studied (Elliott, Dempsey and Maille, 1990) but were confined to alum and ferric chloride materials and not extended to soils treated with the material. Of concern in the current study was the behaviour of metals in soils treated with WTR.

The objectives of this chapter are as follows:-

- to determine the effect of the WTR on metal sorption by soils; and
- to establish the transformation of selected metals in soils on introduction of the WTR.

## **9.2 Materials and methods**

### **9.2.1 Soils**

All 11 soils (Table 3.1a) were used in this study. Samples from the pot experiment (Chapter 4) and the incubated soils (Chapter 6) were included in some aspects of the investigation.

### **9.2.2 Determination of time-sorption relationships**

To duplicate 1 g samples of soil in a centrifuge tube were added 50 mL of 0.005 M calcium chloride solution containing 167  $\mu\text{g}$  of Cd, Ni and Zn. Cadmium was chosen because of its potential toxicity to plants and humans, Ni as an indicator element for disposal of sewage sludge, and Zn as a micronutrient with possible deficiencies. The suspension was shaken end-over-end for 0.25, 1, 2, 4, 8, 24 and 48 hours. After each shaking period, the corresponding tubes were removed for centrifugation and filtration. The metals were analysed by atomic absorption spectrophotometry (AAS).

### **9.2.3 Sorption of metals as affected by amount of water treatment residue**

To duplicate 1 g incubated WTR-treated soil samples were added 50 mL of 0.005 M  $\text{CaCl}_2$  solution containing 50  $\mu\text{g}$  of Cd, Ni or Zn. After 6 hours of end-over-end shaking, the suspensions were centrifuged, filtered and analysed by AAS.

To test whether these three cations would provide effective competition for sorption, the same

procedure as outlined above was followed but with the metals either put in singly or all three simultaneously in the same tube. Samples considered were the incubated soils where the WTR was added at rates of 0 and 1280 Mg ha<sup>-1</sup>.

#### 9.2.4 Fractionation of metals

Metal fractions in WTR and soil samples treated with WTR (and lime in some cases) were determined by the method of McLaren and Crawford (1973) as modified by Johnson and Petras (1998) to be a completely parallel rather than a partly sequential extraction. The method involves separating the fractions into water soluble + exchangeable by calcium chloride extraction, inorganically bound extracted with acetic acid, organically bound extracted with potassium pyrophosphate, that bound in amorphous oxides extracted with acid ammonium oxalate and the mineral lattice (residual) form as analysed in a sulphuric acid/hydrofluoric acid digest. All extractions were in duplicate. The residual fraction was not included in the current study.

Included in this fractionation experiment were soil samples from the pot experiment at 0 and 120 Mg ha<sup>-1</sup> of the WTR, with and without the higher rate of lime for the Ia-C and Nb-F1 soils, and samples of the incubated soils treated with 0, 80, 320 and 1280 Mg ha<sup>-1</sup> of the WTR as well as lime for the Hu-F and Ia-C soils. The metals considered, namely Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, were analysed by AAS.

#### 9.2.5 Depth distribution of metals in the field

The same heavy metals fractionated above were analysed in samples from the two field experiments. The objectives were to determine whether the WTR would have any effect on the concentration of metals, and also to establish if there was any discernible movement of these cations to a lower depth. Exchangeable metal forms, which have been suggested to indicate potential mobility (Sposito, Lund and Chang, 1982) were determined by shaking duplicate soil samples on an end-over-end shaker with 0.05 M CaCl<sub>2</sub> solution (Johnson and Petras, 1998) using a 1:2 soil to solution ratio. The

Brookdale samples analysed were for the years 1998 to 2001 from the 0-200, 200-400 and 400-600 mm depths. Samples from the Ukulinga experiment were from 0-200 mm for the year 1999 and all three depths for the year 2001. The Brookdale samples were from the plots where WTR was applied at rates of 0 and 1280 Mg ha<sup>-1</sup> (mulched and incorporated), and the Ukulinga samples were from plots treated with 0 and 1280 Mg ha<sup>-1</sup> WTR.

### 9.3 Results and discussion

#### 9.3.1 Time-sorption relationships

As expected, sorption of all three metals increased with time in all soils. Sorption at 8 hours was compared with that at the often used equilibration time of 24 hours (e.g. Pardo and Guadalix, 1996; Yuan and Lavkulich, 1997; Escrig and Morell, 1998; Hanafi and Sjiaola, 1998; Mesquita, 1998; Pardo, 2000). More than 90% of the Cd sorbed after 24 hours was sorbed by 8 hours in all soils and the WTR. This was the case also for Ni except in the Av soil (61.5%), Nb-A soil (82%) and Nb-F soil (87.8%). At least 90% of the Zn was also sorbed except in the Ia-C (82%) and Ia-W (72.9%) soils. It was notable that all the soils where amount sorbed by 8 hours was relatively low had comparatively low sorption behaviour according to Figures 9.1a, b and c. Rupa and Tomar (1999) also reported similar sorption results between high and low Zn-sorbing soils; in their experiments 60% of added Zn was sorbed within 4 hours by the former soils, an amount which the low-sorbing soils could only achieve in 24 hours.

#### 9.3.2 Comparative extent of sorption

For all metals, the WTR sorbed more than any of the soils. In fact almost all the added Cd and Zn was sorbed in 48 hours, with the amount of Ni sorbed being the lowest at 160.4 mg kg<sup>-1</sup> (96%). This raises the possibility that application of the WTR to soil would enhance the soil's retention capacity for metals and so reduce their mobility, and maybe their availability to plants. The soils could be divided into three groups with comparatively high, moderate and low sorption capacity for all three

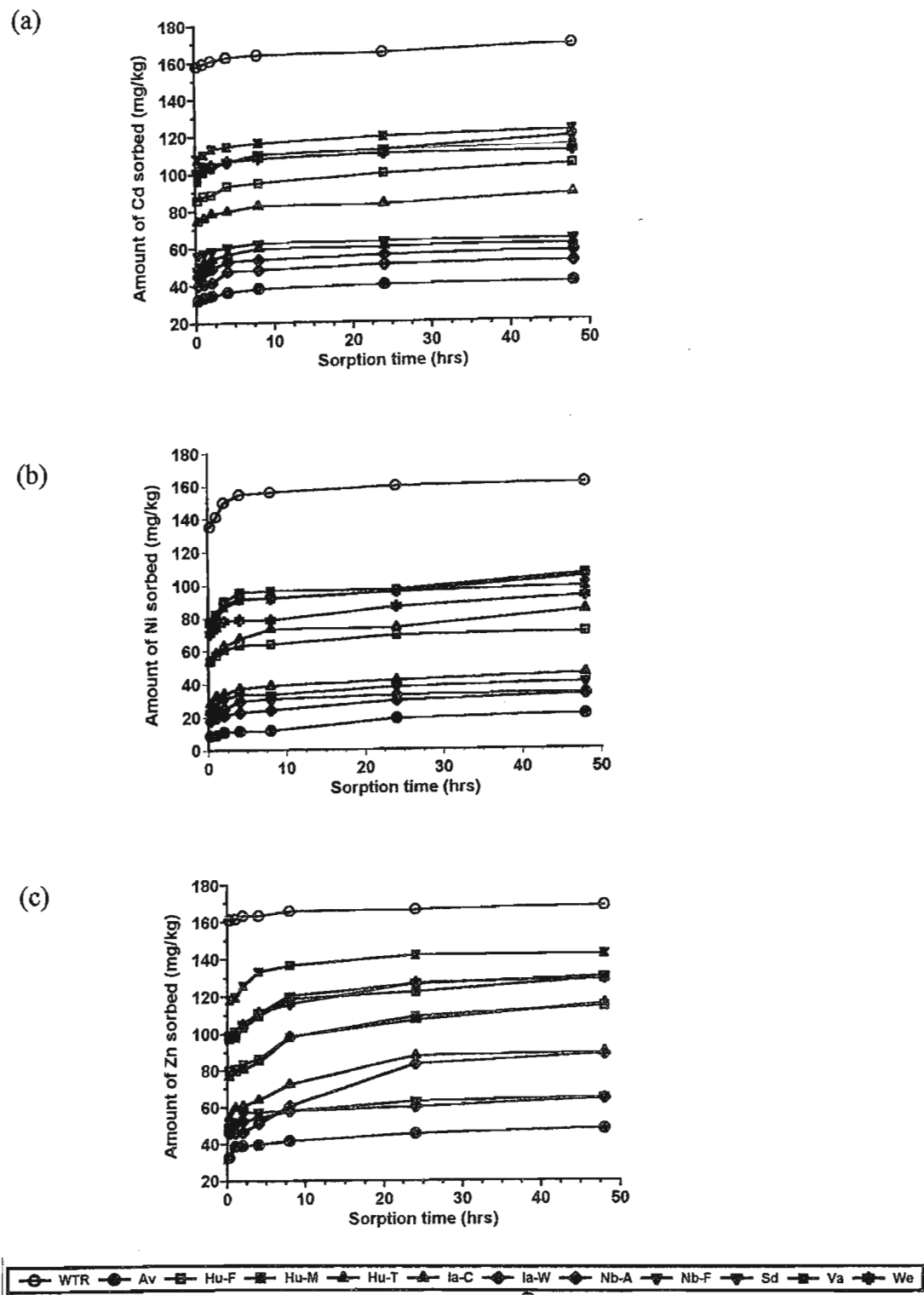


Figure 9.1 Dependence of sorption of (a) Cd; (b) Ni and (c) Zn on shaking time in different soils

metals. The last group consisted of the Av, Ia-C, Ia-W, Nb-A and Nb-F soils where the amount sorbed ranged from 40.2 to 63.3 mg kg<sup>-1</sup> for Cd, 20.8 to 45.1 mg kg<sup>-1</sup> for Ni and 48.0 to 89.5 mg kg<sup>-1</sup> for Zn. The Hu-F and Hu-T soils made up the middle group where the extent of sorption for Cd, Ni and Zn was 103.3 and 87.5 mg kg<sup>-1</sup>, 70.2 and 83.5 mg kg<sup>-1</sup>, and 114.2 and 115.4 mg kg<sup>-1</sup> in the Hu-F and Hu-T soils, respectively. The group with the highest sorption capacity consisted of the Hu-M, Sd, Va and We soils. The highest amounts of metal sorbed were between 110.4 and 121.4 mg kg<sup>-1</sup> for Cd, 92.0 and 105.3 mg kg<sup>-1</sup> for Ni, and 128.8 and 142.1 mg kg<sup>-1</sup> for Zn. The soils with a low sorption capacity were either highly weathered (Av, Ia-C and Ia-W) or coarse-textured (Nb-A and Nb-F). In addition, all the soils except the Ia-C soil had comparatively low cation exchange capacity (CEC) (Table 3.1b). The Hu-F and Hu-T soils had comparatively moderate CECs, as well as being less highly weathered.

Those soils with relatively high metal sorption capacities were moderately weathered and had comparatively high CEC. If the Ia-C soil is omitted, CEC could be considered to be the main factor to influence the extent of sorption of the metals as has been reported elsewhere for Zn (Prasad, Gowrisankar and Shukla, 1997; Singh, McLaren and Cameron, 1997; Pardo, 2000), and Cd and Zn (Hanafi and Sjiaola, 1998). Considering that sorption could increase with amount of clay (Mandal and Hazra, 1997; Prasad *et al.*, 1997; Mesquita, 1998), the Va should have been in the group of low-sorbing soils and the Ia-C in the group of high-sorbing soils. If these two soils were to be removed from consideration, then percent clay could be brought in as a strong factor of influence as well. A stepwise linear regression analysis was performed to test the contributions of acid oxalate-extractable Al and Fe, CEC, clay content, DCB-extractable Al and Fe and organic matter to the sorption of these metals. Only the CEC gave significant R<sup>2</sup> values of 0.759, 0.834 and 0.713 for Cd, Ni and Zn, respectively.

### 9.3.3 Effects of water treatment residue on sorption of metals by soils

The application of the WTR increased the amount of metal sorbed (Figures 9.2a to 9.2k) in all soils. This was an expected result considering that in Figures 9.1a to 9.1c it was established that the WTR

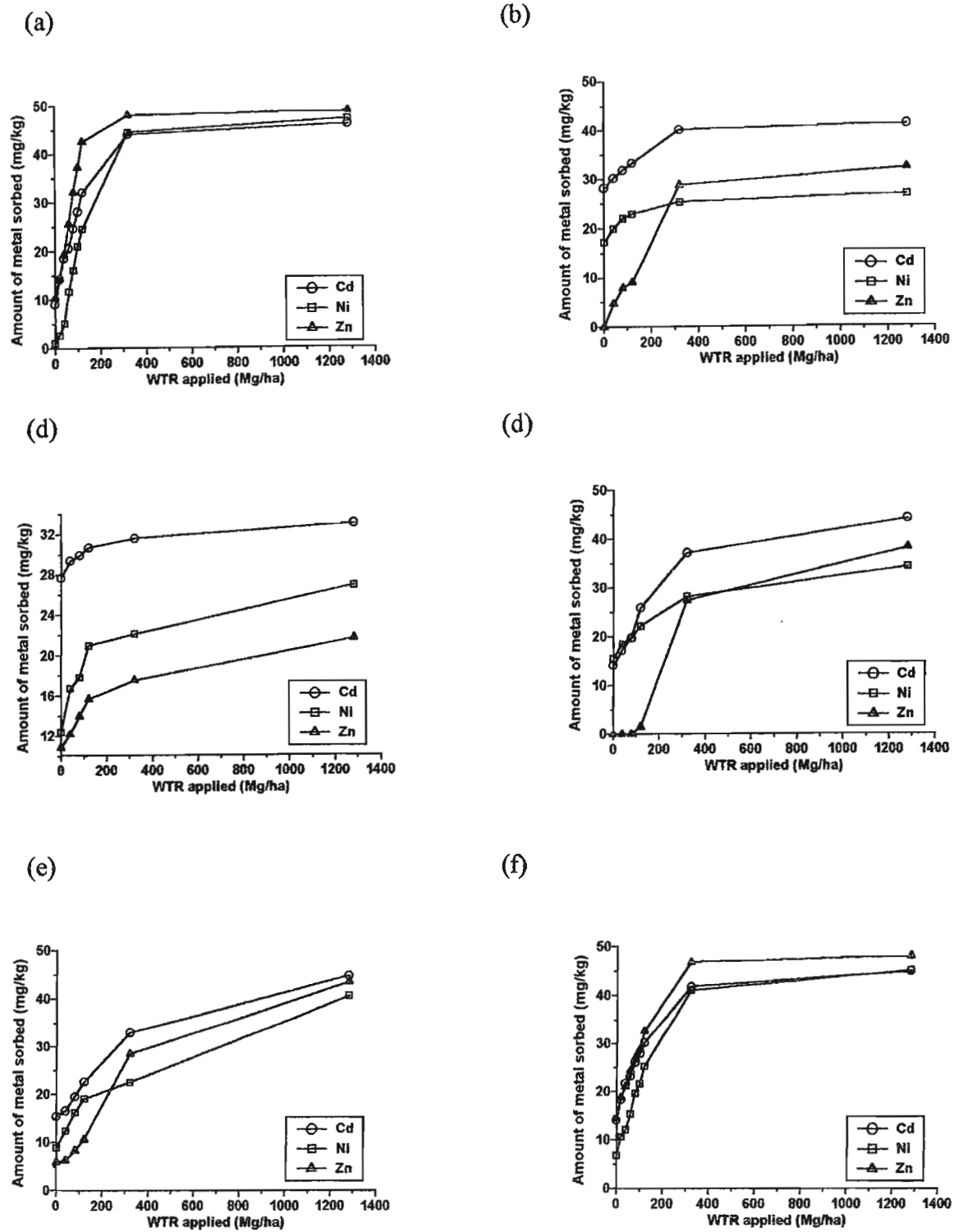
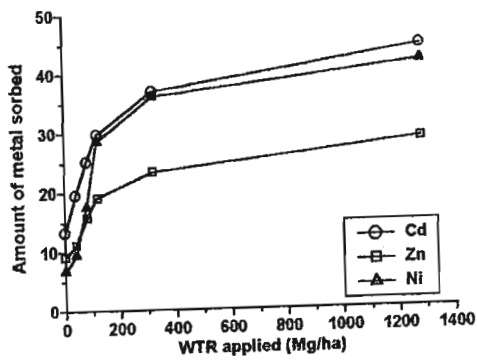


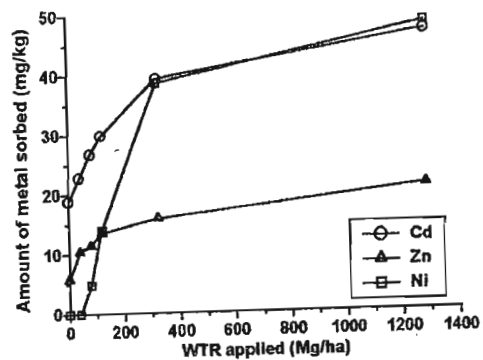
Figure 9.2 Sorption of Cd, Ni and Zn in the (a) Av, (b) Hu-F, (c) Hu-M, (d) Hu-T, (e) Ia-C and (f) Ia-W soils as affected by amount of WTR applied



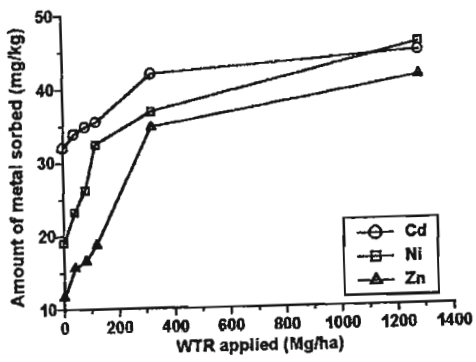
(g)



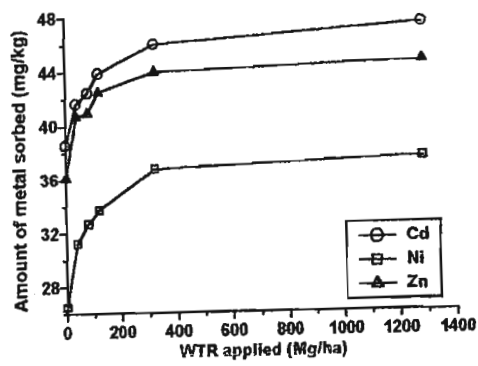
(h)



(i)



(j)



(k)

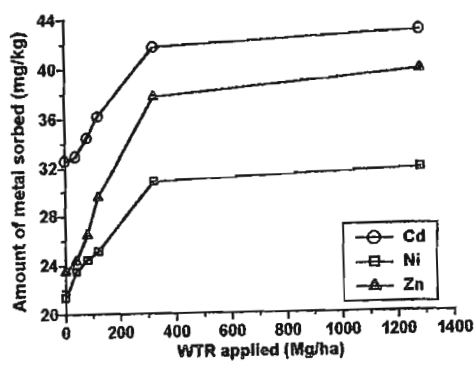


Figure 9.2 cont. Sorption of Cd, Ni and Zn in the (g) Nb-A, (h) Nb-F, (i) Sd, (j) Va and (k) We soils as affected by amount of WTR applied

had a higher sorption capacity than all the soils. No single pattern emerged as to the order of metal sorption by the soils. The Av and Ia-W soils followed  $Zn > Cd > Ni$ . The sequence  $Cd > Ni > Zn$  was associated with the Hu-F, Hu-M, Hu-T and Sd soils. The Nb-A, Va and We soils followed the order  $Cd > Zn > Ni$ . The Ia-C and Nb-F soils conformed to  $Cd > Ni > Zn$  at relatively low WTR levels and to  $Cd > Zn > Ni$  at high rates. Pardo (2000) also reported different preferences of three soils with respect to the extent of sorption for the metals Cd and Zn.

