

# **QUANTIFYING THE FERTILIZER VALUE OF WASTEWATER SLUDGES FOR AGRICULTURE**

Report to the  
**Water Research Commission**

by

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## **EXECUTIVE SUMMARY**

### **BACKGROUND**

Beneficial use of treated municipal sludge in agricultural lands is a well-known practice around the world, because of its soil conditioning effect and as a source of low grade fertilizer. Municipal sludge consists of appreciable amounts of macro and micro nutrients though not all the nutrients are immediately available for consumption by crops. The availability of the macro nutrients N and P from sludge amended soils for consumption by plants (fertilizer value) is a function of sludge composition, climate, and soil. The current South African sludge guideline recommends sludge to be applied according to crop requirement with a maximum rate set  $10 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ . The guideline, however, does not provide detailed instructions on sludge recommendation rates taking into account the fertilizer value of sludge, crop nutrient requirement, and potential long term heavy metal accumulation.

### **OBJECTIVES OF THE STUDY**

The overarching aim of this study was to develop a user friendly sludge application rate advisor computer model that takes into account both the fertilizer value of sludge and crop nutrient requirements. To acquire this overarching objective, the following specific objectives were achieved. The specific objectives were to: a) test existing analytical methods for rapid characterization of sludge N and P pools, b) investigate N release from sludge (fertilizer value) across South African agro-ecological zones and soil textural classes, and c) investigate the fate and dynamics of trace metals in sludge amended soils.

Regarding the first objective, combinations of laboratory incubation and fractionation experiments were conducted to characterize sludge N and P pools. The second objective was mainly achieved by computer model (SWB\_Sci) simulations across five South African agro-ecological zones and four major soil textures. The third objective was achieved from field experiment conducted at East Rand Water Care Company (ERWAT).

### **SUMMARY OF MAIN FINDINGS AND CONCLUSION**

#### **Characterization of sludge N and P pools**

Liquid sludge depth in drying beds as well as drying duration seems to influence the N and C content, organic matter constituents, as well as the N mineralization rate (fertilizer value) of sludge. Liquid sludge dried in thick depths for longer duration appears to decrease sludge N and C content while enhancing the lignified fraction of the sludge organic matter. In contrast, sludges dried in thin layers within short period were characterised by higher C and N contents, lower lignin composition, as well as higher N mineralization (fertilizer value). It was apparent that large fraction of the organic matter in all sludges investigated was soluble compounds, which contributed to about 90% of the total N mineralized.

#### **N release across South African agro-ecological zones and soil textures**

Computer model simulations indicated that annual N release varied significantly ( $P < 0.05$ ) across agro-ecological zones ranging from 25% in arid to 42% in super-humid agro-ecological zones. Similarly, annual N mineralization rates varied significantly between sites within an agro-ecological zone and between soil textures within a site. Therefore, from an

agronomic and environmental perspective it is advisable to have site-and soil-specific annual N release rate.

### **Fate and dynamics of trace metals from sludge amended soils**

There was a direct relationship between trace metal uptake by maize and sludge application rate. In most cases, trace metal concentration in maize plant tissue remained well below phyto toxic levels. Nonetheless, seven consecutive years of sludge application at  $16 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  under dryland maize farming increased canopy Zn concentration to phyto toxic levels. This is in contrast to the soil Zn concentration which remained far below the environmental threshold levels. A large fraction of the trace metals in the soil profile of all sludge treatments was EDTA extractable. While the water soluble fraction of Cd and Pb remained below detection limit ( $<1 \text{ mg kg}^{-1}$ ) while Zn and Pb accounted  $<1\%$  of the EDTA extractable fraction. Therefore, it is of great importance to develop an integrated sludge management practice which comprises monitoring the soil profile for potential heavy metal accumulation and monitoring crop canopy for phyto toxicity.

### **RECOMMENDATIONS FOR FUTURE RESEARCH**

The following research topics need further investigation:

1. The effect of post wastewater treatment dewatering techniques (drying depth and time) on:
  - a. Sludge organic constituents,
  - b. Sludge N composition,
  - c. Nitrogen decomposition rate,
  - d. Sludge fertilizer value, and
  - e. Phosphorus fertilizer value.
2. Water, salt, and nitrogen balances of agricultural lands receiving liquid sludge.
3. Trace metal leaching below the active root zone from sludge amended agricultural soils.

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## **CHAPTER 1 – INTRODUCTION**

### **1.1 GENERAL BACKGROUND**

Agricultural use of municipal wastewater sludge is a well-known practice around the globe because of its soil conditioning effect and as a source of low grade fertilizer (Ogbazghi et al., 2015). Municipal wastewater sludge contains appreciable amounts of N and P and has significant inorganic fertilizer replacement values for these two major plant nutrients (Hall, 1986). Generally, treated municipal sludge with acceptable quality for beneficial agricultural use is applied according to crop N requirements (Mile and Graveland, 1972; Dotson, 1973). A large fraction of the N in municipal wastewater sludge (>75%) is organic and its availability for consumption by crops is dependent on (i) its mineralization rate and (ii) losses to the environment through volatilization, denitrification and leaching (Tesfamariam et al., 2015).

### **1.2 MOTIVATION**

The N content and organic matter composition of wastewater sludge is influenced by the origin of wastewater and wastewater treatment processes (Banegas et al., 2007). These differences in the biochemical composition of sludge have direct effect on the organic matter decomposition and N mineralization of sludges (Serna and Pomares, 1992; Ubierna et al., 2013; Mattana et al., 2014). Furthermore, N mineralization is a biological process and consequently is strongly influenced by abiotic factors such as soil water and temperature. Therefore, injudicious extrapolation of results from laboratory incubation studies conducted at controlled temperature and water or results from field studies conducted at a specific site using specific sludge types can compromise both the environment and crop production.

Similarly, the availability of phosphorus for crop uptake from sludge amended soils is largely influenced by wastewater phosphorus removal methods (biological vs. chemical) (O'Connor et al., 2004). Previous studies indicated high P phytoavailability from biological P removal methods (BPR) relative to chemical methods which used Fe and Al salts. Such plant availability is, however, influenced by soil chemical and physical properties. Proper understanding of the kinetics of P release from biological vs. chemical P removal methods is vital both from agronomic and environmental perspectives.

One of the main concerns with the beneficial use of sludge in agricultural lands is the long-term build-up of trace metals (Smith, 2009). Some trace metals are essential for plant and animals' health while others are not known to be essential to plant and animals. Toxicity occurs when metals are concentrated in the environment above threshold levels (Sterritt and Lester, 1984). The natural background concentration of trace metals in soils play a determining role in the level of threat to groundwater pollution from any anthropogenic additions such as through the application of sludge. The background concentration of a soil is defined as the normal chemical composition of an earth material prior to its contamination (Korte, 1999). The background concentration is a function of the parent material and soil formation processes and is therefore highly variable across sites. Thus site and soil specific heavy metal monitoring protocols are vital from both agronomic and environmental protection perspectives.

### **1.3 PROBLEM STATEMENT**

A large fraction of the N in sludge is organic and its availability for crop uptake is a function of (a) the sludge mineralization rate and (b) losses to the environment through volatilization, denitrification and leaching. Nitrogen mineralization from sludge amended soils is influenced by wastewater sources, wastewater treatment processes, as well as by abiotic factors such as soil water and temperature. The vast number of combinations among the above mentioned factors could never be adequately covered by field trials. Hence, a mechanistic N and P balance cropping systems model (SWB-Sci) model was developed as a reasoning support tool. This model is a fairly complex scientific research tool and requires detailed weather, soil, crop and sludge parameters. Due to its complexity, routine use of this reasoning support tool by industry or extension officers in its current form is highly unlikely.

Proper parameterization of the SWB-Sci model with accurate sludge properties is vital for the accuracy of predictions made by the model. Reliable parameter derivation is often obtained from incubation studies which are time consuming and therefore impractical for real time planning and decision making. The use of surrogate measures (organic compounds) or wastewater treatment processes and post treatment drying techniques could help with real time planning and decision making.

Accumulation of trace metals in agricultural lands is one of the main concerns with the beneficial agricultural use of sludge. Despite the concerns there is presently no local information available on potential short to long-term impacts on agricultural production and the environment.

### **1.4 OBJECTIVES OF THE STUDY**

The main objectives of the study were to:

1. Develop a simple user-friendly database model to aid wastewater treatment plant managers and sludge guideline developers as a reasoning support tool.
2. Test existing objective analytical methods for rapid characterization of sludge N and P pools.
3. Include a simple heavy metal mass balance model into the simple database model.

### **1.5 APPROACH TO THE STUDY**

To achieve the stated objectives, the following activities were undertaken:

1. Literature study,
2. Laboratory incubation studies,
3. Field trial,
4. Model scenario simulations,
5. Simple user-friendly database model development.

#### **1.5.1 Literature study**

A literature study was conducted to identify the best methodologies of extraction and analysis that could be used to determine the various constituents of organic matter in sludge as well as the various compounds which the P in sludge is bound to. Furthermore, a search was done on existing database models and the approaches that they follow to simulate various processes.

### **1.5.2 Laboratory incubation studies**

Laboratory incubation studies were conducted to investigate the effects of wastewater treatment and post treatment dewatering techniques on:

- a) Sludge N content
- b) Sludge C content
- c) Organic matter constituents
- d) Nitrogen mineralization, and
- e) Organic matter decomposition.

Similarly, the effect of wastewater P-removal methods (Biological vs. chemical) on P plant availability and P release rate was investigated.

### **1.5.3 Field trials**

Field trials of dryland maize and irrigated maize-oat rotation were conducted in order to investigate the short-term effects of sludge application according to crop N requirements on heavy metal uptake by crops, accumulation in the soil, and mobility within the soil profile. Maize plant and soil samples were collected from a field experiment, which received class A1a municipal sludge on a yearly basis for 8 consecutive years. Both plant and soil samples were analysed for four selected heavy metals (Zn, Cd, Ni, and Pb).

### **1.5.4 Model scenario simulation**

Model scenario simulations were run using the SWB-Sci model for five of the six South African Agro-ecological zones in order to investigate the possibility of using a single annual N release rate across sites and soil textures within an agro-ecological zone. The scenario simulations were run for two or three sites within each agro-ecological zone, depending on the availability of weather data, using 20 years of historical weather data.

### **1.5.5 Database model development**

A database base model, the Sludge Application Rate Advisor (SARA) model was developed based on information generated from findings of the above four activities.

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# **CHAPTER 2 – THE CHANGE IN CARBON, NITROGEN AND VAN SOEST METHOD EXTRACTABLE ORGANIC FRACTIONS OF MUNICIPAL SEWAGE SLUDGE AS INFLUENCED BY WASTEWATER TREATMENT AND POST TREATMENT DRYING TECHNIQUES**

## **2.1 GENERAL INTRODUCTION**

The biochemical composition of sludge is influenced by wastewater treatment and post treatment dewatering/ drying techniques (Ucisik and Henze, 2008). Thus it is of great importance to identify the effect of pre and post wastewater treatment techniques on the sludge composition. This is because the biochemical composition of sewage sludge dictates the rates of C decomposition and N mineralization (Seneviratne, 2000; Parnaudeau et al., 2004; Smith and Tibbett, 2004).

Anaerobic and aerobic digestion of sludge are the most commonly employed wastewater treatment techniques which produce a stable sludge (Chan et al., 2009) while activated sludge treatment process produce unstable sludge. The most commonly used sludge dewatering/drying techniques include: cake filtration, centrifugation, bed drying, thermal drying, and belt pressing (Dirkzwager & Hermite, 1988; Matsuoka et al., 2006). In South Africa the dominant sludge drying technique used is drying beds (Snyman et al., 2004). Drying beds are relatively cost effective compared to mechanical and thermal drying techniques (WEF, 2009). Post wastewater treatment sludge drying techniques are vital for agricultural use as this significantly influences the transport costs of sludge from wastewater treatment plants to receiving soils (Kouloumbos et al., 2008). The drying techniques could, however, influence the quantity and plant availability of N in the sludge.

The aim of this section of the study is to investigate the effect of selected wastewater treatment techniques (anaerobic digestion, activated sludge, and thermal sludge hydrolyses) and post treatment drying techniques (drying on concrete beds at 10 cm vs. 25 cm drying depth and drying on earth paddy) on the N, C, and organic compounds composition of municipal sewage sludge.

## **2.2 MATERIALS AND METHODS**

### **2.2.1 Sludge material**

The sludge materials investigated in the study were obtained from different wastewater treatment plants and were chosen to represent different wastewater treatment processes and post treatment drying method. The actual sewage treatment processes and dewatering/drying methods evaluated in this experimental work are shown in Table 2.1 while selected chemical properties of the sludge materials are presented in Table 2.2.

These sludge materials were chosen to represent different sewage treatment processes and post treatment drying methods. Three samples of each sludge type were collected from heaps which were ready for collection by farmers. The sludge samples were transported in paper bags to the laboratory for investigation. The sludge organic matter composition fractionation method was conducted using Van Soest (1970) method, which has been previously tested for manure and sludge.