Where all three metals were simultaneously added in solution (labelled with -3 in Figures 9.3a to 9.3k), the amount of metal sorbed tended to be lower than when each metal was added on its own. Suppression of sorption of metals in the presence of others through competitive sorption was reported for Cu, Ni and Zn by Bibak (1997), Cu and Zn by Mesquita (1998), and Cd and Zn by Wilkins, Brummel and Loch (1998). Compared to these workers who used comparatively high concentrations of metals, the differences reported here are not significant. Thus at these concentrations, there was virtually no competitive sorption between the three metals. This was true even for the soils identified as low-sorbing, and at the 0 rate of WTR where no benefits of sorption sites from this material were possible.

#### 9.3.4 Metal fractions in the water treatment residue

Elliott *et al.* (1990) extracted some heavy metals from eight alum WTRs into similar fractions as done in this study although using a different procedure, and suggested caution when interpreting the results. Earlier, when performing fractionation of Cu in soils, McLaren and Crawford (1973), whose modified procedure was used in this study, had established by correlation statistics that the dilute-acid extractable fraction termed “inorganic” actually contained labile organic fractions as well. The result for the organic fraction thus strictly refers to the fraction that is relatively stable under normal soil conditions.

The metal fractions from the analysis of the WTR are presented in Table 9.1. There are zero levels of the metals analysed in the exchangeable fraction from the WTR, implying that were this

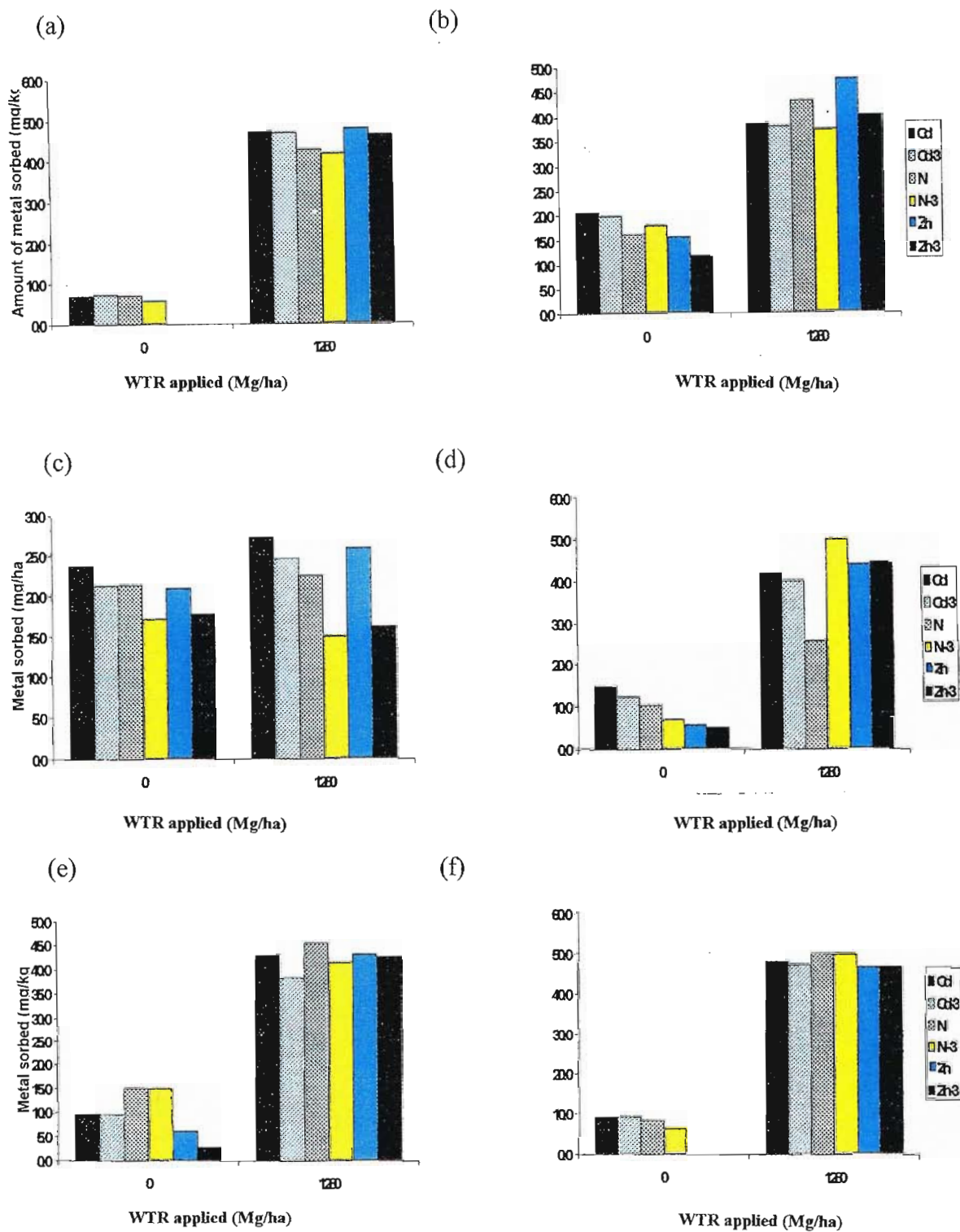


Figure 9.3 Comparative sorption of Cd, Ni and Zn in the (a) Av, (b) Hu-F, (c) Hu-M, (d) Hu-T, (e) Ia-C and (f) Ia-W soils as affected by amount of WTR applied

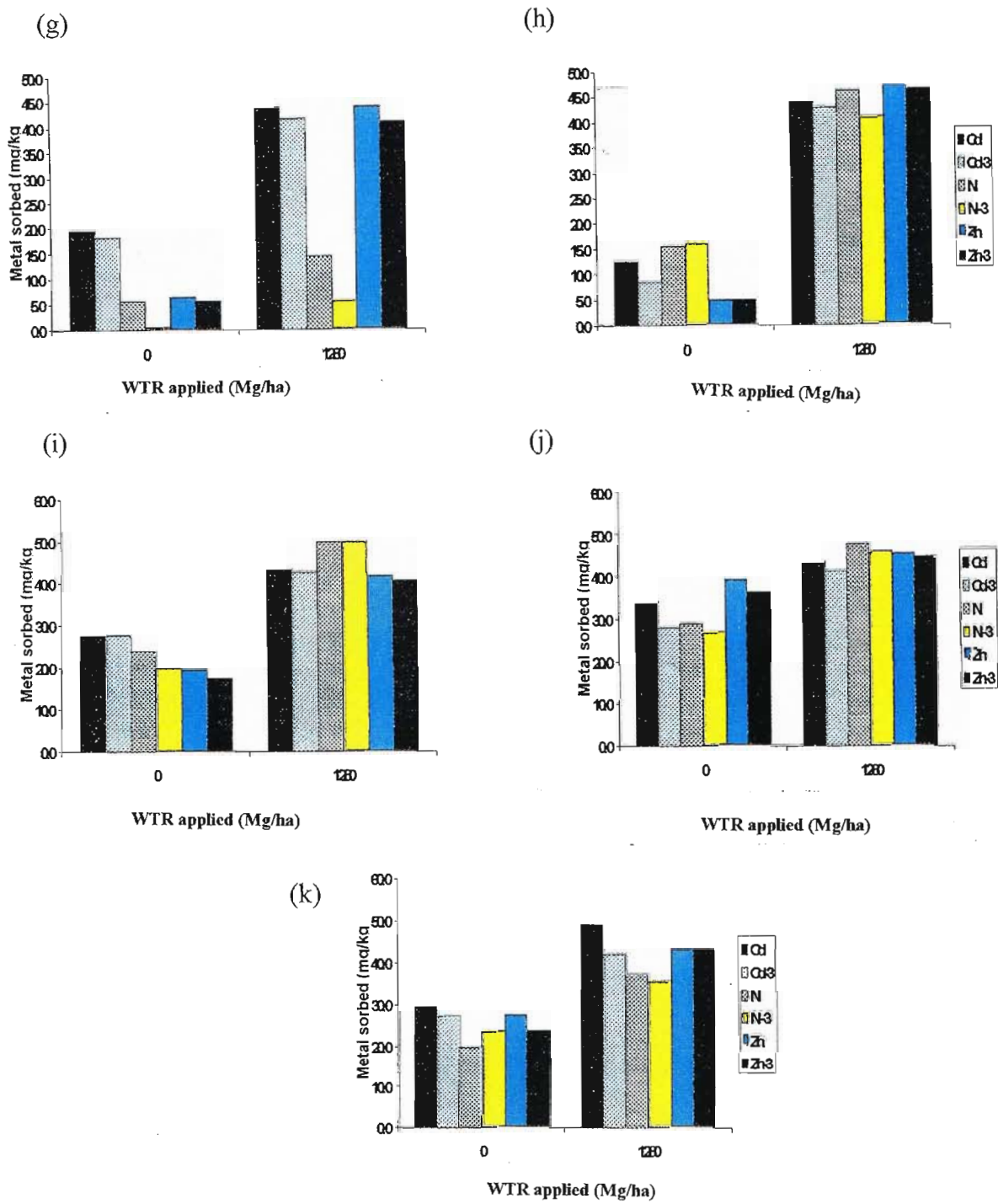


Figure 9.3 cont. Comparative sorption of Cd, Ni and Zn in the (g) Nb-A, (h) Nb-F, (i) Sd, (j) Va and (k) We soils as affected by amount of WTR applied

material to be added to soil, this fraction should either decrease or remain unchanged. This being the potentially mobile fraction (Sposito *et al.*, 1982), concerns about metals migrating down the soil profile in WTR-treated soils should be allayed. Only Mn was in high concentration in the inorganic fraction at 1681.9 mg kg<sup>-1</sup>. The other seven metals were all < 5 mg kg<sup>-1</sup>. Cadmium, Mn and Pb could not be detected in the organic fraction. In WTR-treated soils, the organic fraction of these metals would thus be expected to remain the same or to decrease. Metals which gave relatively high levels in this fraction, at around 20 mg kg<sup>-1</sup>, were Cr, Cu, Ni and Zn. Organic fractions of these metals in

**Table 9.1** Fractionation of selected metals in the water treatment residue

Metal	Exchangeable fraction	Inorganic fraction	Organic fraction	Amorphous fraction
(mg kg <sup>-1</sup> )				
Cd	0.0	0.4	0.0	0.0
Co	0.0	2.7	6.6	7.5
Cr	0.0	3.1	21.9	0.0
Cu	0.0	1.3	18.9	59.2
Mn	0.0	1681.9	0.0	3642.1
Ni	0.0	3.0	25.2	0.0
Pb	0.0	0.3	0.0	0.0
Zn	0.0	4.9	19.5	12.8

soils treated with the WTR would thus be expected to increase significantly or be maintained at a relatively high level. The metals detected in the amorphous fraction were Co at 7.5 mg kg<sup>-1</sup>, Cu at 59.2 mg kg<sup>-1</sup>, Mn at 3642.1 mg kg<sup>-1</sup> and Zn at 12.8 mg kg<sup>-1</sup>. Concentrations of amorphous Cu and Mn would thus be expected to change with application of the WTR to soils, whilst some effect on Co and Zn could also occur.

### 9.3.5 Metal fractions in soil samples from the pot experiment

Soil samples from the pot experiment conformed to the observations above. The exchangeable fraction of the metals were either 0 mg kg<sup>-1</sup> (Cd, Co, Cr, Cu, Ni and Pb) or showed a reduction (Mn, Zn) (Appendices 5.1 to 5.5). Metals whose inorganic fractions were affected by the WTR were Mn and Zn, with their concentrations increasing in all soils. Manganese was the metal which was notably affected in the organic fraction by application of the WTR. Although the Hu-T and Sd soils registered relatively unchanged concentrations, this fraction decreased in the Hu-M, Ia-C and Nb-F1 soils in agreement with earlier expectations. This decrease might be as a result of decomposition of organic matter as reported by Li *et al.* (1997), or may be a straightforward physical dilution brought about by the WTR lacking organic Mn. In the amorphous fraction, Co, Cu and Mn concentrations increased as expected in all soils, although it was only for Mn that these changes were very high. For Cu especially, more significant changes were expected considering its relatively high concentration in the WTR (Table 9.1).

### 9.3.6 Metal fractions in soil samples from the incubation experiment

The incubated fractions (Appendices 6.1 to 6.9) also tended to conform to the expectations created by the metal fractions in the WTR. The metals most affected were Mn and Zn, although Co and Cu were present in some amorphous fractions. In the Hu-F (Appendix 6.1) and Hu-M (Appendix 6.2) soils exchangeable Mn increased with increase in application rate of the WTR, much against expectations. From 0 to 1280 Mg ha<sup>-1</sup>, Mn concentrations increased from 6.8 to 12.4 mg kg<sup>-1</sup> and from 65.0 to 89.1 mg kg<sup>-1</sup> in the Hu-F and Hu-M soils, respectively. The concentrations of Mn and Zn in the inorganic fractions increased in all soils. With respect to the organic fraction, application of the WTR either decreased or did not affect the levels of any of the metals except in the Hu-F (Appendix 6.1), Ia-C (Appendix 6.4), Nb-F (Appendix 6.6) and Sd (Appendix 6.7) soils where Zn concentrations increased. The amorphous forms of Mn and Zn increased in all soils, and in some soils addition of the WTR also affected Co (Va, Appendix 6.8) and Cu (Ia-C, Appendix 6.4; Nb-A, Appendix 6.5; Sd, Appendix 6.7).

### 9.3.7 The effect of lime on metal fractions

There was no consistency concerning the effects of lime in either the samples from the pot experiment or the incubated soils. The generally low concentrations of metals combined with few treatments for comparison made it difficult to pick up any trends. Observations are possible for Mn the concentrations of which were relatively high. Exchangeable Mn decreased with application of lime in the Ia-C (Appendix 5.3) and Hu-F (Appendix 6.1) soils whether the WTR was added or not, and remained virtually unchanged in the Nb-F1 soil (Appendix 5.4) under the same treatments. This behaviour of Mn in the Ia-C and Hu-F soils showed that an increase in pH, caused by either the WTR or the lime, contributed to a reduction in exchangeable Mn. Essentially similar results were observed in the incubated Ia-C soil (Appendix 6.4) where exchangeable Mn was decreased by application of lime. In the presence of 1280 Mg ha<sup>-1</sup> of WTR, however, the lime effect was not evident.

Application of lime increased the inorganic Mn fraction in the Ia-C (Appendix 5.3), Hu-F (Appendix 6.1) and Ia-C (Appendix 6.4) but caused a decrease in the Nb-F1 soil (Appendix 5.4). Although it was only in the Hu-F soil that the changes were statistically significant, the results nevertheless prompted speculation about the fate of the exchangeable Mn. It was in the Nb-F1 soil where no decrease in exchangeable Mn was registered that a slight decrease in the inorganic fraction of the metal was noted. In the other three soils, it is possible that some of the exchangeable Mn was converted to the acid-soluble inorganic fraction with application of either the lime or the WTR. Organic Mn decreased with lime application in all the soils except the Nb-F1. These results could be explained by decomposition of organic matter that breaks down some Mn-organic matter complexes because of an increase in pH. The exception, Nb-F1 soil, had a very low content of organic matter. Statistically non-significant changes in amorphous Mn were noticed in the four soils with all showing an increase except the Ia-C sample from the pot experiment (Appendix 5.3) where this fraction decreased. It would therefore seem that the increase in this fraction with application of the WTR was not only due to the amorphous fraction from this material, but also that an increase in soil pH could favour the formation of such fractions (e.g. Mortvedt, 2000).

### 9.3.8 Comparison of metal fractions in soil samples from pot and incubation experiments

On comparing the soils used in both the pot and incubation experiments, namely the Hu-M, Hu-T, Ia-C, Nb-F1, Nb-F and Sd, it was noted that some metal concentrations were very different. The Nb-F and Nb-F samples used were sampled from different parts of the Farm and had different properties (Table 3.1b) and thus could be expected to yield different results. Similarities were expected from the Hu-M, Hu-T, Ia-C and Sd soils. Consideration was given to the 0 WTR samples only as the others had non-comparable treatments. Except for a few exceptions, the concentrations of all metals were mostly comparable in the two experimental samples with the main exception of Mn. In the Hu-M soil (Appendices 5.1 and 6.2) the other exceptions were amorphous Cu and organic Zn. Copper concentrations were  $2.3 \text{ mg kg}^{-1}$  in the pot soils but  $7.6 \text{ mg kg}^{-1}$  in the incubated samples, with Zn being  $24.8$  and  $10.7 \text{ mg kg}^{-1}$ , respectively. In the Hu-T soil (Appendices 5.2 and 6.3) the differences were in organic Co ( $2.3$  vs  $7.6 \text{ mg kg}^{-1}$ ) and amorphous Cu ( $0$  vs  $7.5 \text{ mg kg}^{-1}$ ) in pot vs incubated samples. There were no obvious differences in corresponding fractions in the Sd soil (Appendices 5.5 and 6.7).

As has been pointed out, Mn showed the greatest differences in all 4 soils and fractions. There were consistencies in the differences in that concentrations of the exchangeable and organic Mn fractions in the incubated samples were higher than in those from the pot experiment samples, and the inorganic Mn from pot experiment samples was higher than from the incubated samples. As the exchangeable fraction would be part of the plant available fraction, it is possible that uptake by the grass plants had reduced this form of Mn compared to incubated samples. Concerning the organic fraction, it could be that alternate wetting and drying as occurred during the pot experiment was more favourable for organic matter mineralization than the stable water conditions experienced by the incubated samples, or that the labile organic fraction was taken up by the plants.

Reasons for metal fractions of the same soil samples from the pot and incubation experiments in some cases not being similar may be explained as follows. The samples were subjected to different environments with respect to moisture regime, soil solution concentration and active cations present,



the last two caused by fertilizer (pot experiment) and no fertilizer application (incubation experiment). Competition between cations (Bibak, 1997; Mesquita, 1998), solution concentration (Pardo and Guadalix, 1996; Escrig and Morell, 1998), *in situ* drainage status (Chowdhury, McLaren, Cameron and Swift, 1997), and continuous flooding or alternate wetting/flooding and drying (Mandal and Hazra, 1997) change the amount of sorption and/or distribution of metals between fractions. Sorption can be by different mechanisms where metals can resort to exchangeable forms by electrostatic attraction, or to less mobile fractions through formation of covalent bonds with specific sorption sites (Pardo and Guadalix, 1996).

### 9.3.9 Depth distribution of metals in the field experiment soils

#### 9.3.9.1 Brookdale Farm

In the soil at Brookdale, only Cd, Mn and Zn (Table 9.2) were detected. As in the fractionation experiments, it was again Mn that was in relatively high quantities. For Cd (all  $< 2 \text{ mg kg}^{-1}$ ) and Zn (from  $0.5$  to  $1.3 \text{ mg kg}^{-1}$ ) the levels were too low to make an informed decision on the effects of either the WTR or time. For Mn, however, the concentrations were relatively high.

At the 0-200 mm depth, there was a reduction in exchangeable Mn where the WTR had been applied at all sampling times, except in 1999 for the incorporated treatment. The dilution of the soil by the WTR, which had virtually no exchangeable Mn, could explain the results for the incorporated treatment. The lower levels on the mulch treatment could be attributed to a cation such as Ca affecting the mobility of the Mn. The longer persistence of moisture under the WTR mulch would also encourage the leaching of Mn by favouring some formation of the more mobile  $\text{Mn}^{2+}$ . At the 200-400 and 400-600 mm depths, the concentrations of this metal were higher where the WTR was applied compared to the control. The Mn lost from the 0-200 mm depth could thus be enriching the lower depths.

There was a decrease of exchangeable Mn with time at the 0-200 mm and 200-400 mm depths for

**Table 9.2** Distribution of some heavy metals ( $\text{mg kg}^{-1}$ ) in selected depth samples from 1999 to 2001 at Brookdale Farm with selected rates of water treatment residue

Metal	WTR rate (Mg/ha)	Year	0-200	200-400 (mm)	400-600
Cd	0	1999	0.2	0.1	0.1
		2000	0.2	0.1	0.1
		2001	0.2	0.2	0.2
	1280i	1999	0.1	0.1	0.1
		2000	0.2	0.2	0.2
		2001	0.2	0.2	0.2
	1280m	1999	0.1	0.1	0.1
		2000	0.2	0.2	0.2
		2001	0.2	0.2	0.2
Mn	0	1999	90.4	51.1	5.9
		2000	52.5	4.0	1.4
		2001	79.5	34.4	4.3
	1280i	1999	86.7	70.1	9.3
		2000	2.8	22.4	3.2
		2001	45.6	41.8	17.9
	1280m	1999	49	79.2	10.7
		2000	0.9	42.4	2.6
		2001	25.2	48.6	29.3
Zn	0	1999	0.9	0.4	0.3
		2000	1.0	0.5	0.4
		2001	1.3	0.7	0.5
	1280i	1999	1.1	0.6	0.4
		2000	0.8	0.6	0.6
		2001	1.1	0.5	0.4
	1280m	1999	0.4	0.5	0.4
		2000	0.5	0.7	0.5
		2001	0.6	0.9	0.6

all three treatments from 1999 to 2001. The increases at the 400-600 mm depth also suggests the mobility of Mn in the conditions of this study. This possibility was also predictable from the incubated soil results (Section 9.3.4) where exchangeable Mn (Appendix 6.1) increased with increase in rate of the WTR applied in the Hu-F soil. The WTR applied by incorporation effected increases from 9.3 to 17.9 mg kg<sup>-1</sup> from 1999 to 2001, whereas the corresponding effects of the mulch treatment were from 10.7 to 29.3 mg kg<sup>-1</sup>. The results of 2000 tended to be anomalous in comparison with the other years, perhaps because of sampling or analytical error. Although there was evidence of downward movement of Mn, there was no evidence of it enriching the groundwater as shown by analytical results of the borehole water (Appendix 7.1).

#### 9.3.9.2 Ukulinga Farm

Manganese was in relatively high concentrations at the 0-200 mm depth (Table 9.3). Other metals detected were Cd, Co, Cu, Ni, Pb and Zn at low concentrations, mostly less than 0.5 mg kg<sup>-1</sup> and with no influence of the WTR apparent. The dilution effect of the application of the WTR was clear with the application of the material decreasing Mn concentrations from 66.5 to 52.8 mg kg<sup>-1</sup> in 1999 and from 20.0 to 1.2 mg kg<sup>-1</sup> in 2001. Since the lower depths did not show any evidence of an increase in exchangeable Mn, the decrease with time could be caused by changing to other forms. In the We soil (Appendix 6.9) it was established that exchangeable Mn decreased with increase in the amount of the WTR applied whilst the inorganic and amorphous fractions, which are not extractable by a neutral salt solution, increased.

**Table 9.3** Distribution of some heavy metals ( $\text{mg kg}^{-1}$ ) in selected depth samples in 1999 and 2001 at Ukulinga Farm with selected rates of water treatment residue

Metal	WTR rate (Mg/ha)	Year	0-200	200-400 (mm)	400-600
Cd	0	1999	0.1	0.0	0.0
		2001	0.1	0.1	0.3
	1280	1999	0.1	0.1	0.1
		2001	0.1	0.0	0.0
Co	0	1999	1.3	0.0	0.0
		2001	2.2	1.3	1.0
	1280	1999	0.7	1.1	1.3
		2001	0.8	0.0	0.0
Cu	0	1999	0.2	0.0	0.0
		2001	0.2	0.1	0.1
	1280	1999	0.2	0.5	0.1
		2001	0.2	0.0	0.0
Mn	0	1999	66.5	0.0	0.0
		2001	20.6	1.0	1.4
	1280	1999	52.8	0.8	1.8
		2001	1.2	0.0	0.0
Ni	0	1999	0.3	0.0	0.0
		2001	0.3	0.2	0.2
	1280	1999	0.2	0.4	0.3
		2001	0.2	0.0	0.0
Pb	0	1999	0.7	0.0	0.0
		2001	0.7	0.6	0.6
	1280	1999	0.5	0.7	0.6
		2001	0.5	0.0	0.0
Zn	0	1999	0.5	0.0	0.0
		2001	0.5	0.2	0.2
	1280	1999	0.3	0.4	0.3
		2001	0.3	0.0	0.0

## 9.4 Conclusions

When applied to soils under laboratory conditions, the WTR increased the amount of Cd, Ni and Zn sorbed, and the amount of sorption increased with time. The form of sorption was, in part, explained by the fractionation of these metals, together with Co, Cr, Cu, Mn and Pb, in soil samples from pot and incubation experiments. The metal fractions which generally increased in all soils were inorganic and amorphous forms, implying specific sorption and mineral layer penetration, respectively. Whichever mechanism is operative, the practical meaning is that the WTR was responsible for converting metals to less mobile forms, which would reduce the risk of groundwater pollution. It was only in the Hu-F and Hu-M soils that exchangeable fractions of Mn increased with application of the WTR, and then only in the incubated samples. It would thus be in soils under fallow that mobility of this metal must be expected. Similar results were observed in the field where Mn was the only one of the eight metals studied which appeared to have leached at the Brookdale experiment on the Hu-F soil.

The established immobilization of metals by introduction of the WTR appeared to reduce mobility of the metals but did not induce any deficiencies in perennial ryegrass and tall fescue grown in either pot or field experiments. The result of a 30-month long field experiment by Geertsema *et al.* (1994) with alum WTR showed essentially the same results. Soil analysis and soil water analysis established that metals incorporated with the WTR were not mobile within the soil profile. Also no differences were observed, with respect to growth and metal concentration (notably Mn), of pine trees growing on their WTR-treated plots.

These results, coupled with those of Chapters 4 and 5, show that land treatment of the WTR is a worthwhile option of disposing of the material. There were no agronomic negatives as plant growth was not adversely affected. Also, no environmental concerns were observed since, except for Mn, there was no evidence of metal movement down the profile.

## CHAPTER 10

### GENERAL DISCUSSION AND CONCLUSIONS

#### 10.1 Introduction

Everyone has a right to a healthy environment according to the constitution of the Republic of South Africa. The health and future of the environment, soil included, depends primarily on how the human inhabitants make use of it. Uses of land include what Logan (1990) referred to as the final solution to society's disposal problem. Land disposal of wastes, however, must not be a transfer of a problem to another location, but a solution and, as a bonus, a benefit.

It was the purpose of this investigation to establish into which of the above categories land disposal of the WTR would fall. This WTR is based on a cation organic polymer and contains calcium carbonate, different from the more researched so-called alum sludges. Its lime value seems to hold with different conditions (e.g. comparing lime contents in Sections 3.3.1 and 6.3.2). If the land disposal would be deemed to be transfer or translocation of a problem, then such an activity would be discontinued, or not started at all. For the purposes of this investigation, a healthy soil is one whose plant productivity is sustained or improved by the application of the WTR, and/or one which is not going to be harmful to the environment and its inhabitants or living organisms. In other words, the permissibility of land disposal of the WTR would be governed by its agricultural and environmental impact.

#### 10.2 Agricultural implications of the land disposal of water treatment residue

Is land application of the WTR of benefit to agriculture from a soil chemical point of view?

According to the results obtained from the two field experiments, it is not. On the other hand, the pot experiment showed benefits such as an increase in dry mass yield of perennial ryegrass and pH (both KCl and H<sub>2</sub>O) of five soils with increase in the amount of WTR applied up to 120 Mg ha<sup>-1</sup>. No such benefits were apparent from field experiments with the same test plant even at the highest rate

of application, namely  $1280 \text{ Mg ha}^{-1}$ . If the agricultural benefit was a key driver in land disposal, then this activity would probably be written off. Of importance, though, is that there were no negative effects on either soil chemical properties or plant growth occurred as a result of the application of the WTR. These results are of even more significance when noting that the soils providing them have dissimilar properties. Despite their differences, the deep, highly weathered, well-drained Hu-F soil gave similar results to the relatively shallow, less weathered, poorly drained We soil. It may thus be assumed that on soils with properties between these two extreme cases disposal of the WTR can be practised with similar results.

It has been established that application of the WTR does not reduce uptake of any nutrients by plants. This includes P and some heavy metals which have been demonstrated in the investigation to be sorbed by the WTR. Also, although the WTR contained some heavy metals, there was no evidence of its application to soil resulting in toxicity to either of the species grown. This was the case in both field experiments, and up to the highest application rate of  $1280 \text{ Mg ha}^{-1}$ . It can thus be deduced that for the plants concerned under the current conditions of the investigation, the WTR had no negative effects on availability of nutrients and subsequent plant growth.

The incorporated and mulched treatments of the WTR gave essentially similar results at the Brookdale field experiment. The results of the mulched treatment suggest that the WTR can be used as a soil substitute when required, as in rehabilitation of eroded lands or stabilization of fragile landscapes. Perennial ryegrass and tall fescue, which have been demonstrated to thrive under this mode of WTR application, or some other grass, could be grown as an aid to the reclamation process as demonstrated by Titshall (2003).

The question arises as to why the positive results of the pot experiment were not repeated in the field situation. In general, results of pot experiments cannot be directly extrapolated to a field situation. Part of the explanation in the current case might lie with the differences in conditions, especially those of the aggregate size of the WTR, and the fate of the soil-WTR products. The aggregate sizes of the WTR applied to the pot experiment were very small ( $< 2\text{mm}$ ) compared to those applied to

the field (50-80 mm). In the pot experiment the reaction of the WTR with the soil would thus occur faster and more readily. The useful products of the reaction, like nitrate, would then be available to be taken up by plants easily, unlike in the field where leaching may occur. Breaking the aggregates prior to field application would both be impractical and expensive, and leaching cannot be prevented. If these are the key differences to plant response in pot and field experiments, then that would mean the situation cannot be rectified. Although there is evidence of the material breaking to smaller aggregates with time (Moodley, 2001), chemical and fertility benefits might not accrue as required since some of its species would have been lost already. If agricultural benefits are considered to be important, then experiments to test the response of other plants might be considered.

### **10.3 Environmental aspects of the land disposal of water treatment residue**

How would it be determined whether land treatment of the WTR is environmentally safe? With the “environment” in the current investigation referring to the soil, plants, groundwater, surface waters, and the atmosphere the answer to this question would be how these mentioned environmental components would respond to the application of this material. The first two of these have been addressed (Section 10.1). The atmospheric environment has not been investigated. However, from the fact that the WTR is basically inorganic, and that it does not create anaerobic conditions in the soil (Moodley, 2001) it can be reasonably assumed that no volatilization or denitrification is likely to occur.

Comparing analytical results from before the establishment of the Brookdale trial, and those acquired in monitoring borehole and dam water during the running of the experiment, it was established that there were no problematic increases in any of the elements Ca, Mg, Cl, N as nitrate, P, Cr and Mn. Thus although there was evidence of removal of solutes from the soil, it was not at such a rate as to cause pollution to either surface water or the groundwater. Although the chemically retentive nature of the WTR for soluble material is established, this might not be the only mechanism by which it reduces, or does not encourage mobility of solutes. Moodley *et al.* (2004) have established with the field trials reported here (Chapter 5) that the WTR can increase water retention of soils at high rates. Because of water percolation rates through the soil profile, less solutes will be transported.



## 10.4 Conclusions

It is safe to dispose of this type of WTR on land. The rate of disposal may be up to 1280 Mg ha<sup>-1</sup>, the highest rate of application of the WTR in this investigation. Based on the different soils used, on the different modes of application (incorporated and mulched), and on the data gathered during the course of this investigation no scientific reason can be forwarded for perceived limitations on its disposal to land. Further details of other aspects of the land disposal of this and other types of WTR can be found in Hughes *et al.* (2005).

Whilst agriculturally it might not be beneficial, the water treatment residue has been demonstrated to be environmentally innocuous. There were no negative effects on plants growing on WTR-treated soils. Supporting this was no evidence of induced nutrient deficiencies or creation of toxicities. To minimize migration of solutes to the groundwater, land disposal would need to be practised with growing vegetation on treated soils. This activity could have positive spin-offs in terms of soil conservation, animal feed and reduction in eutrophication and pollution of groundwater through absorption of soluble species by the growing plants.

There probably are grounds to rethink the policy of considering the water treatment residue as a “waste” in the sense that it might cause pollution. Lombard *et al.* (1994) even concede that the definition of “waste” might be subjective because what is considered a waste in one context might be a resource in another. Whilst the water treatment residue might be a waste because of no perceived benefits agriculturally, it has been proven not to be a waste in terms of pollution. With especially the demonstration that certain grass species can grow directly on it, its disposal is a means of recycling soil to eroded lands for rehabilitation purposes, thus making it a potential resource. For rehabilitation practices the National Ministry of Environmental Affairs and Tourism, for whom maintenance and restoration of the environment would take precedence over economic considerations, could take charge of such an undertaking.