All sludge materials were air dried and milled to pass through a 1 mm sieve. The air dried and milled sludge was extracted with petroleum ether using Soxtec™ 2043 Fat Extraction System to determine the fraction of lipids in the sludge. The lipids extraction was followed by estimation of the Neutral Detergent Fiber (NDF) as described by Goering and Van Soest (1970) and Van Soest (1994). The NDF solution was made up of sodium lauryl sulphate, disodium ethylenediaminetetraacetate (EDTA) dehydrate, sodium borate decahydrate, disodium hydrogen phosphate anhydrous, 2-ethoxyethanol (ethylene glycol monoethyl ether) purified grade and distilled water. A 0.3 g of air dried sample milled to pass 1 mm sieve, was placed in 50 ml crucible and boiled for 1 hour with 100 ml NDF solution at 100°C. After boiling, the extract was filtered through the crucible and the residues that remained in the crucible were oven dried at 60°C and not ashed. Extraction of NDF was conducted using Fibertec™ 2010 Auto Fibre Analysis System. The NDF extraction was followed by Acid Detergent Fiber (ADF) extraction as described by Goering and Van Soest (1970) and Van Soest (1994).

**Table 2.1 Description of sewage sludge used**

Sludge acronym	Sludge treatment process	VSS destruction	Digestion	Age (retention time) (days)			Post treatment drying techniques and duration		
				Primary	Secondary		Drying method	Sludge layer depth during drying	Duration of drying technique
Activated	Activate sludge								
ADS1	Anaerobically digested	33%	Mesophylic	15	2		Conventional concrete drying beds	< 100mm	7 days
ADS2	Anaerobically digested	44%	Mesophylic	25	3		Conventional drying beds	250mm	21 days (summer)
ADS3	Anaerobically digested	35%	Mesophylic	NA	NA		Paddy Conventional drying beds	250mm <100mm	21 days 7 days
THS	Thermally hydrolyzed	47%	140-170°C	NA	NA		NA	NA	NA

**NB.** No information from wastewater treatment plant provided

**Table 2.2 Selected chemical properties of sludges investigated**

Sludge parameter	Unit	Activated	ADS1	ADS2	ADS3	THS
pH (H <sub>2</sub> O)	NA	6.24	5.86	6.34	6.58	6.78
EC	mS m <sup>-1</sup>	264	236	77	211	317
Total C	%	29.7	17	24.8	31.9	18.1
Total N	%	4.95	2.81	2.83	5.47	3.13
NH <sub>4</sub> <sup>+</sup>	mg kg <sup>-1</sup>	1008	2640	250	1449	2697
NO <sub>3</sub> <sup>-</sup> and NO <sub>2</sub> <sup>-</sup>	mg kg <sup>-1</sup>	166	508	254	75.4	325
Total P	%	2.44	3.02	2.34	2.00	2.70
K	%	0.59	0.27	0.26	0.46	0.08
Na	%	0.11	0.15	0.07	0.1	0.06
Ca	%	1.96	2.86	2.76	1.83	3.38
Mg	%	0.53	0.39	0.37	NA	0.15
Zn	mg kg <sup>-1</sup>	1166	2886	3065	1121	523
Mn	mg kg <sup>-1</sup>	175	880	625	NA	291
Al	%	0.74	2.17	2.03	0.77	0.81
Fe	%	1.21	NA	2.15	1.12	NA

The ADF solution was made up of Cetyl trimethyl ammonium bromide (CTAB) and 1N H<sub>2</sub>SO<sub>4</sub>. A 0.3 g air dried sample milled to pass through 1 mm sieve, was placed in 50 ml crucible and boiled for 1 hour with 100 ml ADF solution at 100°C. After boiling, the solvent was filtered through the crucible and the residues that remain in the crucible were oven dried at 60°C and not ashed. Extraction of ADF was conducted using Fibertec™ 2010 Auto Analysis System. Finally the acid detergent lignin (ADL) was determined as reported by Goering and Van Soest (1970) and Van Soest (1994). This procedure had two steps. The first step was to run ADF. The dried residues from ADF were treated with 72% sulfuric acid for 3 hours at room temperature. Afterwards it was filtered through the crucible and the residues that remained in the crucible were oven dried at 60°C. In the second step, the dried residues from the 72% sulfuric acid treatment were ashed. Similar to the NDF and ADF, extraction of ADL was conducted using Fibertec™ 2010 Auto Analysis System.

Fractions of the neutral detergent soluble fraction, hemicelluloses, cellulose and lignified fraction were calculated as follows:

Soluble compounds fraction = original mass – (NDF+ fats fraction),

Hemicellulose = NDF- ADF,

Cellulose = ADF- 72% H<sub>2</sub>SO<sub>4</sub> extraction,

Lignified fraction = 72% H<sub>2</sub>SO<sub>4</sub> extraction – Ash.

The inorganic N (NO<sub>3</sub>-N + NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub>-N) was determined by the steam distillation method as described by Mulvaney (1996). Total N (TN) and C (TC) were determined using the Carlo Erba method. The EC and pH of the sludge materials were determined using 1:2.5 sludge to water ratio. Total P and all heavy metals were determined using Inductively Couple Plasma Optical Emission Spectrometer (ICP-OES) (Spectroflame Modula; Spectro; Kleve Germany) after wet acid digestion.

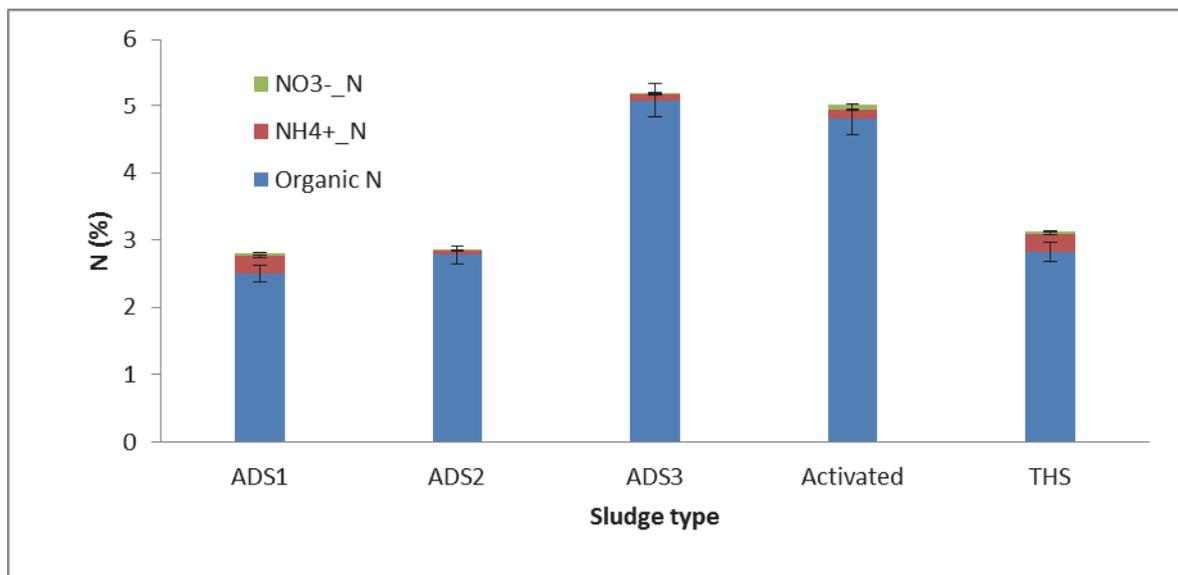
### 2.2.2 Statistical analyses

To evaluate the effect of wastewater treatment and post treatment drying techniques on the total N, C, and organic matter composition of sludges, three samples (replications) were collected randomly from five different sludges that underwent different treatment and post treatment drying techniques. The N, C and organic matter contents of the sludge were analysed using the Statistical Analysis System (SAS) software for Windows v9.3 (Statistical Analysis System Inc., 2002). Data was subjected to analysis of variance and least significant difference (LSD) was calculated at 5% significant level to compare the treatment means using the Tukey's test.

## 2.3 RESULTS AND DISCUSSION

### 2.3.1 Effect of wastewater treatment process and sludge drying techniques on total, organic and inorganic fractions of N in sludge

Sludge N content varied significantly ( $P \leq 0.005$ ) between sludges that were dried in thin layers for short period (ADS3 and Activated) and sludges that were dried in thick layers for relatively longer time (Fig. 2.1).



**Figure 2.1 Total organic and inorganic fraction of N in sludge as affected by wastewater treatment process and drying methods (anaerobically digested dried in concrete beds in layers of 250 mm (ADS1); anaerobically digested dried in paddies in layers of 250 mm (ADS2); anaerobically digested dried on concrete slab in layers of less than 100 mm (ADS3); activated sludge dried in concrete slab in layers of less than 100 mm (Activated); Thermal hydrolysis sludge (THS).**

Activated sludge and anaerobically digested sludge dried as thin layers on concrete slabs (ADS3) had the highest total N compared with ADS 1 & 2 and THS. It was interesting to note that the two sludge types, ADS1 and ADS2, which were all anaerobically digested and dried in concrete beds and paddy in thicker sludge layers (250mm), had similar total N content (2.81 and 2.83%, respectively). However, the  $\text{NH}_4$  content of ADS1 was almost an order of a magnitude greater than for ADS2 (2640 mg/kg for ADS 1 versus 250 for ADS2).

Sludge treated through thermal hydrolyses also had similar total N content (3%) to ADS1 and ADS2. The inorganic N fraction ( $\text{NO}_3$  and  $\text{NH}_4$ ) accounted only 2-3% of the total N in ADS2, ADS3 and Activated sludges and 10-11% of the ADS1 and THS.

ADS1 sludge was anaerobically digested and dried in concrete beds. Similarly, ADS2 was anaerobically digested but was dried in paddy. Both sludges were dried on the beds in thick layers of 250 mm during the drying process. The similarity in the total N content of ADS1 and ADS2 seems to indicate that drying method (concrete or paddy) did not have significant influence on the total N content of anaerobically digested sludges as long as the sludge depth during drying and duration of the drying process remains similar. It was also interesting to note that there was similarity between the total N content of the stable thermally hydrolysed sludge and ADS1 as well as ADS2 sludges.

In contrast, the total N content of ADS3 was 1.8 times higher than ADS1 and ADS2. This is despite the similarity in the wastewater treatment processes (anaerobic digestion). This is most probably attributed to the sludge depth during drying on beds and the drying time (Pescod, 1971) which influence decomposition and volatilization significantly. According to the wastewater treatment plant managers, where sludge ADS3 originated from, this sludge was dried in thin layers of <100 mm depth and often dries within 7 days. While the drying process of ADS1 and ADS2 lasted for 21 days on average during summer and double the time during winter. The activated sludge was also collected from the same wastewater treatment plant as the ADS3 and was dried in drying beds in thin layers of <100 mm depth within approximately 7 days on average. Despite the differences in the sludge treatment process between ADS3 (anaerobically digested) and Activated (activated sludge), there was no significant total N difference between the sludges. This is in contrast to the difference observed between ADS3 and ADS1 as well as between ADS3 and ADS2. This indicates that the depth of sludge in drying beds and the duration of drying process play a significant role in determining the N content of sludges.

As expected, ammonium was the dominant inorganic N species in all sludge types as all sludges were anaerobically digested. This is in line with previous findings of many authors who reported  $\text{NH}_4^+$  as the dominant inorganic N species in anaerobically digested sludges (Wong et al., 2000; Adegbi and Briggs 2003; Doublet et al., 2010; Zarabi and Jalali, 2013). The inorganic N fraction from this study accounted for <10% of each sludge total N content which was similar to the findings of Lasa et al., (1997; Vieira et al., (2005) and Cogger et al. (2001) from an anaerobically digested sludge.