## REFERENCES

- Agbenin, J.G. and Tiessen, H.** 1994. The effects of soil properties on the differential phosphate sorption by semiarid soils from northeast Brazil. *Soil Sci.* 157: 36-45.
- Ahmed, M., Grant, C. D. and Oades, J.M.** 1997. Water treatment residue: potential for use as a soil ameliorant. *Urban Water Research Association of Australia*. Research Report no. 106.
- Ahumada, I., Bustamante, A. and Schalscha, E.B.** 1997. Zinc speciation in phosphate-affected soils. *Commun. Soil Sci. Plant Anal.* 28: 989-995.
- Allison, J.D., Brown, D.S. and Novo-Gradac, K.J.** 1991. MINTEQA/PRODEFAC2, a Geochemical Assessment Model for Environmental Systems: version 3.0 user's manual. U.S. Environmental Protection Agency, Athens, Georgia.
- Allison, L.E. and Moodie, C.D.** 1965. Carbonates. In Black, C.A. (Ed.) *Methods of Soil Analysis*. Part 2: Chemical and Microbiological Properties. ASA, Madison, Wisconsin.
- Arnesen, A.K.M. and Singh, B.R.** 1998. Plant uptake and DTPA-extractability of Cd, Cu, Ni and Zn in a Norwegian alum shale soil as affected by previous addition of dairy and pig manures and peat. *Can. J. Soil Sci.* 78: 531-539.
- Bainbridge, S.H., Miles, N., Praan, R. and Johnston M.A.** 1995. Phosphorus sorption in Natal soils. *S. Afr. J. Plant Soil* 12: 59-64.
- Basta, N.T., Zupancic, R.J. and Dayton, E.A.** 2000. Evaluating soil tests to predict bermudagrass growth in drinking water treatment residuals with phosphorus fertilizer. *J. Environ. Qual.* 29: 2007-2012.
- Bhuiyan, L.R. and Sedberry, J.E. Jr** 1995. Phosphorus sorption characteristics of selected soils of Louisiana. *Commun. Soil Sci. Plant Anal.* 26: 1059-1072.
- Bibak, A.** 1997. Competitive sorption of copper, nickel and zinc by an Oxisol. *Commun. Soil Sci. Plant Anal.* 28: 927-937.
- Bohn, H.L., McNeal, B.L. and O'Connor, G.A.** 2001. *Soil Chemistry*. 3<sup>rd</sup> edition. John Wiley and Sons, Inc., New York.
- Börling, K., Otabbong, E. and Barberis, E.** 2004. Soil variables for predicting potential phosphorus release in Swedish noncalcareous soils. *J. Environ. Qual.* 33: 99-106.
- Bugbee, G.J. and Frink, C.R.** 1985. Alum sludge as a soil amendment: effects on soil properties and plant growth. The Connecticut Agricultural Experiment Station. Bulletin 827.

- Butkus, M.A., Grasso, D., Schulthess, C.P. and Wijnja, H.** 1998. Surface complexation modelling of phosphate adsorption by water treatment residual. *J. Environ. Qual.* 27: 1055-1063.
- Buttigieg, A.D., Klessa, D.A. and Hall, D.A.** 1989. The effects of heavy metals applied in digested sewage sludge to grassland. *XVI International Grassland Congress*, Nice, France.
- Cameron, K.C., Di, R.J. and McLaren, R.R.** 1997. Is soil an appropriate dumping ground for our waste? *Aust. J. Soil Res.* 35: 995-1035.
- Carefoot, J.P. and Whalen, J.K.** 2003. Phosphorus concentrations in subsurface water as influenced by cropping systems and fertilizer sources. *Can. J. Soil Sci.* 83: 203-212.
- Carreira, J.A. and Lajtha, K.** 1997. Factors affecting phosphate sorption along a Mediterranean, dolomitic soil and vegetation chronosequence. *Eur. J. Soil Sci.* 48: 139-149.
- Chen, J-H. and Barber, S.A.** 1990. Effect of liming and adding phosphate on predicted phosphorus uptake by maize on acid soils of three orders. *Soil Sci.* 150: 844-850.
- Chowdhury, A.K., McLaren, R.R., Cameron, K.C. and Swift, R.R.** 1997. Fractionation of zinc in some New Zealand soils. *Commun. Soil Sci. Plant Anal.* 28: 301-312.
- Chung, J-B., Zasoski, R.J. and Burau, R.R.** 1994. Aluminium-potassium and aluminium-calcium exchange equilibria in bulk and rhizophore soil. *Soil Sci. Soc. Am. J.* 58: 1376-1382.
- Cox, A.D., Camberato, J.E. and Smith, B.R.** 1997. Phosphate availability and inorganic transformations in an alum-sludge affected soil. *J. Environ. Qual.* 26: 393-398.
- Dayton, E.A. and Basta, N.T.** 2001. Characterization of drinking water treatment residual for use as a soil substitute. *Water Environ. Res.* 73: 52-57.
- Dayton, E.A., Basta, N.T. and Jakober, C.A.** 2001. Phosphorus sorption capacity of drinking water treatment residuals and potential for use to protect surface water quality. *Joint Residuals and Biosolids Management Conference*. Water Environment Federation. San Diego. CA.
- Djodjic, F., Börling, K. and Bergstrom, L.** 2004. Phosphorus leaching in relation to soil type and soil phosphorus content. *J. Environ. Qual.* 33: 678-684.
- Dodor, D.E. and Oya, K.** 2000. Phosphate sorption characteristics of major soils in Okinawa, Japan. *Commun. Soil Sci. Plant Anal.* 31: 277-288.
- Doula, M., Ioannou, A. and Dimirkou, A.** 1995. Thermodynamics of potassium exchange in calcium bentonite (Ca-b). *Commun. Soil Sci. Plant Anal.* 26: 1535-1545.

- Duffera, M. and Robarge, W.P.** 1999. Soil characteristics and management effects on phosphorus sorption by Highland plateau soils of Ethiopia. *Soil Sci. Soc. Am. J.* 63: 1455-1462.
- Elliott, H.A. and Dempsey, B.A.** 1991. Agronomic effects of land application of water treatment sludges. *J. Am. Water Works Assoc.* 84: 126-131.
- Elliot, H.A., Dempsey, B.A. and Maille, P.J.** 1990. Content and fractionation of heavy metals in water treatment sludges. *J. Environ. Qual.* 19: 330-334.
- Elliott, H.A. and Singer, L.M.** 1988. Effect of water treatment sludge on growth and elemental composition of tomato (*Lycopersicon esculentum*) shoots. *Commun. Soil Sci. Plant Anal.* 19: 345-354.
- Escrig, I. and Morell, I.** 1998. Effect of calcium on the soil adsorption of cadmium and zinc in some Spanish sandy soils. *Water, Air and Soil Pollution* 105: 507-520.
- Escudey, M., Diaz, P., Foerster, J.E. and Galindo, G.** 1997. Adsorbed ion activity coefficients in K-Ca exchange on soil fractions derived from volcanic materials. *Aust. J. Soil Res.* 35: 123-130.
- Eze, O.C. and Loganathan, P.** 1990. Effects of phosphate sorption of some paleudults of southern Nigeria. *Soil Sci.* 150: 612-621.
- Filius, A., Streck, T. and Richter, J.** 1998. Cadmium sorption and desorption in limed topsoils as influenced by pH: isotherms and simulated leaching. *J. Environ. Qual.* 27: 12-18.
- Forster, J.C.** 1995. Soil Nitrogen. In Alef, K. and Nannipieri, P. (Eds). *Methods in Applied Soil Microbiology and Biochemistry*. Academic Press, San Diego.
- Fox, R.L. and Kamprath, E.J.** 1970. Phosphate adsorption for evaluating the phosphate requirements of soils. *Procs Soil Sci. Soc. Am.* 34: 902-906.
- Fuggle, R.F.** 1994. Environmental Management: An Introduction. In Fuggle, R.F. and Rabie, M.A. (Eds) *Environmental Management in South Africa*. Juta and Co, Ltd. Cape Town.
- Gallimore, L.E., Basta, N.T., Storm, D.E., Payton, M.E., Huhnke, R.H. and Smolen, M.D.** 1999. Water treatment residual to reduce nutrients in surface runoff from agricultural land. *J. Environ. Qual.* 28: 1474-1478.
- Garcia-Rodeja, L. and Gil-Sotres, F.** 1995. Laboratory study of phosphate desorption kinetics in soils of Galicia (N.W. Spain). *Commun. Soil Sci. Plant Anal.* 26: 2023-2040.
- Gee, G.W. and Bauder, J.W.** 1986. Particle-size analysis. In Klute, A. (Ed.). *Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods*. ASA, CSS and SSSA, Madison, Wisconsin.

- Geertsema, W.S., Knocke, W.R., Novak, J.T. and Dove, D.** 1994. Long-term effects of sludge application to land. *J. Am. Water Works Assoc.* 86: 64-74.
- Gillman, G.P.** 1979. A proposed method for the measurement of exchange properties of highly weathered soils. *Aust. J. Soil Res.* 17: 129-139.
- Gillman, G.P., Burkett, D.C. and Coventry, R.J.** 2001. A laboratory study of application of basalt dust to highly weathered soils: effect on cation chemistry. *Aust. J. Soil Res.* 39: 799-811.
- Grant, R.F. and Heaney, D.J.** 1997. Inorganic phosphorus transformation and transport in soils: mathematical modelling in ecosystems. *Soil Sci. Soc. Am J.* 61: 752-764.
- Grove, J.W., Sumner, M.E. and Syers, J.W.** 1981. Effect of lime on exchangeable magnesium in variable charge soils *Soil Sci. Soc. Am. J.* 45: 497-500.
- Hanafi, M.M. and Sjaola, J.** 1998. Cadmium and zinc in acid tropical soils. I. Soil physico-chemical properties effect on their adsorption. *Commun. Soil Sci. Plant Anal.* 29: 1919-1931.
- Harter, R.R. and Smith, G.** 1981. Langmuir equation and alternate methods of studying "adsorption" reactions in soils. Chemistry in the Soil Environment. SSSA, Madison, Wisconsin.
- Haustein, G.W., Daniel, D.C., Miller, D.E., Moore, P.A. Jr and McNew, R.W.** 2000. Aluminium-containing residuals influence high-phosphorus soils and runoff water quality. *J. Environ. Qual.* 29: 1954-1959.
- Havlin, J.L., Beaton, J.D., Tisdale, S.L. and Nelson, W.L.** 1999. Soil Fertility and Fertilizers: An Introduction to Nutrient Management. 6th edition. Prentice Hall, Upper Saddle Rivers, New Jersey.
- Hedley, M.J., Stewart, J.W.B. and Chauhan, B.S.** 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46: 970-976.
- Heil, D.E. and Barbarick, K.A.** 1989. Water treatment sludge influence on the growth of sorghum-sudangrass. *J. Environ. Qual.* 18: 292-298.
- Henry, P.C. and Smith, M.F.** 2002. Phosphorus sorption study of selected South African Soils. *S. Afr. J. Plant Soil* 19: 61-69.
- Hopkins, A., Adamson, A.H. and Bowling, P.J.** 1994. Response of permanent and reseeded grassland to fertilizer nitrogen. 2. Effects on concentration of Ca, Mg, K, Na, S, P, Mn, Zn, Cu, Co and Mo in herbage at a range of sites. *Grass and Forage Science* 49: 9-20.
- Hughes, J.C.** 1988. The disposal of leather tannery wastes by land treatment-a review. *Soil Use and Management* 4: 107-111.

**Hughes, J.C. and Girdlestone, S.J.A.** 1994. The effects of leather tannery sludge on the leachates from soil columns. *S. Afr. J. Plant Soil* 11: 90-95.

**Hughes, J.C., Titshall, L.W., Buyeye, M., Johnston, M.A., Moodley, M. and Pecku, S.** 2005. Effects of land application of water treatment residue. Report to the Water Research Commission on the project : "Development of guidelines for the disposal of water treatment sludges to land". WRC Report No. 1148/1/05. Pretoria.

**Ippolito, J.A., Barbarick, K.A. and Redente, E.F.** 1999. Co-application effects of water treatment residuals and biosolids on two range grasses. *J. Environ. Qual.* 28: 1644-1650.

**Jackson, M.L., Lim, C.H. and Zelazny, L.W.** 1986. Oxide, Hydroxides and Aluminosilicates. In Klute, A. (Ed.) *Methods of Soil Analysis. Part 1: Physical and Mineralogical Methods*. 2<sup>nd</sup> Edition, SSSA, Madison, Wisconsin.

**Johnson, C.E. and Petras, R.J.** 1998. Distribution of zinc and lead fractions within a forest spodosol. *Soil Sci. Soc. Am. J.* 62: 782-789.

**Jonasson, B.** 1996: Phosphorus transformation in alum-sludge amended soils. *Swedish J. Agric. Res.* 26: 69-79.

**Karathanasis, A.D.** 1999. Subsurface migration of copper and zinc mediated by soil colloids. *Soil Sci. Soc. Am. J.* 63: 830-838.

**King, L.D.** 1982. Land application of untreated industrial waste water. *J. Environ. Qual.* 11: 638-644.

**Kumar, R., Mehta, S.C., Grewal, K.S. and Singh, M.** 1997. Potassium-calcium exchange equilibria in some soils of Haryana. *Agrochimica* 51: 171-176.

**Lehozcky, I., Szabados, I. and Marth, P.** 1996. Cadmium content of plants as affected by soil cadmium concentration. *Commun. Soil Sci. Plant Anal.* 27: 1765-1777.

**Leij, F.J. and Dane, J.W.** 1990. Determination of exchange isotherms for modelling cation transport in soils. *Soil Sci.* 150: 817-826.

**Li, M., Hue, N.V. and Hussain, S.K.G.** 1997. Changes of metal form by organic amendments to Hawaii soils. *Commun. Soil Sci. Plant Anal.* 28: 381-394.

**Logan, T.J.** 1990. Chemical degradation of soil. *Adv. Soil Sci.* 11: 187-221.

**Logan, T.J.** 1992. Reclamation of chemically degraded soils. *Adv. Soil Sci.* 17: 13-35.

- Lombard, R., Botha, L. and Rabie, M.A.** 1994. Solid Waste. In Fuggle, R.F. and Rabie, M.A. (Eds). Environmental Management in South Africa. Juta and Co, Ltd. Cape Town.
- Lopez-Pineiro, A. and Navarro, A.G.** 1997. Phosphate sorption in Vertisols of Southwestern Spain. *Soil Sci.* 162: 69-77.
- Lucas, J.B., Dillaha, T.A., Reneau, R.B., Novak, J.T. and Knocke, W.R.** 1994. Alum sludge land application and its effects on plant growth. *J. Am. Water Works Assoc.* 86: 75-83.
- Ma, Y.B. and Liu, J.F.** 1997. Adsorption kinetics of zinc in a calcareous soil as affected by pH and temperature. *Commun. Soil Sci. Plant Anal.* 28: 117-126.
- Ma, Y.B. and Uren, N.C.** 1997. The fate and transformation of zinc added to soils. *Aust. J. Soil Res.* 35: 727-738.
- Macks, S., Grant, C., Murray, R. and Drew, E.** 1998. Water treatment sludges for removing phosphorus from contaminated waters. Scientific registration no. 1415. Department of Soil Science. University of Adelaide, South Australia.
- Mandal, B. and Hazra, G.C.** 1997. Zinc adsorption in soils as influenced by different soil management practices. *Soil Sci.* 162: 713-721.
- McBride, M.B. and Evans, L.J.** 2002. Trace metal extractability in soils and uptake by bromegrass 20 years after sewage sludge application. *Can. J. Soil Sci.* 82: 323-333.
- McBride, M.B., Martinez, C.E., Topp, E. and Evans, L.** 2000. Trace metal solubility and speciation in a calcareous soil 18 years after no-till sludge application. *Soil Sci.* 165: 616-636.
- McBride, M.B., Richards, B.K., Steenhuis, T. and Spiers, G.** 1999. Long-term leaching of trace elements in a heavily sludge-amended silty clay loam soil. *Soil Sci.* 164: 613-623.
- McDowell, R.W., Drewry, J.J., Paton, R.J., Carey, P.L., Monaghan, R.M. and Condon, L.M.** 2003. Influence of soil treading on sediment and phosphorus losses in overland flow. *Aust. J. Soil Res.* 41: 949-961.
- McGee, P.A.E.** 1972. Phosphate adsorption in sesquioxenic Transvaal soils. MSc Agric. thesis. University of Natal. Pietermaritzburg. Unpublished.
- McKenzie, F.J. and Jacobs, J.L.** 2002. Effect of application of nitrogen fertilizer on concentrations of P, K, S, Ca, Mg, Na, Cl, Mn, Fe, Cu and Zn in perennial ryegrass/white clover pastures in southwestern Victoria, Australia. *Grass and Forage Sci.* 57: 48-53.

- McLaren, R.R., Clucas, L.M., Taylor, M.D. and Hendry, T.** 2004. Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge. 2. Leaching of metals. *Aust. J. Soil Res.* 42: 459-471.
- McLaren, R.R. and Crawford, D.E.** 1973. Studies on soil copper I. The fractionation of copper in soils. *J. Soil Sci.* 24: 172-181.
- McPharlin, I.R., Jeffrey, R.C., Toussaint, L.F. and Cooper, M.** 1994. Phosphorus, nitrogen and radionuclide retention and leaching from a Joel sand amended with red mud/gypsum. *Commun. Soil Sci. Plant Anal.* 25: 2925-2944.
- Mehra, O.P. and Jackson, M.L.** 1960. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Procs, 7<sup>th</sup> Nat. Conf. on Clays and Clay Minerals.* Pergamon Press, New York.
- Mesquita, M.E.** 1998. Copper and zinc competitive adsorption in schistic and granitic acid soils. *Agrochimica* 52: 235-245.
- Miles, N.** Undated. Plant analysis criteria for pastures. KwaZulu-Natal Department of Agriculture, Cedara, Pietermaritzburg.
- Miller, D.E. and Miller, W.P.** 2000. Land application of wastes. Chapter 8 in Section G, *Interdisciplinary Aspects of Soil Science.* In Sumner, M.E. (Ed.) *Handbook of Soil Science.* CRC Press, Boca Raton, Florida.
- Minyi, T.** 1989. Experiment of trace elements fertilizer spraying on sown pasture. *XVI International Grassland Congress, Nice, France.*
- Mitchell, L.G., Grant, C.A. and Racz, G.J.** 2000. Effect of nitrogen application on concentration of cadmium and nutrient ions in soil solution and in durum wheat. *Can. J. Soil. Sci.* 80: 107-115.
- Moalla, S.N. and Pulford, L.D.** 1995. Mobility of metals in Egyptian desert soils subject to inundation by Lake Nasser. *Soil Use and Management* 11: 94-98.
- Moodley, M.** 2001. Effects of the land disposal of water treatment sludge on soil physical quality. PhD thesis. University of Natal. Pietermaritzburg. Unpublished.
- Moodley, M., Johnston, M.A., Hughes, J.C. and Titshall, L.W.** 2004. Effects of a water treatment residue, lime, gypsum, and polyacrylamide on the water retention and hydraulic conductivity of two contrasting soils under field conditions in KwaZulu-Natal, South Africa. *Aust. J. Soil Res.* 42: 273-282.
- Mortvedt, J.J.** 2000. Bioavailability of micronutrients. Chapter 2 in Section D, *Soil Fertility and Plant Nutrition.* In Sumner, M.E. (Ed.) *Handbook of Soil Science.* CRC Press, Boca Raton, Florida.



- Mundy, G.N., Nexhip, K.J., Austin, N.R. and Collins, M.D.** 2003. The influence of cutting and grazing on phosphorus and nitrogen in irrigation runoff from perennial pasture. *Aust. J. Soil Res.* 41: 675-685.
- Murphy, J. and Riley, J.P.** 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27: 31-36.
- Naidu, R., Kookana, R.R., Sumner, M.E., Harter, R.R. and Tiller, K.G.** 1997. Cadmium sorption and transport in soils: A review. *J. Environ. Qual.* 26: 602-617.
- Naidu, R., Syers, J.W., Tillman, R.W. and Kirkman, J.W.** 1990. Effect of liming on phosphate sorption by acid soils. *J. Soil Sci.* 41: 165-175.
- Nash, D.M. and Halliwell, D.J.** 1999. Fertilizers and phosphorus loss from productive grazing systems. *Aust. J. Soil Res.* 37: 403-429.
- Nissinen, A., Ilvesniemi, H. and Tanskanen, N.** 1998. Apparent cation-exchange equilibria in podzolic forest soils. *Eur. J. Soil Sci.* 49: 121-132.
- Noble, A.D., Randall, P.J. and James, T.R.** 1995. Evaluation of coal-derived organic products in ameliorating surface and subsurface soil acidity. *Eur. J. Soil Sci.* 46: 65-75.
- Orlov, D.S.** 1992. Soil Chemistry. A.A. Balkema. Rotterdam.
- Osei, B.A.** 1995. Effects of different lime application rates and time on some chemical properties of an acid soil in Ghana. *Soil Use and Management* 11: 23-29.
- Owens, L.B. and Bonta, J.V.** 2004. Reduction of nitrate leaching with haying or grazing and omission of nitrogen fertilizer. *J. Environ. Qual.* 33: 1230-1237.
- Owens, L.B., Edwards, W.M. and Van Keuren, R.W.** 1994. Groundwater nitrate levels under fertilized grass and grass-legume pastures. *J. Environ. Qual.* 23: 752-758.
- Owusu-Bennoah, E., Szilas, C., Hansen, H.C.R. and Borggaard, O.K.** 1997. Phosphate sorption in relation to aluminium and iron oxides of Oxisols from Ghana. *Commun. Soil Sci. Plant Anal.* 28: 685-697.
- Papadopoulos, P., Dimirkou, A. and Ioannou A.** 1998. Kinetics of phosphate sorption by goethite and kaolinite-goethite (k-g) system. *Commun. Soil Sci. Plant Anal.* 21: 2191-2206.
- Pardo, M.T.** 2000. Sorption of lead, copper and cadmium by soils: effect of nitroloacetic acid on metal retention. *Commun. Soil Sci. Plant Anal.* 31: 31-40.

**Pardo, M.T. and Guadalix, M.E.** 1996. Zinc sorption-desorption by two Andepts: effect of pH and support medium. *Eur. J. Soil Sci.* 47: 257-263.

**Paterson, J.E., Klessa, D.A. and MacPherson, A.** 1989. Factors influencing the availability of soil cobalt and its uptake by herbage. *XVI International Grassland Congress*, Nice, France.

**Peters, J.M. and Basta, N.T.** 1996. Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial waste. *J. Environ. Qual.* 25: 1236-1241.

**Pleysier, J.L., Juo, A.S.R. and Herbillon, A.J.** 1979. Ion exchange equilibria involving aluminium in a kaolinitic Ultisol. *Soil Sci. Soc. Am. J.* 43: 875-880.

**Poonia, S.R., Mehta, S.C. and Pal, R.** 1986. Exchange equilibria of potassium in soils: 1. Effect of farmyard manure on potassium-calcium exchange. *Soil Sci.* 141: 77-83.

**Poonia, S.R. and Niederbudde, E.A.** 1990. Exchange equilibria of potassium in soils: V. Effect of natural organic matter on K-Ca exchange. *Geoderma* 47: 233-242.

**Prasad, R., Gowrisankar, D. and Shukla, L.M.** 1997. Adsorption and desorption of zinc in soils. *Agrochimica* 51: 241-246.

**Purchase, B.S.** 1974. The influence of phosphate deficiency on nitrification. *Plant Soil* 41: 541-547.

**Quang, V.D. and Dufey, J.E.** 1997. Phosphate desorption from flooded and re-oxidized soils as compared with adsorption characteristics. *Commun. Soil Sci. Plant Anal.* 28: 885-898.

✓ **Quang, V.D., Thai, V.C., Linh, T.T.T. and Dufey, J.E.** 1996. Phosphorus sorption in soils of the Mekong Delta (Vietnam) as described by the binary Langmuir equation. *Eur. J. Soil Sci.* 47: 113-123.

✓ **Rajan, S.S.S. and Fox, R.L.** 1975. Phosphate adsorption by soils. II. Reactions in tropical acid soils. *Procs Soil. Sci. Soc. Am.* 39: 846-851.

**Rengasamy, P., Oades, J.M. and Hancock, T.W.** 1980. Improvement of soil structure and plant growth by addition of alum sludge. *Commun. Soil Sci. Plant Anal.* 11: 533-545.

**Rhoades, J.D.** 1996. Salinity: electrical conductivity and total dissolved salts. In Sparks, L.D. (Ed.) *Methods of Soil Analysis Part 3. Chemical Methods*. SSSA, Madison, Wisconsin.

**Rhue, R.R. and Mansell, R.R.** 1988. The effect of pH on sodium-calcium and potassium-calcium exchange selectivity for Cecil Soil. *Soil Sci. Soc. Am. J.* 52: 641-647.

**Riekert, S. and Bainbridge, S.** 1998. Analytical methods of the Cedara Plant Laboratory. KwaZulu-Natal Department of Agriculture and Environmental Affairs, Pietermaritzburg.

- Rupa, T.R. and Tomar, K.P.** 1999. Zinc sorption kinetics in soils as influenced by equilibration period and soil pH. *Agrochimica* 53: 223-234.
- Sale, P.W.G., Simpson, P.G., Lewis, D.C., Gilkes, R.J., Bolland, M.D.A., Ratkowsky, D.A., Gilbert, M.A., Garden, D.L., Cayley, J.W.D. and Johnson, D.** 1997. The agronomic effectiveness of reactive phosphate rocks 1. Effect of the pasture environment. In "The role of reactive phosphate rock fertilizers for pastures in Australia". (Eds P.W.G. Sale, P.G. Simpson, C.A. Anderson and L.L. Muir) pp 921-936. CSIRO Publishing, Melbourne.
- Sherrell, C.G.** 1990. Effect of cobalt application on the cobalt status of pastures 2. Pastures without previous cobalt application. *New Zealand J. Agric. Res.* 33: 305-311.
- Siemens, J., Ilg, K., Lang, F. and Kaupenjohann, M.** 2004. Adsorption controls mobilization of colloids and leaching of dissolved phosphorus. *Eur. J. Soil Sci.* 55: 253-263.
- Singh, B. and Gilkes, R.J.** 1991. Phosphorus sorption in relation to soil properties for the major soil types of south-western Australia. *Aust. J. Soil Res.* 29: 603-618.
- Singh D., McLaren, R.R. and Cameron, K.C.** 1997. Desorption of native and added zinc from a range of New Zealand soils in relation to soil properties. *Aust. J. Soil Res.* 35: 1253-1266.
- Singh, D., Pal, R. and Poonia, S.R.** 1981. Exchange equilibria of potassium versus calcium-plus-magnesium in soils of arid and semi-arid regions, India. *Geoderma* 25: 55-62.
- Skene, T.M., Oades, J.M. and Kilmore, G.** 1995. Water treatment sludge: a potential plant growth medium. *Soil Use and Management* 11: 29-33.
- Smith, C.J., Goh, K.M., Bond, W.J. and Freney, J.R.** 1995. Effects of organic and inorganic calcium compounds on soil-solution pH and aluminium concentration. *Eur. J. Soil Sci.* 46: 53-63.
- Soil Classification Working Group.** 1991. Soil Classification. A taxonomic system for South Africa. Department of Agricultural Development, Pretoria, South Africa.
- Soil Survey Staff.** 1975. Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys. USDA Natural Resources Conservation Service, Washington D.C.
- Sposito, G.** 1981. Cation exchange in soils: An historical and theoretical perspective. Chemistry in the Soil Environment. SSSA, Madison, Wisconsin.
- Sposito, G., Lund, L.J. and Chang, A.C.** 1982. Trace metal chemistry in arid zone field soils amended with sewage sludge: Fractionation of Ni, Cu, Zn, Cd and Pb in solid phases. *Soil Sci. Soc. Am. J.* 46: 260-268.

- Sumner, M.E. and Miller, W.P.** 1996. Cation exchange capacity and exchange coefficients. In Bigham, J.M. (Ed.) *Methods of Soil Analysis Part 3. Chemical Methods*. SSSA, Madison, Wisconsin.
- Tarkalson, D.D. and Mikkelsen, R.L.** 2004. Runoff phosphorus losses as related to phosphorus source, application method, and application rate on a Piedmont soil. *J. Environ. Qual.* 33: 1424-1430.
- The Non-Affiliated Soil Analysis Work Committee.** 1990. *Handbook of Standard Soil Testing Methods for Advisory Service*. Soil Science Society of South Africa, Pretoria.
- Thomas, G.W.** 1982. Exchangeable cations. In Page, A.L. (Ed.) *Methods of Soil Analysis Part 2. Chemical and Microbiological Properties*. 2<sup>nd</sup> edition. Am. Soc. Agron., Madison, Wisconsin.
- Thomas, G.W.** 1996. Soil pH and Soil Acidity. In Bigham, J.M. (Ed.) *Methods of Soil Analysis Part 3. Chemical Methods*. SSSA, Madison, Wisconsin.
- Tiller, K.G.** 1989. Heavy metals in soils and their environmental significance. *Adv. Soil Sci.* 9:113-142.
- Titshall, L.W.** 2003. The characterisation of some South African water treatment residues and glasshouse pot experiments to investigate the potential of two residues for land disposal. MSc thesis. University of Natal. Unpublished.
- Tolner, L. and Füleký, Gy.** 1995. Determination of the originally adsorbed soil phosphorus by modified Freundlich isotherm. *Commun. Soil Sci. Plant Anal.* 26: 1213-1231.
- Toor, G.S., Condron, L.M., Di, H.J. and Cameron, K.C.** 2004. Seasonal fluctuations in phosphorus loss by leaching from a grassland soil. *Soil Sci. Soc. Am. J.* 68: 1429-1436.
- Turner, B.L., Kay, M.A. and Westermann, D.T.** 2004. Colloidal phosphorus in surface runoff and water extracts from semiarid soils of the western United States. *J. Environ. Qual.* 33: 1464-1472.
- Umgeni Water.** 1994. Investigation of sludge disposal options for Midmar Waterworks. Report no. PP 1/1994.
- United States Salinity Laboratory Staff.** 1954. *Diagnosis and improvement of saline and alkali soils*. USDA, Washington D.C.
- Van der Meer, H.G. and Wedin, W.F.** 1989. Present and future role of grasslands and fodder crops in temperate countries with special reference to over-production and environment. *XVI International Grassland Congress*, Nice, France, 1989.

- Van Es, H.M., Schindelbeck, R.R. and Jokela, W.E.** 2004. Effect of manure application timing, crop, and soil type on phosphorus leaching. *J. Environ. Qual.* 33: 1070-1080.
- Veith, J.A. and Sposito, G.** 1977. On the use of the Langmuir equation in the interpretation of "adsorption" phenomena. *Soil Sci. Soc. Am. J.* 41: 697-702.
- Verma, B.C., Swaminathan, K. and Sud, K.C.** 1977. An improved turbidimetric method for the determination of sulphate in plant and soils. *Talanta*. 24: 49-50.
- Walkley, A.** 1947. A critical examination of a rapid method for determining organic carbon in soils: effect of variations in digestion conditions and of organic soil constituents. *Soil Sci.* 63: 251-263.
- Wang, F., Couillard, D., Auclair, J-C. and Campbell, P.G.C.** 1998. Effects of alum-treated waste water sludge on barley growth. *Water, Air and Soil Pollution* 108: 33-49.
- Wilkins, B.J., Brummel, N. and Loch, J.P.G.** 1998. Influence of pH and zinc concentration on cadmium sorption in acid, sandy soil. *Water, Air and Soil Pollution* 101: 349-362.
- Wooldridge, J.** 1990. Effect of liming and parent material on the potassium quantity/intensity relationships of some upland soils of the Western Cape. *S. Afr. J. Plant Soil* 7: 62-67.
- Yuan, G. and Lavkulich, L.M.** 1997. Sorption behaviour of copper, zinc, and cadmium in response to simulated changes in soil properties. *Commun. Soil Sci. Plant Anal.* 28: 571-587.
- Zhang, T.Q. and MacKenzie, A.F.** 1997. Changes of soil phosphorus fractions under long-term corn monoculture. *Soil Sci. Soc. Am. J.* 61: 485-493.
- Zhang, Z., Zhu, Y., Guo, P. and Liu, G.** 2004. Potential loss of phosphorus from a rice field in Taihu Lake basin. *J. Environ. Qual.* 33: 1403-1412.
- Zhou, M. and Li, Y.** 2001. Phosphorus-sorption characteristics of calcareous soils and limestone from the southern everglades and adjacent farmlands. *Soil Sci. Soc. Am. J.* 65: 1404-1412.