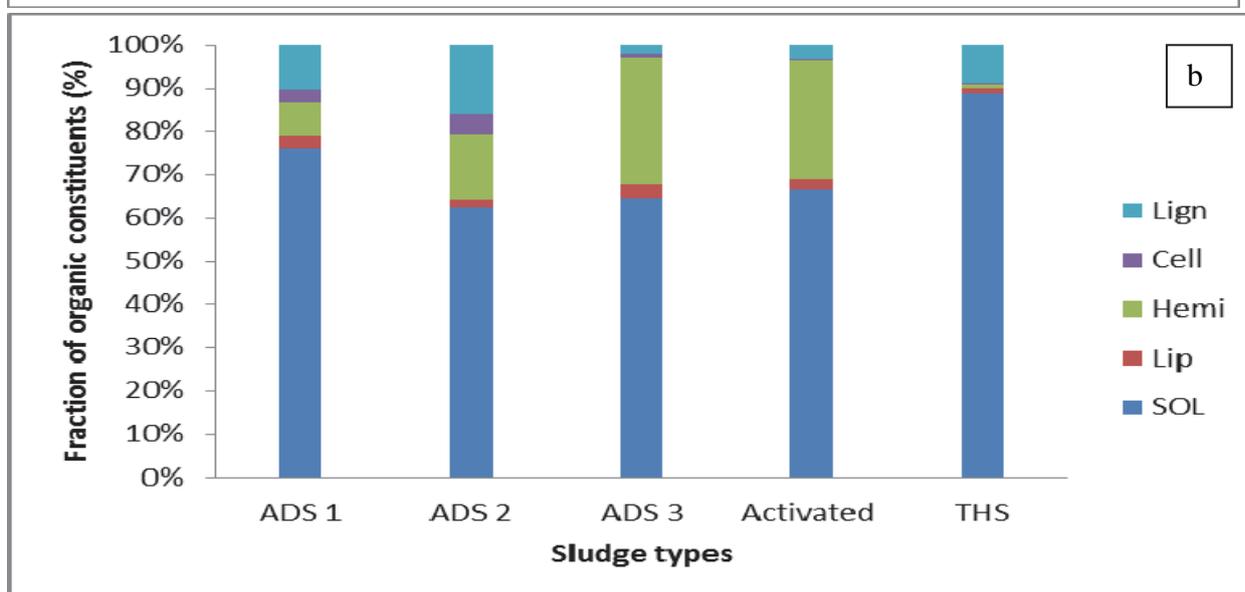
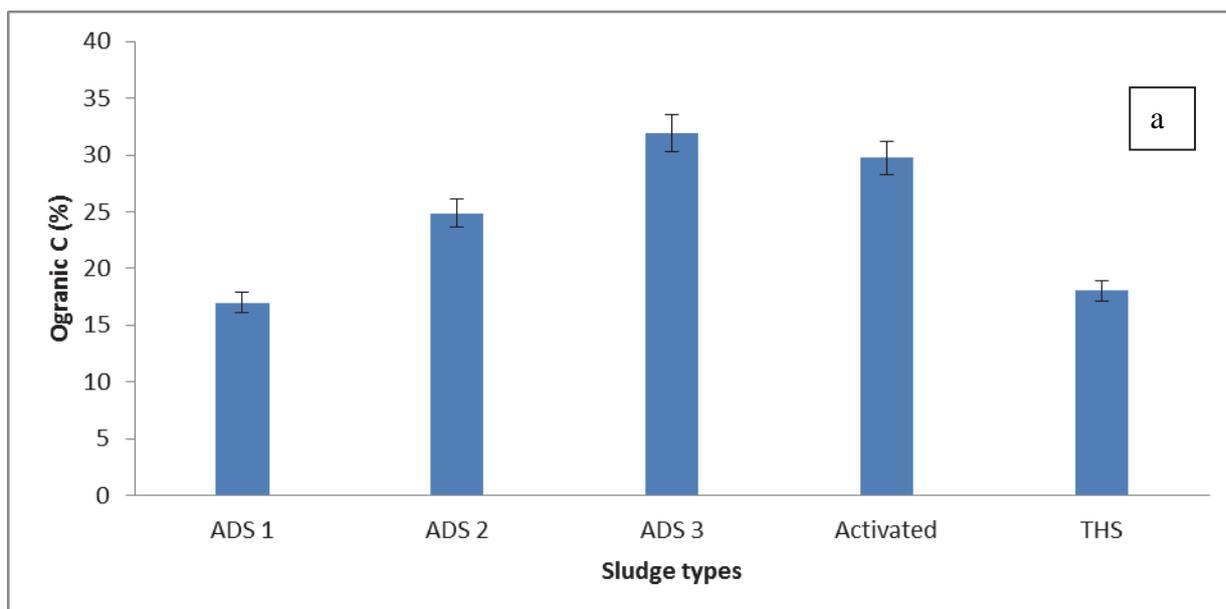
### **2.3.2 Effect of wastewater treatment process and drying time on sludge organic matter content and composition**

The total organic C content and composition of sludge varied significantly among the wastewater treatment processes and drying time. The study showed that ADS3 and activated sludge had highest total organic C followed by ADS2 and ADS1. Unlike the total N, however, ADS2 had relatively higher total organic C than ADS1 (Fig. 2.2a). Similar to the total N, the organic C content of THS remained similar to that of ADS1 but lower than ADS2. It was evident that the soluble compounds comprised of 62-88% of the total organic matter decomposition of all sludge types under investigation (Fig. 2.2b).

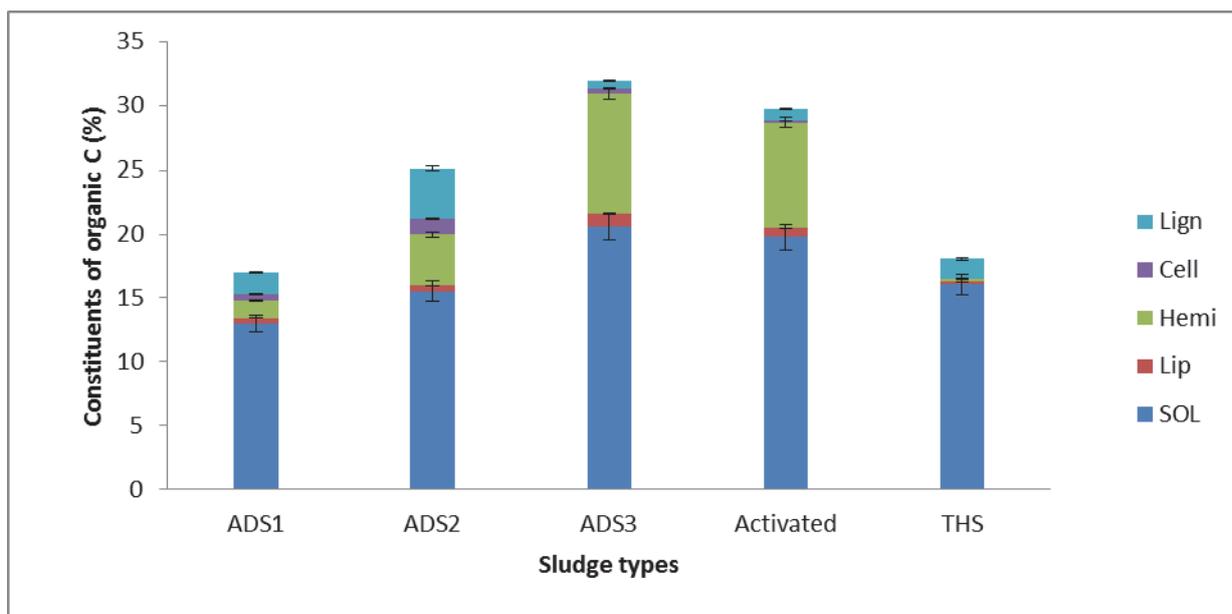
The other major differences among the sludge types were: hemicellulose for ADS3 and activated sludges; lignin for ADS1, ADS2 and THS sludges. Lipids and cellulose together

constituted less than 7% of the total organic matter of all the sludge types considered in this study. Generally, the soluble compounds constituted 13-22% by mass of the sludge solid fraction (Fig. 2.3). Hemicellulose was the next dominant organic compound (2-10%) followed by Lignin (1-4%). In contrast, lipids and cellulose constituted <2%.

Despite the differences in the total organic C contents between ADS1 and ADS2, both sludge types had higher lignin fraction than ADS3, THS and activated sludge. This indicates that both ADS1 and ADS2 are more stable and are expected to have relatively lower N mineralization (Mottet et al., 2010). The difference in the total organic C content between ADS1 and ADS2 despite their similarities in the total N content has implications on N mineralization (Lashermes et al., 2010). This is due to their differences in the C:N ratio which affects the microbial activity (Pansu and Thuriés, 2003). Organic matter decomposition, however, is not only influenced by the C:N ratio or the total N (Lashermes et al., 2010) and C content and therefore is inadequate for predicting decomposition kinetics (Thuriés et al., 2001).



**Figure 2.2 Total organic C contents (a) and percentage distribution of organic constituents (b) for five sludge types (anaerobically digested dried in concrete beds in layers of 250 mm depth (ADS1); anaerobically digested dried in paddy in layers of 250 mm depth (ADS2); anaerobically digested dried on concrete slab in layers of less than 100 mm depth (ADS3); activated sludge dried in concrete slab in layers of less than 100 mm depth (Activated) Thermal hydrolysis sludge (THS). NB. Lip = Lipids, SOL = Soluble organic compounds, Hemi = Hemicellulose, Cell = Cellulose and Lign = Lignified fraction**



**Figure 2.3 Percentage by mass of organic constituents in selected sludge types (anaerobically digested dried in concrete beds in 250 mm depth sludge layers (ADS1); anaerobically digested dried in paddy in 250 mm depth sludge layers (ADS2); anaerobically digested dried on concrete slab in layers of less than 100 mm depth (ADS3); activated sludge dried in concrete slab in layers of less than 100 mm depth (Activated); Thermal hydrolysis sludge (THS) NB. Lip = Lipids, SOL = Soluble organic compounds, Hemi = Hemicellulose, Cell = Cellulose and Lign = Lignified fraction**

Previous studies indicated a strong negative correlation between initial lignin content and N mineralization (Mubarak et al. 2010; Trinsoutrot et al., 2001; Palm et al., 2001) as well as cellulose and N mineralization (Rahn et al., 2003) from organic materials. Consequently, ADS2 is expected to have lowest cumulative N mineralization than the other sludge types due to its highest lignin:N ratio (Table 2.3) (Parnaudeau et al., 2004) and therefore lower fertilizer value. This is despite the similarity in total N content with ADS1 because an increase in lignin content tends to restrict the decomposition of organic matter (Baddi et al., 2004).

**Table 2.3 C:N ratio and lignin:N ratio of anaerobically digested sludges dried on concrete beds (ADS1 and ADS3) and paddy dried (ADS2), activated sludge dried in concrete drying beds (Activated), as well as Thermal hydrolysis sludge (THS).**

	ADS1	ADS2	ADS3	Activated	THS
C:N ratio	6.05	8.78	6.44	5.72	5.77
Lignin:N ratio	0.61	1.40	0.12	0.18	0.50

Similar to previous findings (Morvan et al., 2006; Mottet et al., 2010; Parnaudeau et al., 2004; Doublet et al., 2010; Zhao et al., 2011), large fraction of the organic matter was made up of soluble compounds. These soluble compounds are the main sources of N mineralization and C decomposition during the first few days of organic matter breakdown (Sánchez-Monedero et al., 1999; Trinsoutrot et al., 2001; Alexandra and José, 2005; Brady

and Weil, 2008). This show that higher percentage of organic matter in sewage sludge forms part of the NDF soluble fraction, as it was stated by Parnaudeau and Dignac (2007).

## 2.4 CONCLUSION

Drying sludge in thick layers of more than 250 mm for longer than 20 days seems to decrease the sludge N and C content. There was, however, little or no difference in total N concentration between sludges treated with anaerobic digestion and activated sludge when both were exposed to similar drying techniques (liquid sludge depth in drying beds and drying duration). Large fraction of the organic matter in all sludge types accounted for soluble compounds. The lignified fraction was relatively higher for the sludges that were dried in thick layers for longer time regardless of whether dried in concrete slabs or paddies. Sludges dried in thin layers within shorter period of time (7 days) were characterized by higher N, C, and low lignin fraction and were dominated by soluble compounds and hemicellulose. Nonetheless the sludges used in this study were originated from different sources, therefore, further investigation on the effect of drying depth and time using similar sludge sources and treatment processes is warranted to isolate the effect of sludge source.

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## **CHAPTER 3 – THE EFFECT OF WASTEWATER TREATMENT AND POST TREATMENT DRYING TECHNIQUES ON N AND C MINERALIZATION**

### **3.1 INTRODUCTION**

Different sludge types have different C and N mineralization rates which are attributed to the differences in their composition (Parker and Sommers, 1983; Serna & Pomares, 1992; Parnaudeau et al., 2004; Smith and Tibbett, 2004). Previous studies have shown that sludge treatment processes could influence C and N mineralization of sludges (Epstein et al., 1976; Parker and Sommers, 1983; Serna and Pomares, 1992; Ubierna et al., 2013; Mattana et al., 2014).

According to Parker and Sommers (1983), activated sludge had the highest mineralizable N (40%), followed by raw and primary sludges (25%), anaerobically digested sludge (15%), and composted sludge (8%) of the total N applied during a 16 week incubation study. Other studies conducted by Serna and Pomares (1992) as well as Hernandez et al. (2002) also showed that aerobically digested sludges gave higher N mineralization than anaerobically digested sludges. In contrast, activated sludge was reported to give much higher mineralization than digested sludge due to its high active organic carbon and less stable compounds (Hsieh et al., 1981).

Recent methods of wastewater treatment such as thermal hydrolysis at temperatures ranging from 40 to 180°C break the cell walls of biological organic materials in sludge improving degradability (Neyens and Baeyens, 2003; Wei et al., 2003). Studies conducted by Rigby et al., (2009) showed that thermally dried mesophilic anaerobically digested biosolids had larger mineralizable pool of N than dewatered mesophilic anaerobically digested biosolid, despite its lower total and mineral N content. Similar findings were reported by Smith and Durham (2002), Matsuoka et al., (2006) and Fernández et al., (2007). According to the latter authors, thermal drying increased the easily mineralizable fraction of N and C in the sludge.

Little is known about the combined effect of wastewater treatment methods and sludge drying techniques on C and N mineralization of sludge. In addition, the effect of sludge depth on drying beds and duration of drying during the drying process on C and N mineralization needs investigation.

The aim of this section of the study was to test the hypothesis that a) thermally hydrolyzed sludge (THS) have higher mineralization per unit organic N applied than anaerobically digested sludge with similar initial total and organic N contents because of its low lignin content b) Activated sludge (Activated) dried in thin layers of <100 mm in concrete beds have a higher fertilizer value than thermally hydrolysed and anaerobically digested sludges due to higher initial N and relatively lower lignin fraction.

## 3.2 MATERIALS AND METHODS

### 3.2.1 Sludge materials

Four sludge materials were selected for this study. Detailed characteristics of these sludge materials are presented in Tables 2.1, 2.2, 3.1, and 3.2. All sludge materials were milled to pass 1 mm sieve.