**Appendix 1.1** Nutrient composition and DM yield of perennial ryegrass grown on the Hu-M soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of WTR [means (n = 3) followed by the same letter are not statistically different]

Cut no.	WTR (Mg ha <sup>-1</sup> )	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield (g)
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			
1	0	0.47a	3.79a	0.44a	0.14a	18a	155a	65a	0.90a
	40	0.61ab	4.04a	0.45a	0.17a	18a	171a	55a	1.00a
	80	0.61ab	3.74a	0.47a	0.14a	16a	135a	60a	1.09a
	120	0.67b	3.25a	0.41a	0.13a	13a	117a	60a	0.82a
	LSD (0.05)	0.18	0.96	0.14	0.07	5	54	16	0.30
2	0	0.53a	2.97a	0.55a	0.31ab	15a	198c	61a	3.90a
	40	0.63ab	3.30b	0.52a	0.36b	16a	140b	55a	4.38a
	80	0.66ab	3.27ab	0.64a	0.30a	17a	96a	55a	3.94a
	120	0.79b	3.12ab	0.63a	0.28a	17a	89a	58a	4.02a
	LSD(0.05)	0.13	0.32	0.24	0.06	3	37	9	0.98
4	0	0.74a	1.11a	0.81a	0.26a	7a	459d	42a	0.77a
	40	0.83a	1.43a	0.70a	0.32a	6a	170bc	40a	0.92a
	80	0.96a	1.54a	0.83a	0.33a	7ab	101ab	46a	0.61a
	120	0.99a	1.35a	0.72a	0.19a	9b	72a	40a	0.95a
	LSD(0.05)	0.28	0.86	0.28	0.19	2	78	18	0.36
8	0	0.85a	1.61a	0.64a	0.47ab	6a	806d	44b	1.04a
	40	0.94ab	1.65a	0.70a	0.56b	5a	455bc	34a	0.99a
	80	0.94ab	1.60a	0.68a	0.58b	6a	188a	21a	1.05ab
	120	1.34c	1.35a	0.62a	0.42a	5a	346ab	46b	1.59c
	LSD(0.05)	0.28	0.38	0.17	0.12	3	216	15	0.41

**Appendix 1.2** Nutrient composition and DM yield of perennial ryegrass grown on the Hu-T soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of WTR [means (n = 3) followed by the same letter are not statistically different]

Cut	WTR (Mg ha <sup>-1</sup> )	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield (g)
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			
1	0	0.42a	3.60a	0.41a	0.27b	18a	634c	113ab	3.25b
	40	0.57b	3.96ab	0.41a	0.23b	20a	394ab	114b	2.79ab
	80	0.67bc	4.34b	0.42a	0.22ab	18a	205a	97a	2.65a
	120	0.69c	4.22b	0.45a	0.16a	20a	199a	99ab	2.46a
	LSD(0.05)	0.11	0.47	0.05	0.06	6	229	16	0.60
2	0	0.42a	3.96a	0.48a	0.51b	10a	686d	87a	4.05a
	40	0.57b	3.93a	0.47a	0.43ab	13a	442bc	86a	4.18a
	80	0.61b	4.02a	0.47a	0.43ab	14ab	216ab	83a	4.61b
	120	0.60b	3.84a	0.56a	0.34a	16c	192a	82a	4.61b
	LSD(0.05)	0.07	0.28	0.10	0.05	2	223	24	0.35
4	0	0.45a	1.91a	0.52a	0.29b	5a	465c	58a	0.83a
	40	0.79b	2.00a	0.65ab	0.33b	5a	217a	62a	1.01a
	80	1.00c	1.97a	0.73bc	0.28ab	7ab	220a	74ab	0.98a
	120	1.07c	1.82a	0.84c	0.22a	9b	340b	85b	1.08a
	LSD(0.05)	0.19	0.36	0.14	0.07	3	102	17	0.31
8	0	0.60a	1.60a	0.55a	0.52a	7a	442b	35ab	1.07a
	40	0.84b	1.50a	0.62a	0.51a	4a	321b	29a	1.22ab
	80	1.02c	1.55a	0.52a	0.53a	5a	85a	41ab	1.17a
	120	1.12c	1.41a	0.51a	0.40a	4a	321b	45b	1.67c
	LSD(0.05)	0.12	0.22	0.14	0.16	3	216	16	0.26

**Appendix 1.3** Nutrient composition and DM yield of perennial ryegrass grown on the Sd soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of WTR [means(n = 3) followed by the same letter are not statistically different]

Cut	WTR	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield
	(Mg ha <sup>-1</sup> )	(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			(g)
1	0	0.56a	3.76a	0.49a	0.15a	18a	301c	90a	2.97c
	40	0.62a	3.77a	0.50a	0.15a	20a	207b	85a	2.60ab
	80	0.68a	4.10a	0.50a	0.15a	21a	140a	85a	2.31a
	120	0.72a	3.78a	0.50a	0.14a	19a	165a	81a	2.54a
	LSD(0.05)	0.18	0.36	0.11	0.02	6	31	21	0.36
2	0	0.43a	3.88a	0.45a	0.43b	11a	455c	60a	4.07b
	40	0.58b	3.80a	0.58b	0.37a	13ab	310b	72c	3.44a
	80	0.56b	3.88a	0.51ab	0.40ab	14bc	159a	64ab	4.41bc
	120	0.55b	3.89a	0.55b	0.40ab	15c	174a	62a	4.76c
	LSD(0.05)	0.11	0.32	0.09	0.05	2	61	7	0.47
4	0	0.59a	1.86a	0.57a	0.41a	7b	448c	55a	0.72a
	40	0.65ab	1.89a	0.65b	0.40a	7b	272ab	40a	0.94a
	80	0.75bc	2.07a	0.71bc	0.44a	6ab	129a	57a	0.92a
	120	0.94d	1.77a	0.86d	0.37a	4a	247a	52a	0.99a
	LSD(0.05)	0.11	0.38	0.07	0.11	2	152	33	0.35
8	0	0.79a	1.65a	0.67c	0.46a	5a	1213c	34ab	0.89a
	40	0.78a	1.39a	0.57a	0.40a	4a	388ab	21a	0.93a
	80	0.86ab	1.48a	0.59ab	0.44a	6a	254a	31ab	1.31b
	120	1.02c	1.34a	0.66bc	0.46a	5a	296a	39b	1.63c
	LSD(0.05)	0.10	0.32	0.08	0.12	3	487	14	0.29



**Appendix 1.4** Nutrient composition and DM yield of perennial ryegrass grown on the Ia-C soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L) [means (n = 3) followed by the same letter are not statistically different]

Cut	Treatment	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			(g)
1	L0R0	0.39a	4.08a	0.36a	0.25b	23a	260c	49a	1.26a
	L0R40	0.48ab	4.03a	0.35a	0.24b	18a	176a	42a	1.76b
	L0R80	0.54bc	3.88a	0.36a	0.19ab	18a	189a	42a	1.81b
	L0R120	0.63c	3.28a	0.34a	0.13a	16a	201ab	47a	1.17a
	LSD(0.05)	0.12	0.85	0.07	0.07	10	43	14	0.26
	L1R0	0.72b	3.46a	0.33a	0.14a	18a	108a	46b	1.04a
	L1R40	0.53a	3.62a	0.31a	0.18a	15a	148bc	45ab	1.73b
	L1R80	0.57a	3.83a	0.34a	0.20a	16a	135b	38a	1.74b
	L1R120	0.71b	3.27b	0.35a	0.20a	18a	195d	42ab	1.34a
	LSD(0.05)	0.10	1.30	0.06	0.10	6	27	8	0.34
	L2R0	0.66a	3.26a	0.34a	0.14ab	16a	146ab	36ab	1.54a
	L2R40	0.68a	3.48aa	0.34a	0.17b	17a	142a	38b	1.93ab
	L2R80	0.70ab	3.55ab	0.33a	0.15ab	18a	140a	31a	2.12b
	L2R120	0.78c	3.95b	0.29a	0.13a	18a	179c	31a	1.60ab
	LSD(0.05)	0.05	0.45	0.05	0.03	5	23	5	0.55
	L0R0	0.34a	4.58b	0.38a	0.33b	15ab	215ab	48a	3.84ab
	L0R40	0.57b	3.73a	0.50c	0.25a	13a	296c	47a	3.64a
	L0R80	0.54b	3.83a	0.36a	0.31ab	13a	214a	42a	4.49ab
	L0R120	0.67b	4.16ab	0.39ab	0.31ab	16b	182a	42a	5.18b
	LSD(0.05)	0.14	0.52	0.06	0.07	2	80	7	1.53
2	L1R0	0.59a	4.46b	0.46a	0.30a	18c	170ab	51a	3.69a
	L1R40	0.60a	4.02ab	0.39a	0.30a	13a	206b	49a	4.18a
	L1R80	0.61ab	3.83a	0.40a	0.37c	14a	159a	49a	4.95ab
	L1R120	0.72c	3.74a	0.38a	0.31ab	15ab	169ab	47a	6.19b
	LSD(0.05)	0.09	0.45	0.11	0.05	3	39	11	1.29
	L2R0	0.69a	3.64a	0.43a	0.34bc	15a	106a	47a	4.56a
	L2R40	0.71ab	3.68a	0.40a	0.37c	15a	142b	46a	4.89a
	L2R80	0.80bc	3.78a	0.39a	0.28ab	15a	164bc	38a	4.72a
	L2R120	0.96d	4.01a	0.40a	0.26a	16a	210d	41a	4.59a
	LSD(0.05)	0.09	0.57	0.06	0.08	5	27	10	0.26

continued

**Appendix 1.4 cont.** Nutrient composition and DM yield of perennial ryegrass grown on the Ia-C soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L) [means (n = 3) followed by the same letter are not statistically different]

Cut	Treatment	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			(g)
4	L0R0	1.18ab	2.28d	0.40a	0.20a	9a	534b	45a	0.75a
	L0R40	1.48b	1.38ab	0.96c	0.24a	7a	576b	50a	1.01ab
	L0R80	1.31ab	1.18a	0.75bc	0.20a	8a	391ab	49a	1.23b
	L0R120	1.05a	1.56bc	0.71c	0.17a	8a	233a	44a	1.27b
	LSD(0.05)	0.37	0.25	0.24	0.11	3	203	18	0.30
	L1R0	1.22ab	1.97a	0.50ab	0.19ab	12ab	276a	44a	0.89a
	L1R40	0.90a	1.86a	0.40a	0.20ab	11a	273a	43a	1.13ab
	L1R80	1.12ab	2.42a	0.46ab	0.17a	14c	246a	45a	1.22bc
	L1R120	1.34b	2.17a	0.64b	0.17a	11a	223a	51a	1.71d
	LSD(0.05)	0.35	0.59	0.21	0.03	2	108	14	0.28
	L2R0	0.72a	1.18a	0.56a	0.23b	10a	153a	42a	1.05a
	L2R40	0.81a	1.82a	0.52a	0.19ab	10a	167ab	36a	1.46b
	L2R80	1.14a	2.80a	0.29a	0.14a	13ab	230c	41a	1.57b
	L2R120	1.15a	3.05a	0.29a	0.17a	15b	149a	37a	1.64b
	LSD(0.05)	1.52	1.25	0.41	0.05	3	41	9	0.41
8	L0R0	1.11a	1.36b	0.65ab	0.52a	10b	773b	80b	1.16a
	L0R40	1.36b	1.29ab	0.64a	0.49a	7ab	898b	81b	1.37a
	L0R80	1.54c	1.19a	0.62a	0.44a	5a	613a	66ab	1.64b
	L0R120	1.43bc	1.26ab	0.71c	0.49a	8ab	477a	49a	1.86b
	LSD(0.05)	0.16	0.13	0.03	0.09	4	159	17	0.26
	L1R0	1.50a	1.55c	0.69a	0.60d	11b	646b	69c	1.28a
	L1R40	1.44a	1.25ab	0.73ab	0.45bc	5a	372a	55ab	1.44a
	L1R80	1.46a	1.15a	0.73ab	0.39ab	5a	373a	50a	1.60ab
	L1R120	1.37a	1.08a	0.76b	0.31a	5a	467ab	45a	1.96c
	LSD(0.05)	0.17	0.30	0.06	0.09	4	207	13	0.36
	L2R0	2.30a	1.25b	0.71a	0.58c	17b	373a	40a	1.13a
	L2R40	2.24a	1.10a	0.71a	0.46ab	19b	507a	49a	1.56b
	L2R80	2.05a	1.11a	0.65a	0.43a	11ab	579ab	40a	1.84c
	L2R120	1.96a	1.26b	0.63a	0.35a	8a	822b	35a	2.01c
	LSD(0.05)	0.36	0.12	0.11	0.12	8	301	16	0.22

L0=no lime applied; L1=lower lime treatment; L2=higher lime treatment; R=water treatment residue

**Appendix 1.5** Nutrient composition and DM yield of perennial ryegrass grown on the Nb-F1 soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L) [means (n = 3) followed by the same letter are not statistically different]

Cut	Treatment	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			(g)
1	LOR0	0.22a	4.18c	0.32a	0.45a	12a	174a	56b	0.69a
	LOR40	0.81b	3.98c	0.40b	0.46a	11a	217b	65b	1.12ab
	LOR80	0.98bc	2.67a	0.42b	0.39a	9a	385d	36a	1.65c
	LOR120	1.27d	3.60b	0.45b	0.40a	11a	248bc	45a	0.98a
	LSD(0.05)	0.24	0.31	0.07	0.16	6	35	10	0.48
	L1R0	0.72a	3.15a	0.40a	0.61c	9a	96a	60a	1.77a
	L1R40	1.16b	3.18a	0.45b	0.41ab	16a	270b	62a	1.82a
	L1R80	1.15b	3.33a	0.43ab	0.38a	13a	289b	58a	1.36a
	L1R120	1.18b	3.08a	0.43ab	0.30a	16a	231b	45a	1.49a
	LSD(0.05)	0.34	1.18	0.03	0.12	7	91	35	0.63
	L2R0	0.94a	2.29a	0.41a	0.49b	16a	101a	54a	2.13a
	L2R40	0.95a	2.17a	0.37a	0.32a	16a	182ab	42a	2.28a
	L2R80	1.12a	2.57a	0.40a	0.36ab	11a	207b	41a	2.20a
	L2R120	1.28a	2.97a	0.41a	0.37ab	18a	218b	38a	2.00a
	LSD(0.05)	0.81	1.87	0.15	0.14	9	90	27	0.71
2	LOR0	0.25a	3.41a	0.37a	0.72c	9a	162a	36a	2.80a
	LOR40	0.97c	3.12a	0.61d	0.62ab	10a	384b	58b	2.87a
	LOR80	0.82b	3.25a	0.47b	0.59a	7a	757c	45a	3.21a
	LOR120	1.07d	2.96a	0.48c	0.53a	10a	405ab	47ab	3.43a
	LSD(0.05)	0.10	0.65	0.04	0.10	4	124	12	0.66
	L1R0	0.80a	3.19a	0.50b	0.71c	11a	260a	69c	2.30a
	L1R40	1.00ab	2.95a	0.39a	0.57ab	11a	448a	47ab	3.06b
	L1R80	1.07b	2.74a	0.44ab	0.52a	10a	405a	36a	3.31b
	L1R120	1.07b	3.01a	0.42a	0.55a	12a	268a	43a	3.32b
	LSD(0.05)	0.23	0.73	0.08	0.09	3	247	18	0.49
	L2R0	0.91a	3.47b	0.46a	0.65c	9b	153a	58b	2.58a
	L2R40	0.82a	3.31ab	0.40a	0.59bc	9b	515d	54b	3.51a
	L2R80	1.00a	2.56a	0.48a	0.54ab	5a	315bc	39a	2.82a
	L2R120	1.02a	3.00ab	0.49a	0.48a	9b	294b	40a	3.26a
	LSD(0.05)	0.33	0.89	0.10	0.06	5	128	8	0.49

continued

**Appendix 1.5 cont.** Nutrient composition and DM yield of perennial ryegrass grown on the Nb-F1 soil in a pot experiment at cuts 1, 2, 4 and 8 with different rates of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L) [means (n = 3) followed by the same letter are not statistically different]

Cut.	Treatment	Ca	K	Mg	P	Cu	Mn	Zn	Mean yield
		(g 100g <sup>-1</sup> )				(mg kg <sup>-1</sup> )			(g)
4	L0R0	0.42a	2.10b	0.46a	0.62ab	7a	179a	52a	0.49a
	L0R40	1.19c	1.99b	0.77b	0.80b	7a	1033b	54a	0.49a
	L0R80	0.98b	2.13b	0.54a	0.55a	8a	1061b	41a	0.58a
	L0R120	1.53d	1.54a	0.91c	0.66b	9a	1441b	46a	0.44a
	LSD(0.05)	0.18	0.31	0.13	0.22	6	568	18	0.16
	L1R0	1.01a	2.25b	0.58a	0.80c	7a	188a	48b	0.35a
	L1R40	1.13a	2.21b	0.59a	0.62b	7a	823b	44ab	0.49ab
	L1R80	1.64b	2.03ab	0.68a	0.47a	5a	1764d	42ab	0.66bc
	L1R120	1.77b	1.67a	0.64a	0.46a	6a	1066bc	33a	0.77c
	LSD(0.05)	0.30	0.41	0.18	0.15	3	263	12	0.23
	L2R0	1.38c	1.89d	0.93a	0.62b	8a	150a	41b	0.44a
	L2R40	1.14b	1.44bc	0.75a	0.55b	7a	766b	33ab	0.73b
	L2R80	1.31bc	1.20b	0.72a	0.58b	8a	974b	27a	0.81b
	L2R120	0.74a	0.61a	0.69a	0.41a	8a	783b	28a	0.86b
	LSD(0.05)	0.20	0.44	0.27	0.13	2	514	8	0.15
8	L0R0	0.84a	2.07c	0.55a	0.88a	5a	511a	64a	0.50a
	L0R40	1.40b	1.39ab	0.56a	0.84a	7ab	606ab	78a	0.86b
	L0R80	1.50b	1.33a	0.50a	0.69a	7ab	503a	46a	0.85b
	L0R120	1.70b	1.19a	0.62a	0.74a	9b	1597c	58a	0.84b
	LSD(0.05)	0.47	0.32	0.15	0.38	4	362	38	0.21
	L1R0	1.29a	1.90b	0.48a	0.95b	9a	287a	60a	0.59a
	L1R40	1.61b	1.53ab	0.49a	0.61a	8a	422ab	41a	0.72ab
	L1R80	1.77b	1.29a	0.66b	0.64a	10a	794b	45a	0.84b
	L1R120	1.77b	1.40a	0.63b	0.77ab	10a	752ab	41a	0.83b
	LSD(0.05)	0.30	0.41	0.13	0.23	7	494	32	0.23
	L2R0	1.51a	0.48a	0.48a	1.02b	8ab	137a	49c	0.74a
	L2R40	1.45a	0.46a	0.46a	0.71a	7a	295ab	35a	0.88a
	L2R80	1.96b	0.61a	0.61a	1.07b	9ab	476c	32a	0.84a
	L2R120	2.03b	0.55a	0.55a	0.93b	10b	275a	36ab	0.90a
	LSD(0.05)	0.34	0.21	0.16	0.23	3	174	7	0.18

L0=no lime applied; L1=lower lime treatment; L2=higher lime treatment; R=water treatment residue

**Appendix 2.1** Chemical analysis of soil samples from the pot experiment with different rates of water treatment residue (R) ( $\text{Mg ha}^{-1}$ ) and lime (L) [means ( $n = 3$ ) followed by the same letter are not statistically different]