**Table 3.1 Biochemical composition of sludge materials: Activated sludge (Activated) anaerobically digested dried in concrete beds (ADS1), anaerobically digested dried in paddy (ADS2) and Thermal hydrolysis sludge (THS)**

Sludge type	Organic constituents				
	Lipids	Soluble compounds	Hemicellulose	Cellulose	Lignin
	%				
Activated	2.33	66.47	27.51	0.48	3.21
ADS1	2.79	76.19	7.9	3	10.14
ADS2	1.74	62.55	14.84	4.91	15.96
THS	1.07	88.88	1.12	0.23	8.7

**Table 3.2 C:N ratio and lignin:N ratio of sludge materials**

Parameter	Sludge type			
	ADS1	ADS2	Activated	THS
C:N ratio	6.05	8.78	5.72	5.77
Lignin:N ratio	0.61	1.40	0.18	0.50

### 3.2.2 Soil

A soil sample for the incubation study was collected from a long term field study trial at East Rand Water Care Works (ERWAT), near Johannesburg, South Africa. The site from which the soil sample was collected has never received inorganic fertilizer or sludge. The soil is a red clay loam Hutton soil (Soil Classification Working Group, 1991). Selected properties of the soil used in the incubation study are presented on Table 3.3.

**Table 3.3 Selected properties of the soil used for the incubation study**

	Units	
Total N	%	0.09
Organic C	%	1.7
Organic N*	%	0.084
C:N		20
NH <sub>4</sub> <sup>+</sup>	mg/kg	33.964
NO <sub>3</sub> <sup>-</sup>	mg/kg	20.384
pH		6.1
EC	mS m <sup>-1</sup>	52
Silt	%	24
Clay	%	26
Sand	%	46

\*Calculated as the difference between total N and total inorganic N (NH<sub>4</sub><sup>+</sup>, and NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>).

### 3.2.3 Method

#### 3.2.3.1 Incubation

Two consecutive incubation experiments were carried out at the Soil Science Laboratory of the University of Pretoria. The incubation was conducted in room insulated with air conditioner to maintain room temperature of 25 ±1 °C. The incubation for N mineralization was conducted in 1163 cm<sup>3</sup> volume airtight containers where 100 g soil was mixed with the candidate sludge to meet a 300 kg N ha<sup>-1</sup> application rate. Inorganic N in the form of KNO<sub>3</sub> was added during the second incubation study to increase the soil NO<sub>3</sub><sup>-</sup>-N level to 60 mg kg<sup>-1</sup> (Parnaudeau *et al.*, 2004) in order to minimize N immobilization. The soil moisture was maintained at field capacity by adding water based on mass difference.

The C decomposition study was conducted in airtight 2000 cm<sup>3</sup> volume desiccators where 100 g soil was also mixed with the candidate sludge to meet 300 kg N ha<sup>-1</sup>. During the first incubation, only one sludge type (anaerobically digested dried in concrete beds (ADS1)) was used. In the second incubation, however, three sludge types (ADS2, Activated and THS) were investigated. Similar to the N mineralization studies, KNO<sub>3</sub> was added in the second incubation study to increase the initial inorganic N content of the soil-sludge mix to 60 mg kg<sup>-1</sup>. A zero control treatment, which did not receive sludge, was included for each incubation study.

The sludge, soil and inorganic fertilizer were thoroughly mixed at the commencement of the study. Both CO<sub>2</sub> evolution and inorganic N release analysis were conducted at similar time intervals during the incubation study. The analyses intervals were set at days (d) 0, 1, 3, 7, 15, 30, 65, and 100. Both N mineralization and CO<sub>2</sub> evolution experiments were aerated during sampling intervals for the first seven days of incubation. After day seven, the N-mineralization experiment was opened and weighed once a week and at sampling time to replenish water to field capacity while CO<sub>2</sub> evolution set up was opened only at sampling time.

### 3.2.3.2 Chemical analyses methods

#### ***Inorganic N determination***

Inorganic N (NO<sub>3</sub>-N and NH<sub>4</sub>-N) release from sludge amended soils and control were determined by the steam distillation method described by Mulvaney (1996). A soil sample of 10 g on dry mass base was extracted with 100 ml 1 M KCl after 1 hour of shaking time. After shaking, the extracts were filtered through Whatman No. 42 filter papers and analyzed for inorganic N using Eq. 1.

A titre of 1 cm<sup>3</sup> 0.0025 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> equals to 35 µg N and 10 g soil was extracted with 100 cm<sup>3</sup> KCl, therefore:

$$\text{Inorganic N (mg kg}^{-1}\text{)} = \frac{A \times 100 \times 39}{c \times 10} \quad \text{Eq.1}$$

Where A = volume (mL) of 0.0025 M H<sub>2</sub>SO<sub>4</sub> needed for titration  
C = volume (ml) of aliquot sample used for distillation

The cumulative amount of net N mineralized from sludge was calculated using Eq. 2.

$$\text{Net N mineralized} = N(\text{sludge amended soil}) - [N(\text{control}) - N(\text{initially in sludge})] \quad \text{Eq.2}$$

Where N is inorganic nitrogen at each sampling time.

The net-N mineralized was calculated to net-N mineralized per organic C applied (g kg<sup>-1</sup>) and net-N mineralized per organic N applied (g kg<sup>-1</sup>) using Eqs. 3 and 4, respectively.

$$\text{Net N (per organic C applied)} = \frac{\text{Net N mineralized}}{\text{Organic C added from sludge per kg soil}} \quad \text{Eq. 3}$$

$$\text{Net N (per organic N applied)} = \frac{\text{Net N mineralized}}{\text{Organic N added from sludge per kg soil}} \quad \text{Eq. 4}$$

#### ***CO<sub>2</sub> evolution measurement***

A 20 ml of 1M NaOH was used as a carbon dioxide trap placed together with the incubated samples in air tight desiccators. A 100 ml beaker having 20 ml of distilled water was also placed in the dissectors to minimize drying out of the samples. The amount of CO<sub>2</sub> respired was measured by titration with 0.5 M HCl after the addition of 4 ml of 1 M barium chloride (BaCl<sub>2</sub>) and 2 ml of phenolphthalein. CO<sub>2</sub> flux was estimated from the titration using Eq. 5. The CO<sub>2</sub> flux was computed according the equation of Anderson (1982) per mass of soil incubated.

$$\text{CO}_2 \text{ flux (mg kg}^{-1} \text{ soil)} = (B - V) \times \frac{NE}{m} \quad \text{Eq. 5}$$

Where B = volume (mL) of 0.5 M HCl needed to titrate the NaOH in the control,  
 V = volume (mL) of 0.5 M HCl needed to titrate the NaOH in the sample,  
 N = molarity of the HCl (0.5M),  
 E = equivalent weight; to express as milligrams of CO<sub>2</sub>, (22)  
 m = mass of soil (kg)

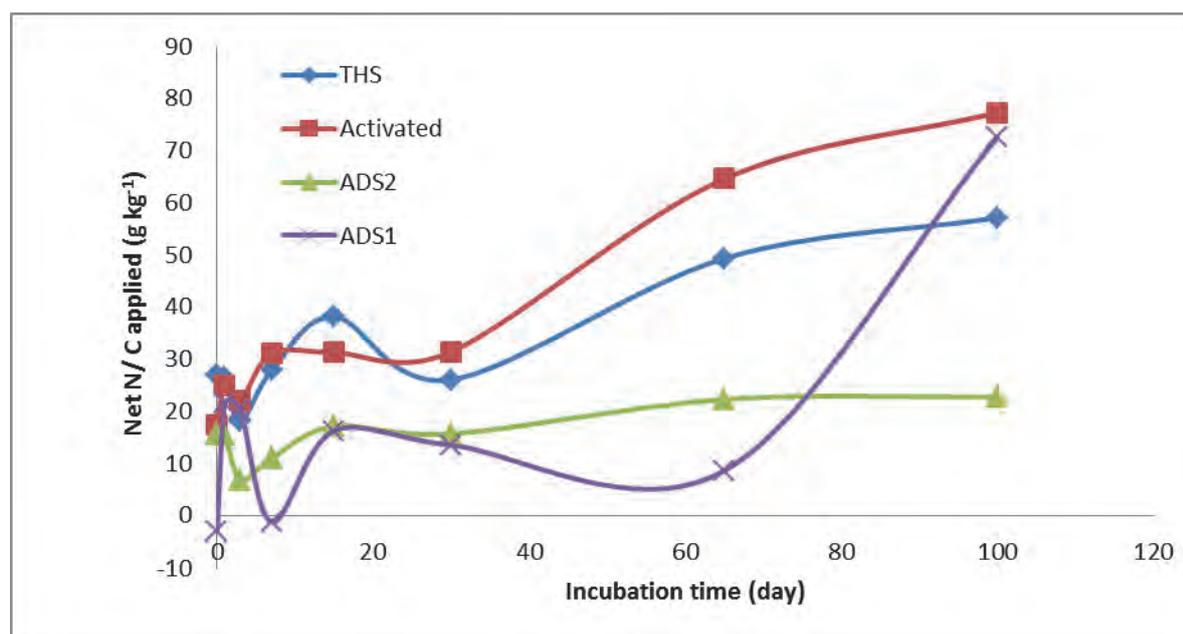
The decomposed C was converted to decomposed C per organic C applied using Eq. 6.

$$\text{Decomposed C per organic C applied (g kg}^{-1}\text{)} = \frac{\text{Decomposed C}}{\text{Organic C applied from sludge per kg soil}} \quad \text{Eq. 6}$$

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 N mineralization

Nitrogen mineralization varied significantly across sludge types (Fig. 3.1). The amount of N mineralized per kg C applied remained lowest for ADS2. While net N mineralization from the Activated sludge remained highest after day 30. The net N mineralization from ADS2 remained lowest at most of the time in the study period.

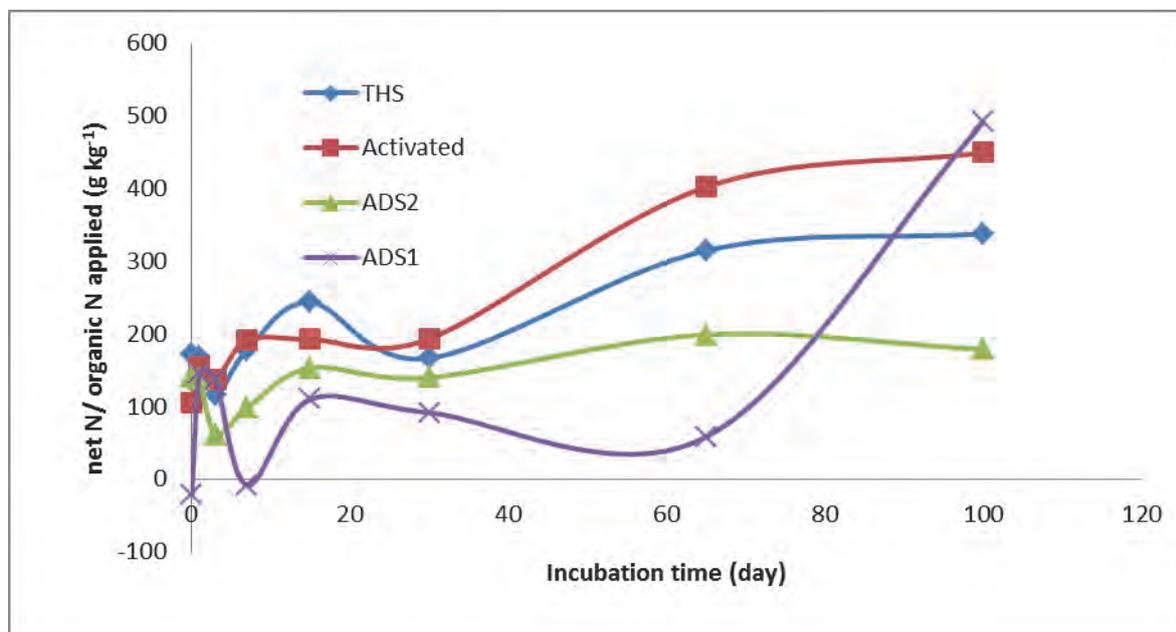


**Figure 3.1 N mineralization from anaerobically digested dried in concrete beds in thick layers of 250 mm (ADS1) dried in paddy in thick layers of 250 mm (ADS2), Activated sludge dried in thin layers of less than 100 mm (Activated) and Thermal hydrolysis sludge (THS) (KNO<sub>3</sub> added at commencement of study only for ADS2, Activated & THS)**

There were visible N immobilization events on days 1, 3, and 30 for THS, day 3 for Activated, days 1, 3, and 30 for ADS2, and days 3, 7, 30, and 65 for ADS1 (Fig. 3.1). This was despite the addition of KNO<sub>3</sub> to all but ADS1. However, the amount and intensity of immobilization was lower for the sludge treatments that received KNO<sub>3</sub>. The first incubation study, which was conducted using anaerobically digested sludge dried on concrete beds without the addition of KNO<sub>3</sub> (ADS1), showed more immobilization events than the second

batch incubation (Fig. 3.1). This is despite the similarity in the total N contents as well as the sludge treatment processes between ADS1 and ADS2, which were both anaerobically digested (Table 3.2).

The net N mineralization per kg organic N applied was highest for ADS1 ( $491.89 \text{ g kg}^{-1}$ ) and lowest for ADS2 at day 100 (Fig. 3.2). For most of the study period, however, ADS1 had the lowest net N mineralization.



**Figure 3.2 N mineralized per unit kg organic N applied from anaerobically digested dried in concrete beds in thick layers of 250 mm (ADS1) dried in paddy in thick layers of 250 mm (ADS2), activated sludge dried in thin layers of less than 100 mm (Activated) and Thermal hydrolysis sludge (THS) (KNO<sub>3</sub> added at commencement of study only for ADS2, Activated & THS)**

The initial N content and C:N ratio are the first litter chemistry that highlight the potential decomposition rate of a biological organic material (Tian et al., 1993; Valenzuela-Solano and Crohn, 2006; Lashermes et al., 2010). Previous studies with plant litter have shown that low C:N ratio materials are characterized by rapid decomposition and less immobilization than materials with higher C:N ratios (Muhammad et al., 2011). It is also well documented that organic materials which are rich in lignin, cellulose and hemicellulose are characterized by low decomposition rates (Trofymow et al., 2002; Santiago, 2007; Baddi et al., 2004; Parnaudeau et al., 2004).

Cumulative N mineralization varied among sludge types significantly. This is in agreement with previous studies which reported that N mineralization from sludge is a function of sludge treatment processes (Parker and Sommers, 1983; Serna & Pomares, 1992; Smith and Tibbett, 2004; Zarabi and Jalali, 2013). Generally net N mineralization from the anaerobically digested sludges (ADS1 and ADS2) was higher than mineralization from similar sludge types reported by Parnaudeau et al. (2004). This is because of the relatively higher initial N content (Table 3.2) and lower C:N ratio (Table 3.2) of the sludges from our study compared to that of Parnaudeau et al. (2004).

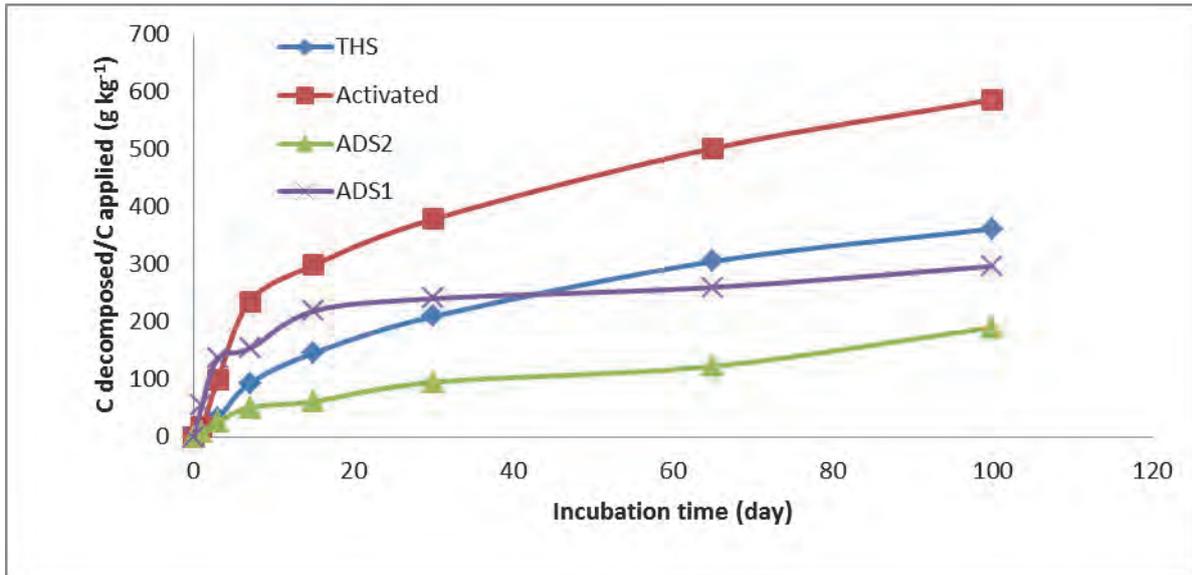
Net N mineralization per kg C applied after 100 days of incubation was highest from activated sludge than the other three (ADS1, ADS2, and THS). This was mainly attributed to the higher initial N content of the sludge (4.95%) compared with the other three which ranged between 2.81 and 3.13% (Table 3.2) because the initial N concentration influences the amount of N that can be mineralized (Valenzuela-solano and Crohn, 2006; Lashermes et al., 2010). In addition Activated sludge had the lowest lignin fraction (3.21%) compared with the other three, which ranged between 8.7 and 15.96% by mass of the total organic matter. Previous studies have shown that lignin affects N mineralization negatively (Baddi et al., 2004). On the other hand, cumulative net N mineralization per kg organic N applied at the end of 100 day incubation was highest for ADS1.

Despite a 9.6% difference in the initial total N content between THS (3.13%) and ADS2 (2.83%), N mineralization from THS (57.11 g N kg<sup>-1</sup> C applied) on day 100 was 61% higher than ADS2 (22.27% g N kg<sup>-1</sup> C applied). Such a difference is most probably attributed to the higher lignin fraction (15.96%), lignin:N ratio (1.40), and C:N ratio (8.78) of ADS2 compared with THS (lignin=8.7%, lignin:N ratio=0.50, C:N ratio=5.77). It is well documented that higher Lignin:N ratio results in low net N mineralization due to N immobilization (Baddi et al., 2004; Parnaudeau et al., 2004).

Cumulative net N mineralized on day 100 from ADS1 was three times higher than ADS2. This is despite a very small total N (0.7%) and organic N (10%) differences. Carbon concentration of ADS2 sludge (24.84%) was, however, 32% higher than ADS1 (17%). Thus, the C:N ratio of ADS2 (8.78) was 2.73 times higher than ADS1 (6.05). In addition, ADS2 had about 18% lower soluble compounds by mass (62.55%) than ADS1 (76.19%). It was also apparent that the lignin (15.96%), cellulose (4.91%), and hemicellulose (14.84%) fractions for ADS2 were 37%, 39%, and 47% higher than that of ADS1, respectively. Therefore, the main reason for the higher cumulative N mineralization from ADS1 relative to ADS2 was the lower C:N ratio, lower lignin, lower cellulose, lower hemicellulose but higher soluble compounds of ADS1.

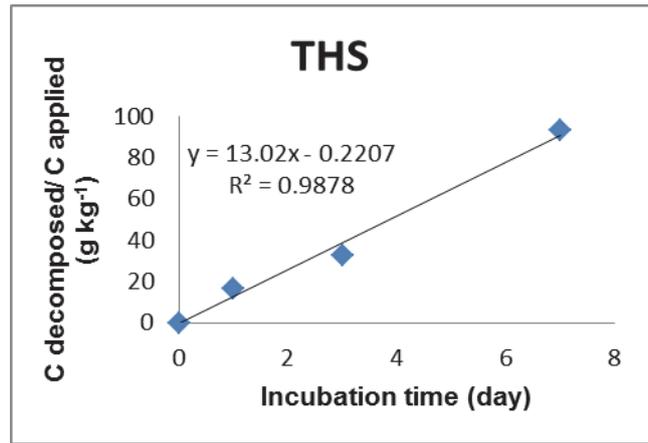
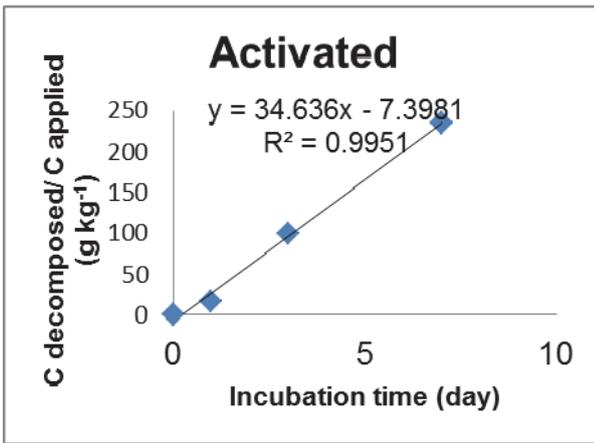
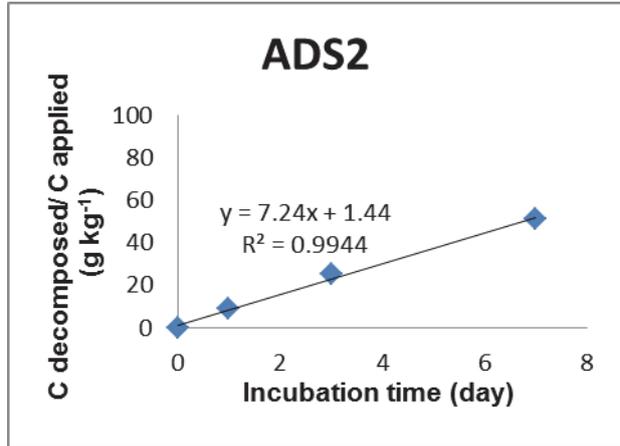
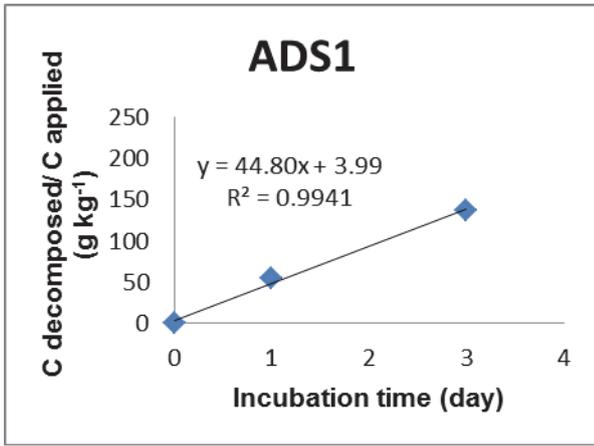
### **3.3.2 Carbon decomposition**

Generally cumulative C decomposition per kg organic C applied was highest for activated sludge and lowest for ADS2 (Fig. 3.3). Carbon decomposition rate was very high during the first seven days for ADS2, Activated, and THS sludges and during the first three days for ADS1 sludge (Fig. 3.3). Cumulative C decomposition at day 100 was highest from Activated (587 g kg<sup>-1</sup> organic C applied), followed by THS (362 g kg<sup>-1</sup> C applied) and was lowest for ADS2 (191 g kg<sup>-1</sup> C applied).



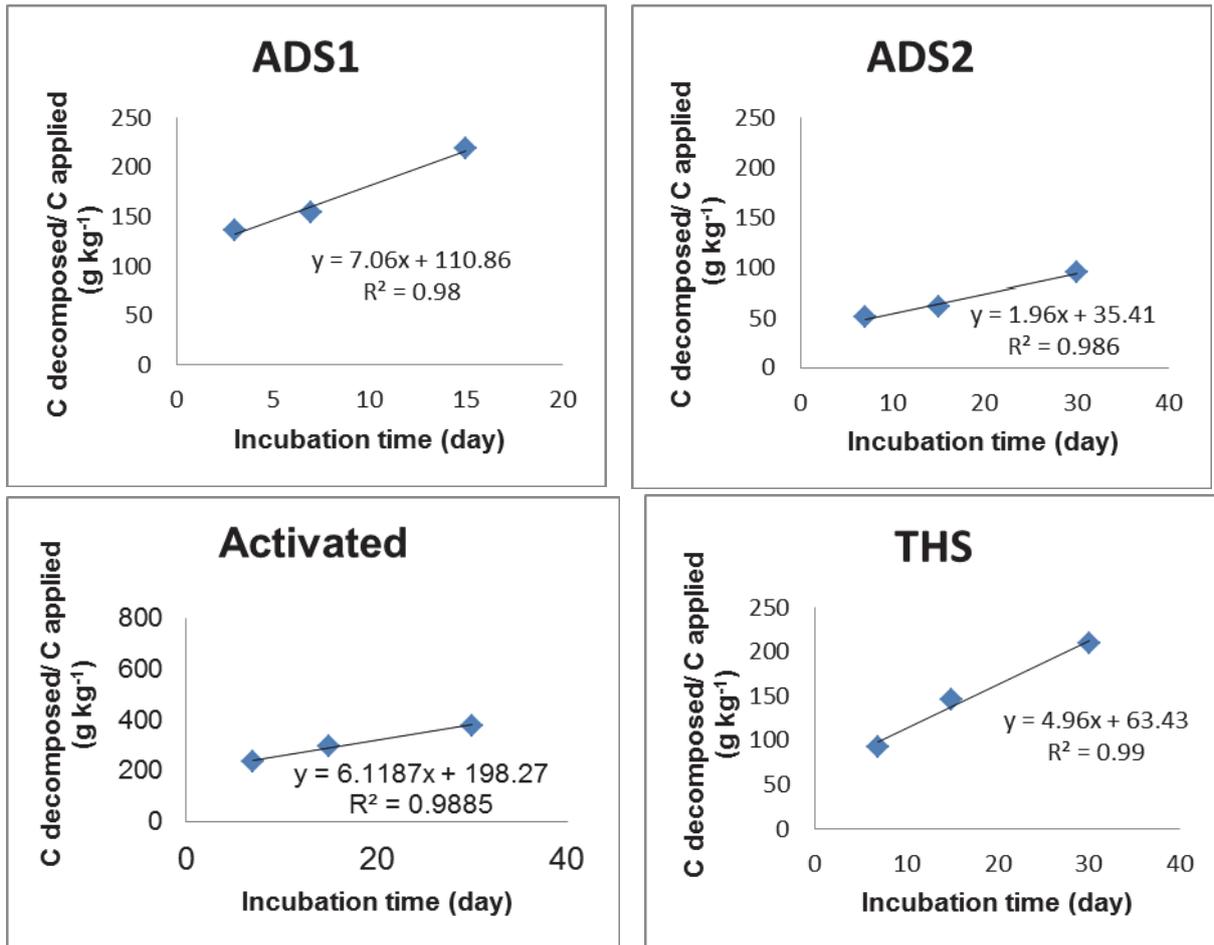
**Figure 3.3 Carbon decomposition of anaerobically digested sludge dried in concrete paddies in thick layer of 250 mm (ADS2), activated sludge dried in thin layers of less than 100 mm (Activated) and Thermal hydrolysis sludge (THS) during a 100 day incubation study (KNO<sub>3</sub> added at commencement of study only for ADS2, Activated & THS)**

The C decomposition rate of the fast cycling organic C fraction for the first three days was highest from ADS1 (44.80 g.kg<sup>-1</sup>) followed by Activated (34.64 g kg<sup>-1</sup>), THS (13.02 g kg<sup>-1</sup>), and was lowest for ADS2 (7.24 g kg<sup>-1</sup>) (Fig. 3.4).