Soil	Treatment	pH (KCl)	pH ( $\text{H}_2\text{O}$ )	Extr. Acidity	Ca ( $\text{cmol}_e \text{kg}^{-1}$ )	Mg	Acid sat. ( $\text{g } 100\text{g}^{-1}$ )	P ( $\text{mg kg}^{-1}$ )	Total yield (g)
Hu-M	LOR0	4.48a	5.54a	0.19c	5.23a	4.73a	1.9b	7a	12.58a
	LOR40	4.85b	5.72ab	0.04a	6.22ab	4.73a	0.4a	5a	13.63ab
	LOR80	5.23c	5.87bc	0.04a	7.25bc	4.76a	0.3a	5a	13.55a
	LOR120	5.73d	6.19d	0.06ab	9.08d	4.86a	0.4a	5a	14.96c
	LSD 0.05	0.23	0.23	0.05	1.36	0.18	0.4	3	1.15
Hu-T	LOR0	4.24a	5.30a	0.18d	2.49a	1.82ab	3.9c	13b	15.10a
	LOR40	4.99b	5.82b	0.07bc	3.58b	1.86ab	1.2b	7a	15.40ab
	LOR80	5.76c	6.28c	0.03a	4.63c	2.00b	0.4a	8a	16.62bc
	LOR120	6.20d	6.60d	0.04ab	5.03c	1.70a	0.6a	8a	18.40d
	LSD 0.05	0.07	0.05	0.04	0.44	0.38	0.6	4	1.28
Ia-C	LOR0	4.25a	5.45a	1.26c	2.40a	1.82a	23.0c	5a	13.22a
	LOR40	4.60b	5.68b	0.29b	4.85b	1.69a	4.2b	6a	14.82a
	LOR80	4.97c	5.78c	0.13a	6.71c	2.23b	1.4a	6a	17.48b
	LOR120	5.37d	5.94d	0.18a	8.07d	2.36b	0.7a	5a	17.88b
	LSD 0.05	0.06	0.05	0.06	0.43	0.28	1.09	4	1.85
	L1R0	4.78a	5.67a	0.22b	5.97a	1.57a	2.9c	6a	13.79a
	L1R40	5.20b	5.78b	0.09a	8.47b	1.77b	0.9ab	5a	15.15ab
	L1R80	5.70c	5.85c	0.06a	10.95c	1.82bc	0.5a	4a	16.34bc
	L1R120	5.79c	6.56d	0.09a	12.23c	1.95c	0.7a	5a	20.22d
	LSD 0.05	0.23	0.04	0.06	1.33	0.17	0.7	2	1.86
	L2R0	5.42a	6.05a	0.05a	9.16a	1.41a	0.5a	6a	15.10a
	L2R40	5.78b	6.33b	0.11a	10.93b	1.53b	0.8a	6a	17.32b
	L2R80	6.03c	6.52c	0.08a	11.83bc	1.52b	0.6a	6a	18.29b
	L2R120	6.31d	6.63	0.07a	13.28d	1.59b	0.5a	6a	17.31b
	LSD 0.05	0.08	0.07	0.08	1.15	0.10	0.6	1	1.40
Nb-F1	LOR0	3.91a	4.72a	0.47c	0.48a	0.21a	40.5c	96c	6.87a
	LOR40	4.78b	5.36b	0.06ab	1.76b	0.28b	2.7ab	59b	10.02b
	LOR80	5.71c	5.90c	0.03a	2.18c	0.37c	1.2a	36a	10.56b
	LOR120	6.46d	6.51d	0.03a	2.76d	0.39c	0.8a	36a	11.19b
	LSD 0.05	0.15	0.10	0.04	0.20	0.05	2.3	9	1.67
	L1R0	4.55a	5.32a	0.09c	1.42a	0.24a	5.3c	80c	7.36a
	L1R40	5.62b	6.31b	0.04ab	1.90b	0.25ab	2.1a	40ab	9.30b
	L1R80	6.44c	6.45c	0.07bc	2.55c	0.31bc	2.3ab	36a	11.39c
	L1R120	6.77d	6.84d	0.02a	2.97d	0.39d	0.5a	32a	11.85c
	LSD 0.05	0.31	0.03	0.03	0.40	0.08	2.7	23	1.70
	L2R0	5.46a	6.12a	0.04a	2.24a	0.27a	1.5a	69d	9.19a
	L2R40	6.12b	6.45b	0.01a	2.89b	0.34b	0.3a	53bc	11.49b
	L2R80	6.84c	6.77c	0.04a	2.99b	0.33ab	1.3a	37a	11.62b
	L2R120	6.84c	6.96d	0.01a	3.01b	0.33ab	0.5a	47b	12.90b
	LSD 0.05	0.22	0.08	0.04	0.35	0.07	1.4	9	1.75
Sd	LOR0	4.60a	5.72a	0.10b	7.52a	9.39b	0.6b	6a	15.06a
	LOR40	5.00b	5.96b	0.07ab	8.78ab	9.32b	0.4ab	4a	14.05a
	LOR80	5.32c	6.26c	0.02a	10.62bc	9.02ab	0.1a	4a	15.91ab
	LOR120	5.75d	6.58d	0.06ab	12.96d	8.62a	0.3a	6a	17.80b
	LSD 0.05	0.25	0.03	0.06	2.32	0.65	0.3	5	2.01

L0=no lime applied; L1=lower lime treatment; L2=higher lime treatment; R=water treatment residue; extr.=extractable

**Appendix 3.1**      Soil profile description of the Hutton soil at Brookdale Farm

Soil code:           Hu 3100  
Soil Form:         Hutton  
Soil Family:       Stella  
Location:          Brookdale Farm, Howick  
Parent material:   Dolerite  
Land use:          Dryland cropping

Horizon	Depth (m)	Description
A	0 - 0.38	Very dark brown (10YR 2/2); clay; weak crumb; dry; firm; many fine roots; gradual transition to B1.
B1	0.38 - 0.60	Dark brown (7.5YR 3/2); clay; weak, subangular blocky; moist, friable; gradual transition to B2.
B2	0.60 - 1.20+	Dark red (2.5YR 3/6); weak, subangular blocky; moist, firm.

Particle size distribution (%)						
Horizon	-----Sand-----			-----Silt-----		Clay
	Coarse	Medium	Fine	Coarse	Fine	
	0.5 - 2.0	0.25 - 0.5	0.053 -	0.02 -	0.002 -	
	mm	mm	0.25 mm	0.053 mm	0.02 mm	
A	7	2	5	16	18	52
B1	6	1	6	20	11	56
B2	8	2	6	8	13	63

Horizon	pH		Exchangeable cations ----- (cmol <sub>c</sub> kg <sup>-1</sup> ) -----				Exch. acidity (cmol <sub>c</sub> kg <sup>-1</sup> )	Organic carbon (g kg <sup>-1</sup> )
	(KCl)	(H <sub>2</sub> O)	Ca	Mg	Na	K		
A	4.22	5.21	5.57	2.29	0.10	0.17	0.37	33.5
B1	4.14	5.50	4.38	2.60	0.24	2.17	0.40	23.2
B2	4.04	5.82	5.34	1.95	0.12	1.00	1.42	15.2

**Appendix 3.2**      Soil profile description of the Westleigh soil at Ukulinga Farm

Soil code:                We 1000  
 Soil Form:              Westleigh  
 Soil Family:            Helena  
 Location:                Ukulinga Farm, Mkondeni, Pietermaritzburg  
 Parent material:        Ecce shale  
 Land use:                Pasture

Horizon	Depth (m)	Description
A	0 - 0.26	Very dark brown (10YR 2/2); silty clay loam; weak, crumb; hard when dry; gradual transition to B.
B	0.26 - 0.55	Dark reddish gray (5YR 4/2); gravelly silty clay loam; moderate, subangular blocky; very hard when dry; numerous yellowish-brown mottles; hardpan concretions.

Horizon	Particle size distribution (%)					
	-----Sand-----			-----Silt-----		Clay
	Coarse	Medium	Fine	Coarse	Fine	
	0.5 - 2.0 mm	0.25 - 0.5 mm	0.053 - 0.25 mm	0.02 - 0.053 mm	0.002 - 0.02 mm	
A	9	2	6	25	25	33
B	not determined					

Horizon	Exchangeable cations						Exch. acidity (cmol <sub>c</sub> kg <sup>-1</sup> )	Organic carbon (g kg <sup>-1</sup> )
	pH		----- (cmol <sub>c</sub> kg <sup>-1</sup> ) -----					
	(KCl)	(H <sub>2</sub> O)	Ca	Mg	Na	K		
A	4.90	5.91	6.24	3.06	0.14	0.17	0.06	21.70
B	not determined							

**Appendix 4.1** Colorimetric determination of Al by the pyrocatechol violet method

Calibration standards were between 0 and 5  $\mu\text{g mL}^{-1}$  of Al.

Into a 50 mL volumetric flask were put 2 mL of sample or standard, followed by 10 mL of 2% w/v hydroxylamine hydrochloride, and then 2 mL of 0.15% 1,10 phenanthroline. After mixing, a 10 mL aliquot of 0.03% w/v pyrocatechol violet solution was added and followed, after again mixing, by 20 mL of a pH 6.3 ammonium acetate-acetic acid buffer solution prepared by 1M ammonium acetate and 40% w/v acetic acid. The solutions were then diluted to the mark before again mixing. After 30 minutes the concentrations of Al in the samples were determined against standards using a UV/visible spectrophotometer at a wavelength of 575 nm.



**Appendix 5.1** Fractionation of metals in the Hu-M soil samples from the pot experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.0	0.0	1.1	0.0
	R120	0.0	0.0	1.6	0.0
Co	R0	0.0	4.2	4.0	0.0
	R120	0.0	2.5	3.7	0.0
Cr	R0	0.0	0.4	21.3	0.1
	R120	0.0	0.3	21.4	0.1
Cu	R0	0.0	30.5	18.3	2.3
	R120	0.0	97.2	18.1	4.0
Mn	R0	42.4	0.1	132.8	261.1
	R120	6.4	0.1	87.8	904.9
Ni	R0	0.0	0.0	26.5	0.0
	R120	0.0	0.0	26.6	0.0
Pb	R0	0.1	0.0	0.0	0.4
	R120	0.1	0.0	0.0	0.2
Zn	R0	0.9	2.0	24.8	0.0
	R120	0.3	2.8	24.2	0.0

**Appendix 5.2** Fractionation of metals in the Hu-T soil samples from the pot experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0 R120	R0 R120	0.0 0.0	0.0 0.0	1.9 1.7
Co	R0 R120	R0 R120	0.0 0.0	4.0 3.5	7.8 5.3
Cr	R0 R120	R0 R120	0.0 0.0	1.5 1.6	20.6 19.0
Cu	R0 R120	R0 R120	0.0 0.0	0.5 0.4	16.5 16.2
Mn	R0 R120	R0 R120	58.3 13.1	82.4 142.9	272.6 268.7
Ni	R0 R120	R0 R120	0.0 0.0	1.0 0.8	25.3 26.1
Pb	R0 R120	R0 R120	0.0 0.0	0.1 0.1	0.7 0.8
Zn	R0 R120	R0 R120	2.7 0.3	2.2 3.1	31.9 27.2

**Appendix 5.3** Fractionation of metals in the Ia-C soil samples from the pot experiment for selected treatments of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L)

Metal	Treatment	Exchangeable	Inorganic	Organic	Amorphous
(mg kg <sup>-1</sup> )					
Cd	R0	0.0	0.0	0.4	0.0
	R120	0.0	0.0	2.4	0.0
	L1R0	0.0	0.0	0.9	0.0
	L1R120	0.0	0.0	0.8	0.0
Co	R0	0.0	2.6	3.1	2.0
	R120	0.0	2.4	3.9	3.6
	L1R0	0.0	1.8	1.7	5.1
	L1R120	0.0	2.4	1.6	5.8
Cr	R0	0.0	1.4	16.0	0.0
	R120	0.0	1.5	15.8	0.0
	L1R0	0.0	0.7	12.5	0.0
	L1R120	0.0	1.0	12.4	0.0
Cu	R0	0.0	0.5	19.3	0.0
	R120	0.0	0.3	18.3	3.1
	L1R0	0.0	0.3	17.9	0.7
	L1R120	0.0	0.2	18.5	1.9
Mn	R0	31.0	54.1	139.4	132.3
	R120	30.5	113.5	0.0	665.9
	L1R0	10.5	69.4	104.9	112.2
	L1R120	0.0	157.0	0.0	609.5
Ni	R0	0.0	0.6	22.9	0.0
	R120	0.0	0.6	24.4	0.0
	L1R0	0.0	0.4	22.8	0.0
	L1R120	0.0	0.7	22.8	0.0
Pb	R0	0.0	0.1	0.0	0.6
	R120	0.0	0.1	0.0	0.5
	L1R0	0.0	0.1	0.0	0.2
	L1R120	0.0	0.1	0.0	0.2
Zn	R0	1.2	1.2	22.7	0.0
	R120	0.3	2.2	21.5	0.0
	L1R0	0.1	2.0	20.7	0.0
	L1R120	0.3	1.3	22.1	0.0

L1=lime applied

**Appendix 5.4** Fractionation of metals in the Nb-F1 soil samples from the pot experiment for selected treatments of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L)

Metal	Treatment	Exchangeable	Inorganic	Organic	Amorphous
(mg kg <sup>-1</sup> )					
Cd	R0	0.0	0.4	0.2	1.5
	R120	0.0	0.4	0.4	1.4
	L1R0	0.0	0.1	0.9	1.4
	L1R120	0.0	0.0	0.8	0.2
Co	R0	0.0	2.6	0.0	0.8
	R120	0.0	2.8	0.0	1.4
	L1R0	0.0	0.6	0.7	0.1
	L1R120	0.0	0.7	0.9	1.0
Cr	R0	0.0	3.0	2.5	6.8
	R120	0.0	3.2	2.6	7.4
	L1R0	0.0	0.5	7.1	2.3
	L1R120	0.0	0.4	8.7	0.0
Cu	R0	0.0	1.2	13.0	55.3
	R120	0.0	0.5	15.4	9.0
	L1R0	0.0	0.3	14.4	6.9
	L1R120	0.0	0.2	14.0	6.9
Mn	R0	2.3	42.5	107.1	0.0
	R120	0.2	136.6	0.0	451.2
	L1R0	2.3	43.6	102.3	0.0
	L1R120	0.0	112.9	0.0	511.0
Ni	R0	0.0	0.1	22.0	2.9
	R120	0.0	0.4	22.4	2.8
	L1R0	0.0	0.3	19.4	5.1
	L1R120	0.0	0.4	22.3	0.4
Pb	R0	0.0	0.2	0.1	0.2
	R120	0.0	0.2	0.3	0.2
	L1R0	0.0	0.1	0.4	0.1
	L1R120	0.0	0.1	0.0	0.1
Zn	R0	2.7	0.8	13.4	0.0
	R120	0.3	2.7	12.1	0.0
	L1R0	2.3	3.7	27.3	0.0
	L1R120	0.1	6.8	25.7	0.0

L1=lime applied

**Appendix 5.5** Fractionation of metals in the Sd soil samples from the pot experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.0	0.0	0.5	0.0
	R120	0.0	0.0	2.4	0.0
Co	R0	0.0	3.0	2.1	37.9
	R120	0.0	2.4	0.0	40.8
Cr	R0	0.0	1.9	9.0	1.0
	R120	0.0	2.1	8.6	0.1
Cu	R0	0.0	0.5	26.9	9.8
	R120	0.0	0.5	23.7	12.0
Mn	R0	51.8	30.3	158.8	1010.4
	R120	24.3	126.0	193.2	1354.3
Ni	R0	0.0	1.3	3.8	10.2
	R120	0.0	1.2	4.5	7.4
Pb	R0	0.0	0.1	0.0	0.0
	R120	0.0	0.1	0.0	0.0
Zn	R0	1.1	1.1	12.9	0.0
	R120	2.1	2.1	9.7	0.0

**Appendix 6.1** Fractionation of heavy metals in the Hu-F soil samples from the incubation experiment for selected treatments of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L)

Metal	Treatment	Exchangeable	Inorganic	Organic	Amorphous
		(mg kg <sup>-1</sup> )			
Cd	LOR0	0.0	0.4	0.0	1.6
	LOR80	0.0	0.3	0.0	1.4
	LOR320	0.0	0.3	0.0	1.5
	LOR1280	0.0	0.5	0.0	1.6
	L1R0	0.0	0.4	0.0	1.8
	L1R1280	0.0	0.6	0.0	2.1
Co	LOR0	0.0	5.2	4.4	17.2
	LOR80	0.0	5.4	2.8	16.6
	LOR320	0.0	4.7	2.4	16.1
	LOR1280	0.0	2.8	5.6	9.9
	L1R0	0.0	4.9	1.9	11.8
	L1R1280	0.0	1.9	6.6	7.4
Cr	LOR0	0.0	2.4	22.8	0.0
	LOR80	0.0	2.3	21.5	0.0
	LOR320	0.0	2.6	21.3	0.0
	LOR1280	0.0	2.8	21.2	0.0
	L1R0	0.0	1.0	19.9	0.7
	L1R1280	0.0	1.5	19.2	1.8
Cu	LOR0	0.0	0.5	19.8	5.8
	LOR80	0.0	0.4	19.6	5.1
	LOR320	0.0	0.4	20.0	5.8
	LOR1280	0.0	0.7	19.5	7.4
	L1R0	0.0	1.9	17.2	8.1
	L1R1280	0.0	0.9	14.2	12.5
Mn	LOR0	6.8	68.3	205.6	215.0
	LOR80	9.0	192.0	8.0	604.7
	LOR320	8.8	277.2	11.1	931.8
	LOR1280	12.4	306.5	0.0	1855.0
	L1R0	5.0	113.3	152.2	225.1
	L1R1280	4.7	518.7	0.0	1866.4
Ni	LOR0	0.0	0.5	17.3	0.0
	LOR80	0.0	1.0	14.2	0.0
	LOR320	0.0	1.1	16.5	0.0
	LOR1280	0.0	1.3	15.4	0.0
	L1R0	0.0	0.6	21.0	0.0
	L1R1280	0.0	1.3	18.0	0.0
Pb	LOR0	0.0	0.2	1.4	0.0
	LOR80	0.0	0.3	1.3	0.0
	LOR320	0.0	0.3	1.2	0.0
	LOR1280	0.0	0.2	1.3	0.0
	L1R0	0.0	0.2	1.2	0.0
	L1R1280	0.0	0.2	1.3	0.0
Zn	LOR0	0.0	4.0	12.5	4.4
	LOR80	0.0	7.7	18.7	28.3
	LOR320	0.0	14.3	29.2	63.9
	LOR1280	0.0	41.1	31.8	94.0
	L1R0	0.0	2.3	26.9	0.0
	L1R1280	0.0	3.6	19.9	1.7