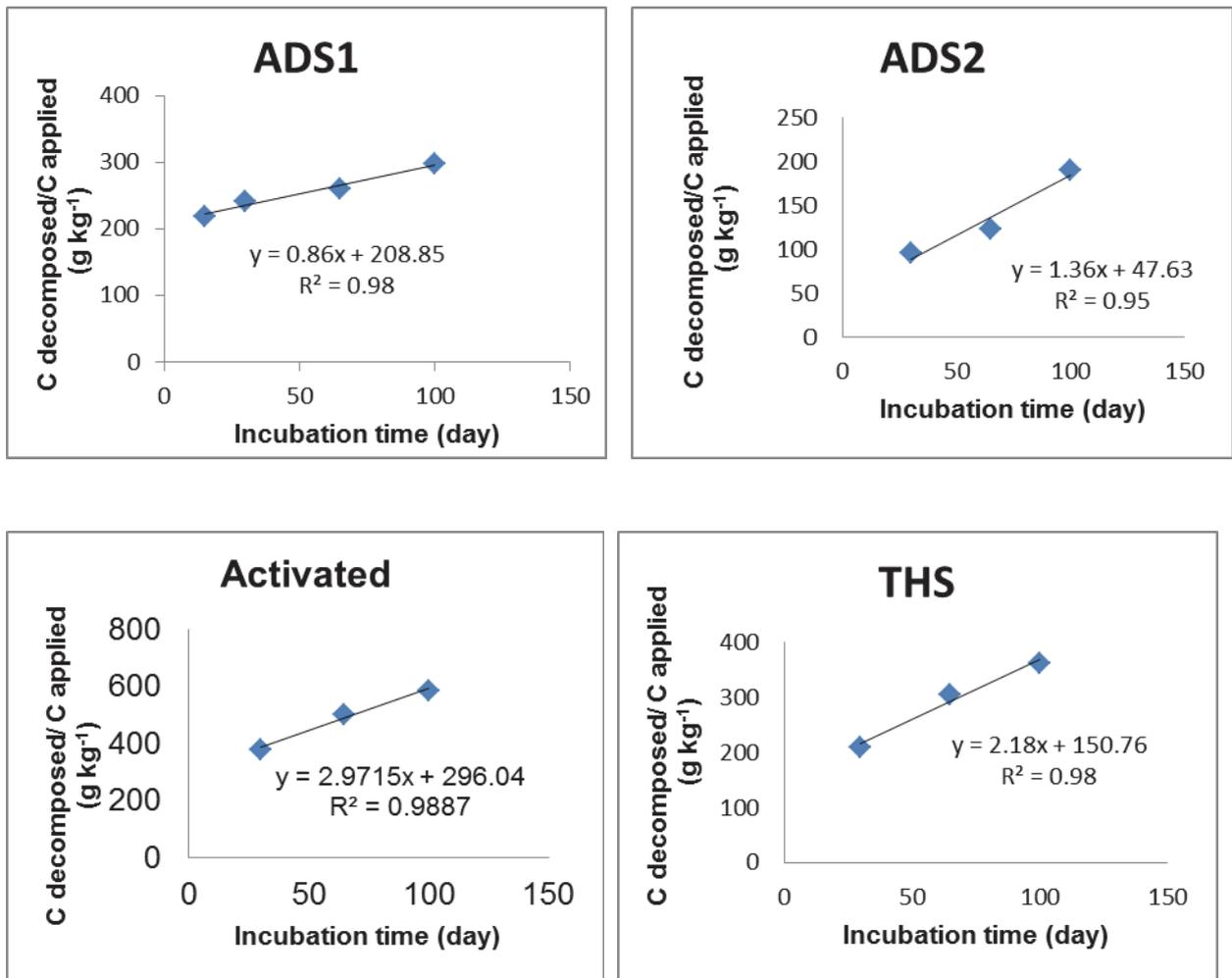
**Figure 3.4 Carbon decomposition rate (g kg<sup>-1</sup>) of the fast cycling fraction of an anaerobically digested sludge dried on paddy in thick layers of 250 mm (ADS1) dried on concrete beds in thick layers of 250 mm (ADS2), activated sludge dried in thin layers of less than 100 mm (Activated) and Thermal hydrolysis sludge (THS)**

The second set of C decomposition data which can be categorized under the same slope (moderately slow pool) with high  $r^2$  (>98%) was between days 3 and 15 (ADS1) and days 7 and 30 (ADS2, Activated, & THS) (Fig. 3.5). The decomposition rate of the relatively slow organic C fraction was also highest for ADS1 (7.06 g kg<sup>-1</sup>) followed by Activated (6.12 g kg<sup>-1</sup>), THS (4.96 g kg<sup>-1</sup>) and was lowest for ADS2 (1.96 g kg<sup>-1</sup>).



**Figure 3.5 Carbon decomposition rate (g kg<sup>-1</sup>) of the moderately slow cycling fraction of an anaerobically digested sludge dried on paddy in thick layers of 250mm (ADS1) dried on concrete beds in thick layers of 250 mm (ADS2), activated sludge dried in thin layers of less than 100 mm (Activated) and Thermal hydrolysis sludge (THS)**

The third set of C decomposition data (slow pool) which was categorized under the same slope with high  $r^2$  (>95%) was between days 15 and 100 (ADS1) and days 30 and 100 for ADS2, Activated, and THS (Fig. 3.6). Unlike the decomposition rate of fast and moderately slow, the decomposition rate of slow organic C pool was highest for Activated (2.97 g kg<sup>-1</sup>) and lowest for ADS1 (0.86 g kg<sup>-1</sup>).



**Figure 3.6 Carbon decomposition rate (g kg<sup>-1</sup>) of the slow cycling fraction of an anaerobically digested sludge dried on paddy in thick layers of 250 mm (ADS1) dried on concrete beds in thick layers of 250 mm (ADS2), activated sludge dried in thin layers of less than 100 mm (Activated) and Thermal hydrolysis sludge (THS)**

Similar to N mineralization (Fig. 3.1), ADS2 had the lowest and Activated the highest C decomposition per kg mass of organic C added during a 100 day incubation study. The C decomposition pattern from this study fits well into three phase (pool) system and has similarity to the findings of Parnaudeau et al. (2004). It was interesting to note that the cumulative organic C decomposed per kg organic C applied at day 100 from anaerobically digested sludges (ADS1 and ADS2) from this study were within the same ranges to the findings by Parnaudeau et al. (2004) for anaerobically digested limed and thickened anaerobically digested centrifuged sludges.

Carbon decomposition from ADS1 during the first three days was 6, 1.3, and 3.4 times higher than ADS2, Activated, and THS, respectively. The net N mineralization during those three days, however, remained similar for all sludge types. Similarly, C decomposition rate of the moderately slow carbon fraction was highest for ADS1 and was 4, 1.2, and 1.4 times higher than ADS2, Activated, and THS, respectively. Net N mineralization during the same time period was, however, lowest for ADS1. This is most probably attributed to immobilization because ADS1 unlike other treatments did not receive KNO<sub>3</sub> at the beginning

of the incubation. Carbon decomposition rate during the last 70 to 85 days, however, was highest from Activated and lowest from ADS1. The net N mineralization from ADS1 between days 7 and 65 remained lowest but turned to be the highest in day 100. The sudden flush of net N release on day 100 despite the lowest C decomposition could probably be attributed to the cell lysis due to excessive turgor pressure caused by influx of water through cell membrane (Mikha et al., 2005), or transport of intercellular solutes out of cells which results in the release of the cell solutes, such as amino acids, ammonium compounds, and glycerol (Kieft et al., 1987).

### 3.4 CONCLUSION

Carbon decomposition and N mineralization are functions of sludge treatment methods and post treatment drying processes. Sludge treatment and drying processes affect C and N mineralization by altering the chemical composition of sludges. Similar to previous findings, sludge C and N decomposition was significantly influenced by the initial N concentration, C:N ratio, lignin content, and lignin:N ratio. Carbon and N mineralization per unit organic C applied was highest for activated sludge and lowest for anaerobically digested paddy dried sludge. However, N mineralization per unit organic N applied was highest from anaerobically digested sludge dried in concrete beds. Considering the higher N content of activated sludge and higher N release rate per unit organic N applied, the fertilizer value of activated sludge is higher than the other sludge types investigated.

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## **CHAPTER 4: THE EFFECT OF WASTEWATER TREATMENT AND POST TREATMENT DRYING TECHNIQUES ON THE DYNAMICS OF SELECTED ORGANIC COMPOUNDS**

### **4.1 INTRODUCTION**

Sewage sludge is a biological waste which is made up of both organic and inorganic constituents. The organic fraction of sewage sludge is usually influenced by the origin of wastewater and the treatment process (Banegas et al., 2007). The biochemical composition of sewage sludge dictates the rate of C decomposition and N mineralization (Seneviratne, 2000; Parnaudeau et al., 2004; Smith and Tibbett, 2004). Thus understanding the rate of degradation of the dominant biochemical compounds in sludge is crucial to the understanding of C and N release differences between sludge types.

Previous studies conducted by Charest et al. (2004); Jouraiphy et al. (2005); Banegas et al. (2007); Francou et al. (2008); Doublet et al. (2010); Doublet et al., 2011; Mottet et al. (2010) and Zhao et al. (2011) investigated the transformation of sludge biochemical compounds during a composting process. Other studies conducted by Chantigny et al. (2000) investigated the transformation and decay of de-inking paper sludge in agricultural soils. Unlike municipal sludge, which is dominated by soluble compounds (Parnaudeau and Dignac, 2007; > 60% by mass of organic matter), de-inking paper sludge is characterized by high hemicellulose, cellulose and lignin fraction (Chantigny et al., 2000). There is, however, little information on the transformation of dominant biochemical compounds from municipal sludge as a function of time.

The aim of this study was to investigate the dynamics of biochemical compounds in general and the compounds responsible for the periodic release of C and N during sludge decomposition in particular.

### **4.2 MATERIALS AND METHODS**

#### **4.2.1 Sludge materials**

Four sludge materials were selected for this study. Detailed characteristics of these sludge materials are presented in Tables 2.1, 2.2, 3.1, and 3.2. All sludge materials were ground and milled to pass a 1 mm sieve after drying in oven at 40°C.

#### **4.2.2 Soil**

Soil for the incubation study was collected from the experimental plots of the long term field study trial at East Rand Water Care Works (ERWAT), near Johannesburg, South Africa. Selected properties of the soil used for the incubation study are presented on Table 3.3.

#### **4.2.3 Methods**

##### **4.2.3.1 Incubation**

Two consecutive incubation experiments were carried out at the Soil Science Laboratory of the University of Pretoria. The incubation was conducted at a constant room temperature of 25 ±1 °C. The incubation was conducted in 1163 cm<sup>3</sup> volume airtight containers where 100 g soil was mixed with the candidate sludge to meet a 300 kg N ha<sup>-1</sup> application rate. Unlike the

first batch incubation, inorganic N in the form of  $\text{KNO}_3$  was added during the second incubation study to increase the soil  $\text{NO}_3^-$ -N level to  $60 \text{ mg kg}^{-1}$  (Parnaudeau et al., 2004) in order to minimize N immobilization. The soil moisture was maintained at field capacity by adding water based on mass difference.

The treatments during the first batch include: ADS1 treated soil and a zero sludge control (soil alone) replicated three times. The second batch incubation treatments include: ADS2 amended soil, THS amended soil, Activated amended soil and a zero sludge control all replicated three times. During the second incubation a sludge alone incubation was conducted for sludges ADS2 and Activated without the addition of inorganic N. Results from the soil-sludge mix gave very high variation between replications (very big standard errors) and inconsistencies across time. Thus, this chapter will deal with results from the sludge alone incubation.

The sludge was thoroughly mixed at the commencement of the study. Analyses on residual organic compounds across time from the soil-sludge mix as well as sludge alone incubation study was done on days (d) 0, 1, 3, 7, 15, 30, 65, and 100. The experiments were aerated during sampling intervals for the first seven days of incubation. After day seven, the experiments were opened once a week and at sampling time to replenish water to field capacity.

The sludge was freeze dried before biochemical composition analyses using the Van Soest fractionation method (Goering and Van Soest, 1970; Van Soest, 1994).

#### **4.2.3.2 Biochemical composition fractionation**

Freeze dried samples were extracted with petroleum ether using Soxtec™ 2043 lipid extraction system to determine the fraction of lipids. The lipids extraction (lip) was followed by estimation of the Neutral Detergent Fiber (NDF) as described by Goering and Van Soest (1970). The NDF solution was made up of sodium lauryl sulphate, disodium ethylenediaminetetraacetate (EDTA) dehydrate, sodium borate decahydrate, disodium hydrogen phosphate anhydrous, 2-ethoxyethanol (ethylene glycol monoethyl ether) purified grade and distilled water. A freeze dried sample (1 g) was placed in a 50 ml crucible and boiled for 1 hour with 100 ml NDF solution at  $100^\circ\text{C}$ . After boiling, the solvent was filtered through the crucible and the residues that remained in the crucible were oven dried at  $60^\circ\text{C}$  and not ashed. Extraction of NDF was conducted using Fibertec™ 2010 Auto Fibre Analysis System.

The NDF extraction was followed by Acid Detergent Fiber (ADF) extraction as described by Goering and Van Soest (1970). The ADF solution was made up of cetyltrimethyl ammonium bromide (CTAB) and 1 N  $\text{H}_2\text{SO}_4$ . A 1 g of freeze dried sample milled to pass 1 mm sieve, was placed in 50 ml crucible and boiled for 1 hour with 100 ml ADF solution at  $100^\circ\text{C}$ . After boiling, the solvent was filtered through the crucible and the residues that remain in the crucible were oven dried at  $60^\circ\text{C}$  and not ashed. Extraction of ADF was conducted using Fibertec™ 2010 Auto Analysis System.

Finally the Acid detergent lignin (ADL) was determined as reported by Goering and Van Soest (1970). This procedure is a two-step process; initially the dried residue from the ADF extraction was treated with 72% sulphuric acid for 3 hours at room temperature. The 72%

sulphuric acid digested sample was filtered through the crucible and the residues that remained in the crucible were oven dried at 60°C and weighed before ashing. This is followed by ashing of the dried residue. Similar to the NDF and ADF, extraction of ADL was conducted using Fibertec™ 2010 Auto Analysis System.

Fractions of the neutral detergent soluble fraction, hemicelluloses, cellulose and lignified fraction were calculated as follows:

Soluble compounds fraction (SOL) = original mass – NDF- lipids fraction,

Hemicellulose (Hem) = NDF- ADF,

Cellulose (Cel) = ADF- 72% H<sub>2</sub>SO<sub>4</sub>,

Lignified fraction (Lign) = 72% H<sub>2</sub>SO<sub>4</sub> – Ash.

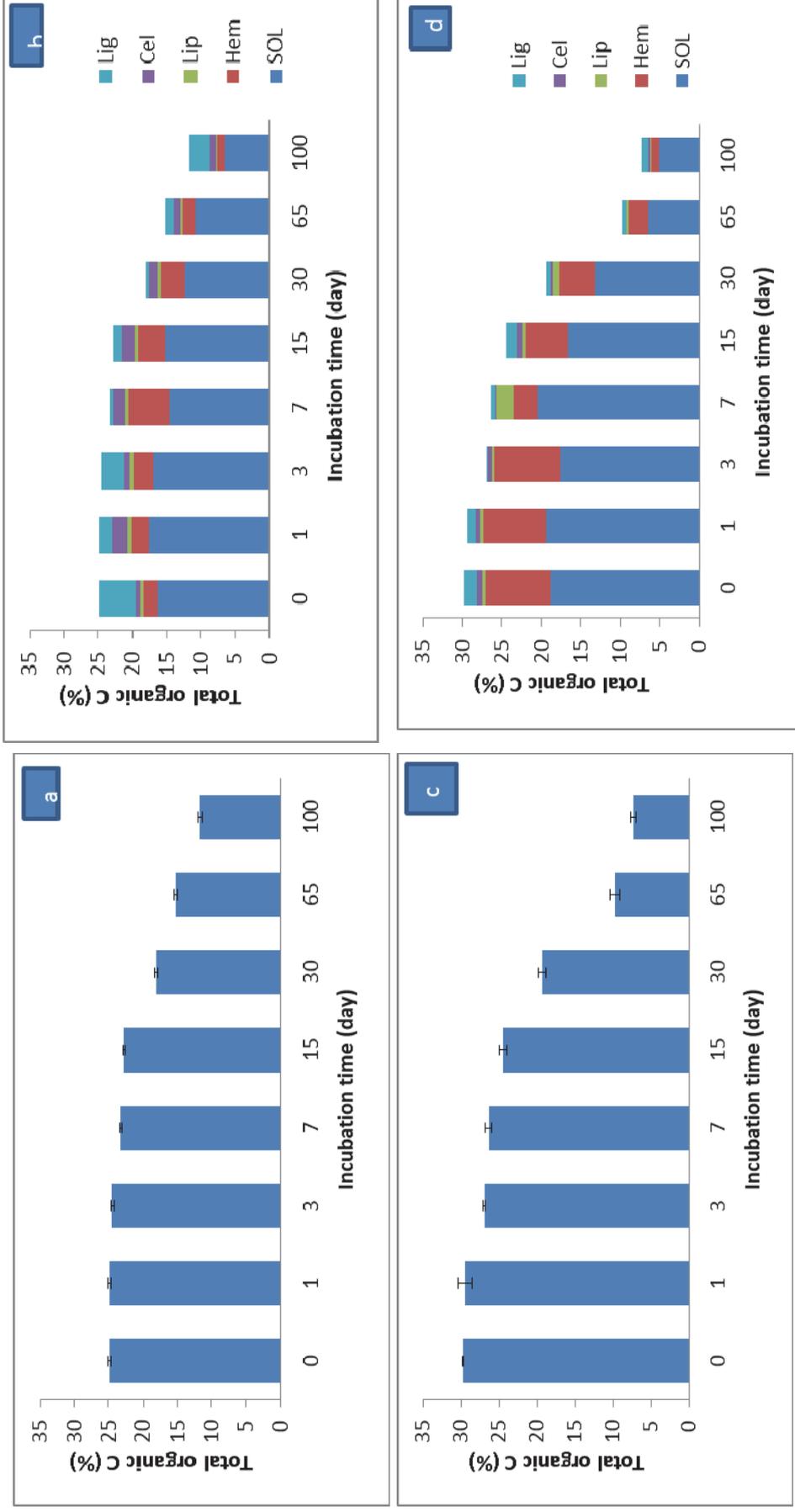
Total C was determined using Carlo Erba method.

### 4.3 RESULTS AND DISCUSSION

The residual carbon of both sludges (ADS2 and Activated) decreased with time during the 100 day incubation (Fig. 4.1a and c). The fraction of soluble compounds in the residue decreased as incubation time progressed for both sludge types. The second dominant residual compound, hemicellulose, showed a different pattern across time between sludge types. For sludge ADS2, the hemicellulose fraction increased gradually until day 7 but decreased thereafter as the time progressed (Fig. 4.1b). In contrast, with Activated sludge the hemicellulose fraction remained fairly similar until day 3 then suddenly decreased by 70% compared to the first three days (Fig. 4.1d). On day 15, however, the hemicellulose for Activated sludge was doubled compared with day 7 but gradually decreased with time (Figure 4.1d).

Lignin fraction, which accounted for 21% of the total C in ADS2 at the beginning of study showed an alternate decreasing and increasing patterns between sampling times until day 65, which finally showed a triple increase on day 100 compared with day 65 (Fig. 4.1b). The pattern of lignin fraction on residual Activated sludge, however, differed from that of ADS2 (Fig. 4.1d). During the first three days, the lignin fraction of Activated sludge decreased gradually followed by a gradual increase for the next three days until day 15. It suddenly decreased on day 30 compared with day 15 followed by a gradual increase for the rest of the incubation study (Fig. 4.1d). The cellulose fraction remained low and with almost no distinct degradation pattern throughout the incubation study for Activated sludge (Fig. 4.1d). It, however, showed a distinct decreasing pattern for ADS2 sludge after day 7 until end of incubation. The lipid fraction remained similar throughout the incubation period for ADS2 (Fig. 4.1b) but showed a sudden increase on day 7 for Activated (Fig. 4.1d).

At the end of 100 days of incubation, 60 and 51% of the organic C from the Activated and ADS2 sludges were decomposed, respectively. The relatively lower decomposition from ADS2 is most probably attributed to the relatively higher initial lignin content of the sludge. The presence of lignin in appreciable amount slows down organic matter degradation (Chantigny et al., 2000; Baddi et al., 2004; Parnaudeau et al., 2004).



**Figure 4.1** Residual organic C (a and c) and transformation and degradation of organic compounds (b and d) during a 100 day incubation period of anaerobically digested dried in paddy in thick sludge layers of 250 mm (ADS2) (a and b) and activated sludge dried in concrete beds in thin layers of about 100 mm (Activated) (c and d)

The soluble compounds fraction of both sludges decreased by 23% during the first 30 days of incubation period. In contrast, 27% of the total carbon in the sludge was decomposed during the same time period. Therefore, 23% of the decomposition could most probably have come from the soluble fraction. This is because soluble fraction is made up of organic compounds which are easily decomposable (Charest et al., 2004; Doublet et al., 2010; Zhao et al., 2011). The remaining 4% might have come from other compounds. Between days 30 and 65, 12% and 38% of the residual soluble fraction for ADS2 and Activated, respectively, was decomposed. It was also interesting to note that between days 65 and 100, 39% and 10% of the residual soluble compound fractions of the ADS2 and Activated sludges, respectively, disappeared. Higher soluble fraction decomposition from the ADS2 sludge took place at a later stage between days 65 and 100. This is in contrast to Activated sludge, whose most decomposition took place at earlier stage. This could be attributed to the higher initial lignin fraction of the ADS2 which slowed down the organic matter decomposition.

On day 7, the soluble organic carbon fraction of Activated sludge increased by about 3%. This is most probably attributed to the hydrolyses of the relatively stable fractions such as hemicellulose to soluble organic compounds (Francou et al., 2008; Sánchez-Monedero et al., 1999; Charest et al., 2004; Doublet et al., 2010; Zhao et al., 2011). One of the main reasons being the sudden decline of the hemicellulose fraction by half between days 3 and 7 (Fig 4.1d). The increase in the hemicellulose fraction observed between days 1 to 7 on ADS2 sludge as well on day 15 of Activated sludge are mostly attributed to the transformation of soluble compounds to more complex forms through synthesis during the decomposition process. It can be clearly observed from the figures that during those periods where an increase in hemicellulose was observed, the soluble fraction decreased.

The lipid fraction remained more or less similar throughout the incubation period for ADS2 but showed a sudden increase on day 7 for Activated sludge. This indicates little contribution to C decomposition. The cellulose fraction showed some dynamics on sludge ADS2, which increased on day 1, most probably due to synthesis from simple soluble compounds by microbial activity. It then decreased on day 3 which could have either decomposed or transformed to much stable Lignin fraction. From day 7 onwards, however, the cellulose fraction decreased gradually and could be considered as a third contributor to C decomposition after hemicellulose. The lignin fraction trend was not as expected, to increase as time progressed; however, this is not the first time such events have been reported. Others studies by Sánchez-Monedero et al. (1999) and Jouraiphy et al. (2005) also reported a decline in lignin fraction.

#### **4.4 CONCLUSION**

The Van Soest method was successfully used to determine the periodic degradation and transformation of biochemical compounds in ADS2 and Activated sludges. Results from this study showed that 90% of the total C decomposition came from the soluble organic carbon fraction. The next main contributor to C decomposition was hemicellulose, which accounted to 5-7% of the total C decomposition.

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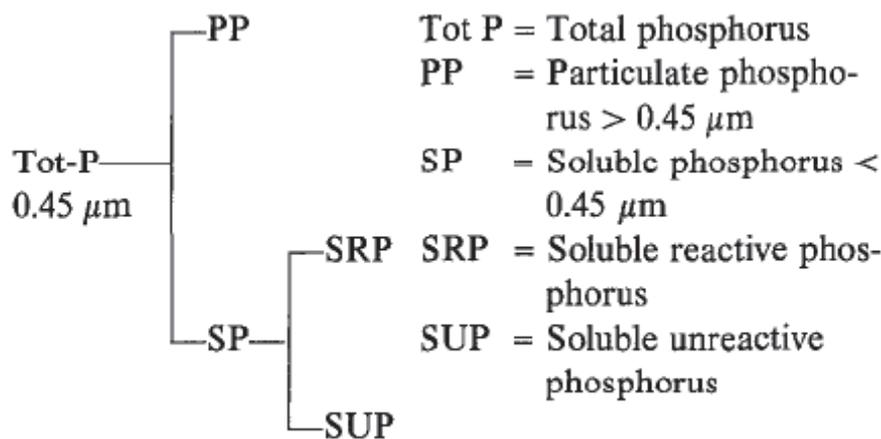
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## CHAPTER 5 – PHOSPHORUS FORMS AND KINETICS IN SOILS AMENDED WITH SLUDGES THAT UNDERWENT BIOLOGICAL VS. TERTIARY PHOSPHORUS REMOVAL METHODS

### 5.1 INTRODUCTION

The most common forms of inorganic P in wastewater aqueous solutions are orthophosphates and polyphosphates. Orthophosphates are available for biological metabolism without further breakdown while polyphosphates usually should undergo hydrolysis and revert to orthophosphates (Crites et al., 2005). Polyphosphates discharged in wastewaters are unstable and eventually get hydrolysed to orthophosphates (Alexander, 1978). Organic Phosphorus are dissolved in organic substances and usually get hydrolysed during the chemical and biological reactions (Holtan et al., 1988). Usually the organic matter content of the sample does not directly influence the organic and inorganic fractions of P (Pardo et al., 2003 and Medeiros et al., 2005). The total P in sludge and/or soil can be fractionated as particulate phosphorus, soluble Phosphorus, soluble reactive Phosphorus, and soluble unreactive phosphorus (Rigler, 1973) (Fig 5.1).