L0=no lime applied, L1=lime applied

**Appendix 6.2** Fractionation of heavy metals in the Hu-M soil samples from the incubation experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.1	0.3	1.4	0.5
	R80	0.1	0.3	1.6	0.2
	R320	0.1	0.3	1.5	0.4
	R1280	0.1	0.3	1.6	0.5
Co	R0	0.0	3.9	4.1	14.6
	R80	0.0	4.6	3.4	15.7
	R320	0.0	3.8	3.8	15.6
	R1280	0.0	3.1	5.5	14.5
Cr	R0	0.0	0.8	20.9	0.0
	R80	0.0	0.8	18.5	0.0
	R320	0.0	0.8	24.8	0.0
	R1280	0.0	0.9	21.8	0.0
Cu	R0	0.0	0.4	13.0	7.6
	R80	0.0	0.4	11.8	8.7
	R320	0.0	0.5	12.1	10.0
	R1280	0.0	0.3	13.2	9.6
Mn	R0	65.0	12.0	244.8	121.9
	R80	59.9	29.8	228.5	264.1
	R320	71.7	27.6	255.0	302.3
	R1280	89.1	28.0	237.6	313.6
Ni	R0	0.0	0.3	21.4	0.0
	R80	0.0	0.6	20.7	0.0
	R320	0.0	0.5	22.1	0.0
	R1280	0.0	0.5	22.1	0.0
Pb	R0	0.0	0.1	1.0	0.0
	R80	0.0	0.2	0.1	0.1
	R320	0.0	0.3	0.1	0.1
	R1280	0.0	0.2	0.0	0.3
Zn	R0	0.0	2.4	10.7	0.0
	R80	0.0	2.3	11.3	5.6
	R320	0.0	3.0	14.5	6.4
	R1280	0.0	4.7	16.8	8.6

**Appendix 6.3** Fractionation of heavy metals in the Hu-T soil samples from the incubation experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.1	0.3	0.8	1.2
	R80	0.2	0.2	0.8	1.3
	R320	0.2	0.2	0.8	1.8
	R1280	0.2	0.3	0.9	1.3
Co	R0	0.0	4.2	3.8	16.0
	R80	0.0	3.6	4.2	12.0
	R320	0.0	3.6	4.2	10.4
	R1280	0.0	2.2	5.9	9.4
Cr	R0	0.0	1.4	24.2	0.0
	R80	0.0	1.6	28.9	0.0
	R320	0.0	1.8	28.1	0.0
	R1280	0.0	2.0	20.1	0.0
Cu	R0	0.0	0.4	11.8	0.2
	R80	0.0	0.2	11.5	10.4
	R320	0.0	0.2	12.6	9.5
	R1280	0.0	0.8	13.5	7.7
Mn	R0	210.3	1.7	307.1	362.3
	R80	92.6	148.0	260.2	650.1
	R320	62.7	275.8	126.3	1052.8
	R1280	13.9	424.9	0.0	2074.9
Ni	R0	0.0	1.1	17.2	0.0
	R80	0.0	1.2	19.4	0.0
	R320	0.0	1.4	18.6	0.0
	R1280	0.0	1.8	15.5	0.0
Pb	R0	0.0	0.1	0.0	0.2
	R80	0.0	0.2	0.0	0.2
	R320	0.0	0.3	0.0	0.2
	R1280	0.0	0.2	0.0	0.2
Zn	R0	4.3	1.7	30.9	0.0
	R80	3.5	14.8	37.3	23.0
	R320	1.3	34.8	30.0	24.7
	R1280	0.3	47.6	33.1	92.3



**Appendix 6.4** Fractionation of heavy metals in the Ia-C soil samples from the incubation experiment for selected treatments of water treatment residue (R) (Mg ha<sup>-1</sup>) and lime (L)

Metal	Treatment	Exchangeable	Inorganic	Organic	Amorphous
		(mg kg <sup>-1</sup> )			
Cd	LOR0	0.0	0.2	2.0	0.0
	LOR80	0.0	0.2	2.0	0.0
	LOR320	0.0	0.2	2.5	0.0
	LOR1280	0.0	0.4	1.7	0.0
	LIR0	0.0	0.3	1.9	0.0
	LIR1280	0.0	0.4	1.6	0.0
Co	LOR0	0.0	2.0	10.3	0.0
	LOR80	0.0	2.0	10.9	0.0
	LOR320	0.0	1.9	12.1	0.0
	LOR1280	0.0	0.8	9.5	0.0
	LIR0	0.0	1.2	11.0	0.0
	LIR1280	0.0	1.0	8.6	0.0
Cr	LOR0	0.0	0.6	19.0	0.0
	LOR80	0.0	0.8	18.2	0.0
	LOR320	0.0	0.9	12.2	0.0
	LOR1280	0.0	0.9	15.8	0.0
	LIR0	0.0	0.7	19.3	0.0
	LIR1280	0.0	1.1	16.4	0.0
Cu	LOR0	0.0	0.7	14.0	3.1
	LOR80	0.0	0.8	14.5	2.8
	LOR320	0.0	0.9	14.9	6.4
	LOR1280	0.0	0.8	13.0	10.0
	LIR0	0.0	0.6	13.0	4.3
	LIR1280	0.0	0.6	13.8	11.1
Mn	LOR0	66.5	2.8	72.7	66.1
	LOR80	63.5	30.3	64.2	276.2
	LOR320	64.0	244.1	48.4	998.5
	LOR1280	13.0	363.2	0.0	1844.8
	LIR0	32.2	7.9	50.4	73.4
	LIR1280	18.6	389.7	0.0	1942.0
Ni	LOR0	0.0	0.5	2.8	3.5
	LOR80	0.0	0.6	2.9	3.6
	LOR320	0.0	0.7	3.2	4.6
	LOR1280	0.0	1.0	3.0	4.9
	LIR0	0.0	0.5	1.6	5.2
	LIR1280	0.0	1.2	2.7	6.0
Pb	LOR0	0.0	0.1	1.2	0.0
	LOR80	0.0	0.1	1.2	0.0
	LOR320	0.0	0.2	1.1	0.0
	LOR1280	0.0	0.2	1.1	0.0
	LIR0	0.0	0.2	1.3	0.0
	LIR1280	0.0	0.2	1.1	0.0
Zn	LOR0	1.7	0.5	7.6	1.6
	LOR80	1.0	5.6	26.2	13.9
	LOR320	0.6	22.5	44.0	72.1
	LOR1280	0.1	34.6	41.4	88.5
	LIR0	0.5	3.3	3.8	6.2
	LIR1280	0.2	35.6	34.9	88.3

L0=lime not applied, L1=lime applied

**Appendix 6.5** Fractionation of heavy metals in the Nb-A soil samples from the incubation experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.2	0.2	1.7	0.3
	R80	0.2	0.2	1.5	0.7
	R320	0.1	0.2	1.7	0.4
	R1280	0.1	0.3	1.4	0.4
Co	R0	0.0	0.9	8.6	0.0
	R80	0.0	1.0	9.7	0.0
	R320	0.0	1.1	10.6	0.0
	R1280	0.0	1.3	12.1	0.0
Cr	R0	0.0	0.5	16.7	0.0
	R80	0.0	0.7	17.3	0.0
	R320	0.0	0.8	18.6	0.0
	R1280	0.0	1.3	18.1	0.0
Cu	R0	0.0	0.3	9.0	0.0
	R80	0.0	0.7	8.9	0.0
	R320	0.0	0.8	9.0	2.8
	R1280	0.0	0.9	11.4	4.5
Mn	R0	23.3	0.0	202.7	0.0
	R80	16.1	49.7	109.2	338.7
	R320	11.6	142.7	32.3	354.8
	R1280	2.9	514.1	0.0	1674.8
Ni	R0	0.0	0.4	20.9	0.0
	R80	0.0	0.4	20.2	0.0
	R320	0.0	0.4	20.7	0.0
	R1280	0.0	1.6	20.5	0.0
Pb	R0	0.0	0.1	1.2	0.0
	R80	0.0	0.1	1.3	0.0
	R320	0.0	0.2	1.2	0.0
	R1280	0.0	0.2	1.2	0.0
Zn	R0	0.4	0.5	22.6	0.0
	R80	0.1	10.5	19.5	7.3
	R320	0.1	29.0	19.3	47.5
	R1280	0.0	58.0	17.3	96.6

**Appendix 6.6 Fractionation of heavy metals in the Nb-F soil samples from the incubation experiment for selected treatments of water treatment residue (R)**

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.2	0.2	0.6	1.3
	R80	0.2	0.2	0.8	1.3
	R320	0.2	0.2	0.9	1.3
	R1280	0.1	0.4	0.4	1.4
Co	R0	0.0	1.8	2.4	0.0
	R80	0.0	1.9	3.2	0.0
	R320	0.0	2.0	3.2	0.0
	R1280	0.0	2.2	2.3	0.0
Cr	R0	0.0	1.7	20.7	0.0
	R80	0.0	1.8	21.2	0.0
	R320	0.0	2.1	19.7	0.0
	R1280	0.0	2.3	20.4	0.0
Cu	R0	0.0	0.2	8.0	0.0
	R80	0.0	0.2	8.4	0.0
	R320	0.0	0.2	9.3	0.0
	R1280	0.0	0.8	12.0	0.0
Mn	R0	8.5	14.4	57.4	0.0
	R80	7.8	70.5	44.8	168.6
	R320	6.9	179.3	0.0	516.1
	R1280	6.2	361.0	0.0	1499.5
Ni	R0	0.0	0.3	27.9	0.0
	R80	0.0	0.5	27.1	0.0
	R320	0.0	0.7	26.1	0.0
	R1280	0.0	1.3	24.2	0.0
Pb	R0	0.0	0.2	0.0	0.0
	R80	0.0	0.2	0.0	0.0
	R320	0.0	0.3	0.0	0.0
	R1280	0.0	0.1	0.0	0.0
Zn	R0	1.3	0.7	14.5	0.0
	R80	1.8	9.6	21.8	16.4
	R320	1.2	29.6	15.7	55.5
	R1280	0.2	47.5	37.3	77.4

**Appendix 6.7** Fractionation of heavy metals in the Sd soil samples from the incubation experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.0	0.2	2.2	0.0
	R80	0.0	0.2	2.0	0.0
	R320	0.0	0.2	1.9	0.0
	R1280	0.0	0.3	2.1	0.0
Co	R0	0.0	1.7	1.7	30.9
	R80	0.0	1.3	1.8	27.4
	R320	0.0	1.0	1.5	29.0
	R1280	0.0	0.6	1.6	37.6
Cr	R0	0.0	0.3	13.5	0.0
	R80	0.0	0.3	13.4	0.0
	R320	0.0	0.5	13.1	0.0
	R1280	0.0	0.6	12.7	0.0
Cu	R0	0.0	0.5	24.8	6.9
	R80	0.0	0.9	22.0	7.3
	R320	0.0	0.8	18.3	8.3
	R1280	0.0	0.9	21.6	10.8
Mn	R0	141.5	0.0	362.8	794.7
	R80	103.9	96.4	262.0	1182.1
	R320	78.7	207.5	142.4	1585.2
	R1280	14.0	393.5	0.0	2322.1
Ni	R0	0.0	1.5	4.4	4.6
	R80	0.0	1.5	4.3	4.7
	R320	0.0	1.7	4.4	3.6
	R1280	0.0	2.1	3.8	5.9
Pb	R0	0.0	0.2	1.3	0.0
	R80	0.0	0.2	0.8	0.0
	R320	0.0	0.3	0.5	0.0
	R1280	0.0	0.1	0.3	0.0
Zn	R0	2.4	1.5	16.1	0.0
	R80	2.4	7.9	21.9	46.5
	R320	1.1	16.0	29.0	61.2
	R1280	0.0	40.0	36.3	93.0

**Appendix 6.8** Fractionation of heavy metals in the Va soil samples from the incubation experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.1	0.3	0.8	1.1
	R80	0.1	0.2	0.8	0.8
	R320	0.1	0.2	0.8	0.9
	R1280	0.1	0.3	0.4	1.5
Co	R0	0.0	2.4	1.7	5.6
	R80	0.0	2.3	1.7	6.7
	R320	0.0	2.4	2.1	6.9
	R1280	0.0	2.4	1.4	7.2
Cr	R0	0.0	2.1	20.3	0.0
	R80	0.0	2.1	20.2	0.0
	R320	0.0	2.3	20.3	0.0
	R1280	0.0	2.7	20.2	0.0
Cu	R0	0.0	0.5	12.3	0.0
	R80	0.0	0.6	14.0	0.0
	R320	0.0	0.8	13.9	4.8
	R1280	0.0	0.8	13.9	6.2
Mn	R0	6.2	92.0	89.5	222.4
	R80	6.1	113.5	92.6	435.5
	R320	5.7	206.7	73.3	1042.3
	R1280	6.7	350.9	0.0	1753.0
Ni	R0	0.0	0.7	18.8	0.0
	R80	0.0	0.7	16.1	0.0
	R320	0.0	1.0	15.4	0.0
	R1280	0.0	1.4	16.6	0.0
Pb	R0	0.0	0.1	0.3	0.0
	R80	0.0	0.3	0.7	0.0
	R320	0.0	0.4	0.6	0.0
	R1280	0.0	0.2	1.3	0.0
Zn	R0	1.2	1.9	13.4	0.2
	R80	1.1	10.5	13.8	30.5
	R320	1.1	29.8	15.7	84.2
	R1280	1.9	41.5	29.3	99.5

**Appendix 6.9** Fractionation of heavy metals in the We soil samples from the incubation experiment for selected treatments of water treatment residue (R)

Metal	WTR (Mg ha <sup>-1</sup> )	Exchangeable	Inorganic (mg kg <sup>-1</sup> )	Organic	Amorphous
Cd	R0	0.1	0.3	0.0	1.7
	R80	0.1	0.2	0.0	1.8
	R320	0.1	0.2	0.0	1.8
	R1280	0.1	0.4	0.0	1.6
Co	R0	0.0	3.0	4.8	9.7
	R80	0.0	2.7	5.2	12.5
	R320	0.0	2.8	5.2	10.8
	R1280	0.0	2.8	4.7	9.8
Cr	R0	0.0	2.6	21.3	0.0
	R80	0.0	2.7	21.3	0.0
	R320	0.0	2.8	20.2	0.0
	R1280	0.0	3.1	21.0	0.0
Cu	R0	0.0	0.4	15.8	8.3
	R80	0.0	0.9	16.0	7.4
	R320	0.0	1.0	15.5	10.5
	R1280	0.0	1.0	16.7	6.2
Mn	R0	22.8	114.0	537.6	1238.2
	R80	26.2	145.1	428.5	1381.0
	R320	13.3	194.3	240.9	1455.6
	R1280	10.7	345.5	0.0	2272.3
Ni	R0	0.0	1.0	16.5	0.0
	R80	0.0	1.9	16.5	0.0
	R320	0.0	1.4	15.9	0.0
	R1280	0.0	1.5	17.3	0.0
Pb	R0	0.0	0.1	1.4	0.0
	R80	0.0	0.2	1.3	0.0
	R320	0.0	0.2	1.2	0.0
	R1280	0.0	0.2	1.3	0.0
Zn	R0	0.3	1.6	13.6	16.6
	R80	0.2	12.7	13.6	26.7
	R320	0.2	24.2	20.6	63.9
	R1280	0.2	42.7	24.7	98.3

**Appendix 7.1** Manganese, chromium and phosphorus in borehole (B) and dam (D) water at Brookdale Farm from 1997 to 2002 (data supplied by Umgeni Water)

Sample date	Mn		Cr		P	
	B	D	B	D	B	D
	(mg L <sup>-1</sup> )		(µg L <sup>-1</sup> )			
04.12.1997	0.02	nd	<3	nd	24.7	nd
11.12.1997	nd	0.06	nd	<3	nd	nd
26.03.1998	0.04	0.04	22	5.3	25.6	105
04.06.1998	<0.01	<0.01	20.7	4.8	21.9	20.4
10.09.1998	0.04	<0.01	3.6	<3	19.7	33.0
03.12.1998	<0.01	0.01	<3	<3	21.9	43.6
06.05.1999	0.05	0.02	<3	<3	25.4	22.6
03.06.1999	0.04	0.07	<3	<3	20.8	16.4
02.09.1999	nd	0.07	nd	<3	nd	46.2
02.12.1999	0.04	0.03	<3	<3	22.4	37.0
30.03.2000	<0.01	0.06	<3	<3	<15	32.6
08.06.2000	<0.01	0.02	<3	<3	<15	<15
07.09.2000	0.24	0.02	<3	<3	nd	30.9
10.04.2001	0.09	0.06	<3	<3	nd	nd
07.06.2001	0.03	<0.01	<3	<3	nd	nd
07.09.2001	<0.01	0.03	<3	<3	<15	16.5
04.04.2002	nd	nd	nd	<3	nd	21.6
13.06.2002	0.13	<0.01	<3	<3	19.2	15.5
12.09.2002	<0.01	0.02	<3	<3	<15	<15

nd=not determined