**Figure 5.1 The outline of Phosphorus fractions. (From Rigler, 1973)**

Generally the concentration of total P in municipal wastewaters may range between 4 to 12 mg L<sup>-1</sup> of which 1 to 4 mg L<sup>-1</sup> is organic. Secondary wastewater treatments can only remove 1 to 2 mg L<sup>-1</sup> P (Metcalf and Eddy, 2003). This is in contrast to the soil solution P concentration benchmark of 1 mg L<sup>-1</sup> for wastewater discharge to rivers and streams (Sims and Pierzynski, 2000). Therefore, direct discharge of wastewater effluents after secondary treatments without further P removal processes could cause eutrophication of surface waters. Wastewater treatment plants, therefore, use either chemical or biological phosphorus removal methods to reduce the concentration below the benchmark before they could discharge it to rivers and streams. Chemical precipitation is used to remove the inorganic forms of phosphate by the addition of coagulants and mixing of wastewater and coagulant. The most commonly used coagulants are calcium, aluminium, and iron (Tchobanoglous et al., 2003). In the biological phosphorus removal method, the P accumulating organisms are encouraged to grow and consume P and are subsequently removed (Storm et al., 2004).

Sewage sludge treatment methods and chemical or biological nutrient removal (BNR) processes influence the availability of P (Frossard et al., 1996; Maguire et al., 2001; Penn and Sims, 2002; Kirkham, 1982; McCoy et al., 1986). The predominant form of P in sludges that have undergone tertiary treatment is inorganic P (McLaughlin, 1984). Chemicals used in tertiary treatments such as Al or Fe salts, decrease the plant available P fraction (Elliott et al., 2002; Häni, et al., 1981; Kyle and McClintock, 1995). Previous studies conducted by Penn and Sims (2002) showed that the plant available fraction of P from soils amended with BNR sludge was higher than soils amended with sludges that underwent chemical P removal methods. Such fundamental differences in the form and availability of P from BNR vs. chemical P removal methods indicate the need for critical and proper understanding of the P release dynamics from biological vs chemical P removal methods.

In work done by Penn and Sims (2002), a significant increase in total soil P was observed in sludge amended silty clay loam and sandy loam soils compared with their control (no sludge). The labile forms of soil P (M3-P, M1-P, FeO-P, and water soluble P) were especially high for soils treated with sludges that underwent biological nutrient removal, compared with the control and soils that received Fe and lime treated sludge. Soils that received sludge treated with Fe and Al salts, slightly increased the labile soil P, but soils which received sludge treated with Fe and lime resulted in an intermediate labile P increment (Penn and Sims, 2002). Therefore, it is of the utmost importance to consider the type of sludge used when quantifying sludge application rates. This can help to optimise crop harvests by minimising the environmental impacts.

## **5.2 MATERIALS AND METHODS**

### **5.2.1 Sludge Materials**

Two sludge types from two contrasting P removal methods namely: chemical removal (by means of ferric chloride precipitation) and biological removal were used in this study. Both sludge types were anaerobically digested. The BNR sludge was dried on earth paddies while the chemically treated sludge was dried in concrete drying beds. Selected chemical properties of the sludge used are presented in Table 5.1.

**Table 5.1 Selected sludge properties**

Variables	Biological phosphorus removal (BPR)	Fe-salt treated sludge	Units
pH *	6.02	6.79	
Moisture	6.1	31.5	%
Tot. solids	93.9	68.5	%
Organic Matter	512	433	g kg <sup>-1</sup>
Ash	489	567	g kg <sup>-1</sup>
Total C	275	234	g kg <sup>-1</sup>
Total N	31.7	28.6	g kg <sup>-1</sup>
C/N Ratio	8.65	8.17	NA
P	23.6	26.0	g kg <sup>-1</sup>
Water soluble P	1.16	0.05	g kg <sup>-1</sup>
Water soluble Cl-	0.25	1.72	g kg <sup>-1</sup>
K	3.21	2.58	g kg <sup>-1</sup>
Na	0.86	1.87	g kg <sup>-1</sup>
Ca	24.7	22.8	g kg <sup>-1</sup>
Mg	5.58	3.67	g kg <sup>-1</sup>
Fe	24.1	101.5	g kg <sup>-1</sup>
Al	21.8	17.6	g kg <sup>-1</sup>
Total S	8.18	20.5	g kg <sup>-1</sup>
Cu	376	328	mg kg <sup>-1</sup>
Mn	1129	827	mg kg <sup>-1</sup>
Zn	3845	8232	mg kg <sup>-1</sup>

**5.2.2 Soil types**

Soil samples were collected from the top 20 cm layer of three soil forms: A horizons of Clovelly (low P fixing), Shortlands (high P fixing) and Hutton (low P fixing) soil forms (Soil Classification Working Group, 1991). Selected chemical (Table 5.2) and Physical (Table 5.3) properties of these soils are presented below.

**Table 5.2 Selected chemical properties of the soils**

Characteristic	Low P fixing (a)	High P fixing	Low P fixing(b)	Units
pH (water)	5.67	5.72	6.46	
Total N	983.0	262.0	1142.0	mg kg <sup>-1</sup>
Total C	1.17	0.388	1.53	%
C/N Ratio	11.9	14.8	13.4	NA
Total P	575.0	415.0	780.6	mg kg <sup>-1</sup>
P Bray 1	33.2	2.01	77.3	mg kg <sup>-1</sup>
Total K	1786.0	552.2	420.4	mg kg <sup>-1</sup>
Total Ca	1208.5	626.7	1452.3	mg kg <sup>-1</sup>
Total Mg	981.0	1064.5	737.9	mg kg <sup>-1</sup>
Ammonium acetate extractable				
K	0.921	0.155	0.201	mg kg <sup>-1</sup>
Ca	4.584	1.747	4.662	mg kg <sup>-1</sup>
Mg	1.740	3.576	2.351	mg kg <sup>-1</sup>
Na	0.000	0.044	0.016	mg kg <sup>-1</sup>

**Table 5.3 Selected physical properties of the soils**

Soil	Soil colour (wet)	Sand (%)	Silt (%)	Clay (%)	Bulk density	Texture
Low P fixing (a)	Brown 7.5YR 5/2	70.0	6	24	1.2	Sandy loam
High P fixing	Red 10 R 4/6	20	16	64	1.0	Sandy loam clay
Low P fixing (b)	Dark Red Red	52	8	40	1.0	Sandy clay loam

### 5.2.3 Treatments and experimental layout

The sludge were mixed thoroughly with the candidate soils to make an equivalent P supply rate of 236 kg P per ha. Additional unamended control soil was included for each treatment and each treatment was replicated three times. At the commencement of the study, de-ionized water was added to each experimental unit to fill the soil pores to field capacity. The soil-sludge mix was incubated in sealed plastic containers in dark room at a constant temperature of 25°C for 56 days under aerobic conditions. Destructive sampling was done on days 1, 7, 14, 28, and 56 from which P fractionation study was conducted.

### 5.2.4 Analytical methods

Soil P exists in several chemical forms that include soil solution and exchangeable or labile phase, organic matter phase, Ca-bound phase, Fe and Al bound phases Hedley et al., 1982). These P forms are often named according to the name of extractants which are used to dissolve them to the soil solution H<sub>2</sub>O-P (labile P or water soluble P), KCl-P (soluble/exchangeable P), NaOH-P (Fe and Al bound P), HCL-P (Ca bound P), and HNO<sub>3</sub>-P (Residual P) (Jalali and Tabar, 2011).

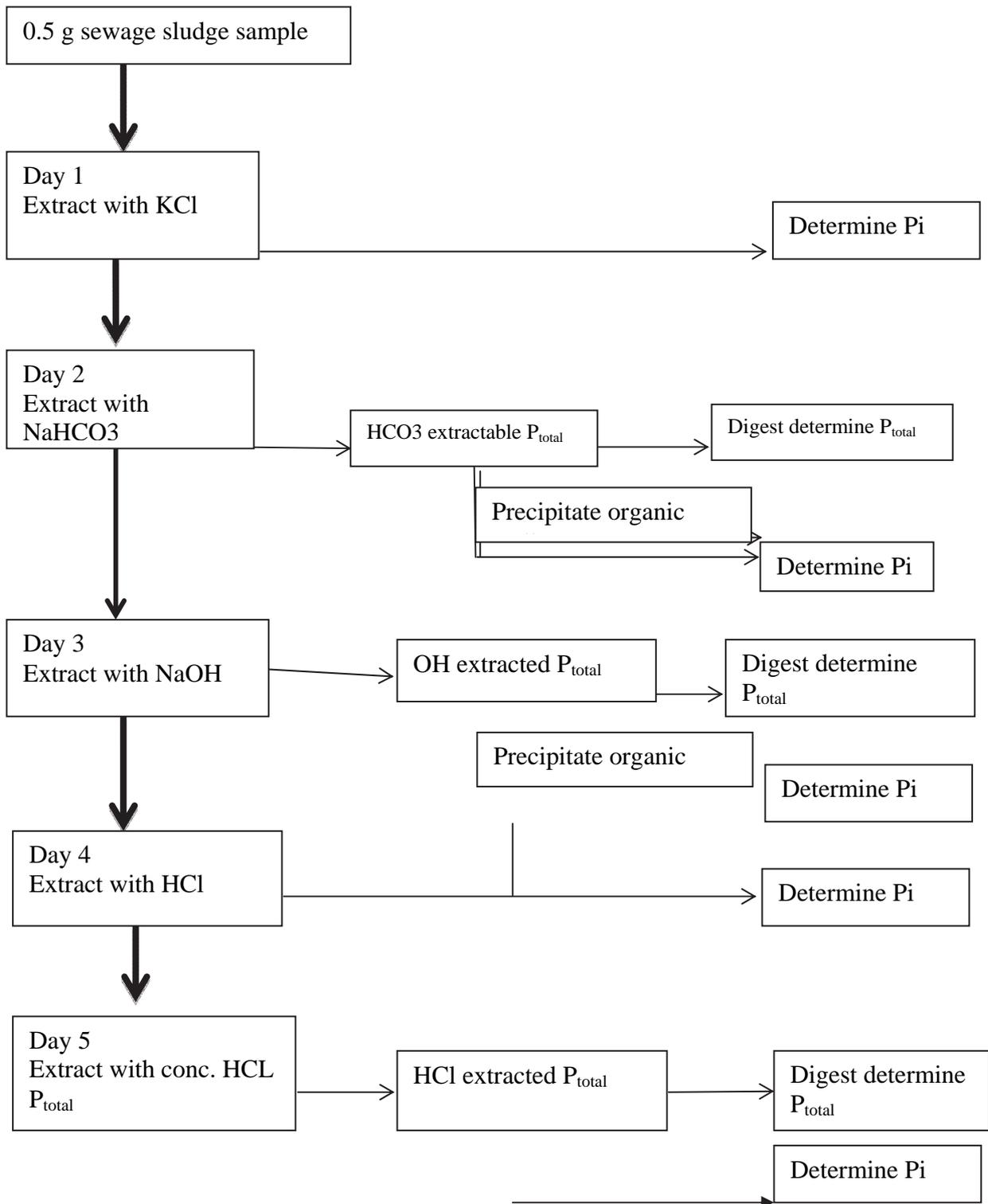
#### **5.2.4.1 Sequential phosphorus fractionation method**

##### *KCl extractable P*

0.5 g of the sample was weighed into a 50 ml centrifuge tube and 1M KCl was added and shaken for two hours, three times for a day. The solution was centrifuged at 4000 rpm for 15 min then 15 ml of the aliquot was collected and centrifuged further using an ultra-centrifuge for 5 min at 15000 rpm. Then solution extract was filtered through a Whatman no.42 filter paper into a clean 50 ml beaker. 5 ml of the filtrate was pipetted into a 50 ml volumetric flask and the soluble-P was determined calorimetrically using the method of Murphy and Riley (1962). The sequence of the fractionation is illustrated in Fig. 5.2.

##### *0.5 M NaHCO<sub>3</sub> extractable P*

After the KCl supernatant was decanted, 30 ml of 0.5 M NaHCO<sub>3</sub> was pipetted to the 0.5 g of the residue and was shaken for two hours three times a day. The samples were then centrifuged at 4000 rpm for 15 min thereafter 15 ml of the aliquot was collected and pipetted centrifuged using an ultra-centrifuge for 5 min at 15000 rpm.



**Figure 5.2 Flow chart of sequential P extraction method.**

The solution extract was filtered through a Whatman no.42 filter paper into a clean 50 ml beaker. 5 ml of the filtrate was into a 50 ml volumetric flask and the  $\text{HCO}_3\text{-P}_i$  (inorganic P) was determined colourimetrically with the method of Murphy and Riley (1962). Another 5 ml aliquot was pipetted into a 50 ml volumetric flask and oxidised with 0.5 g  $\text{K}_2\text{S}_2\text{O}_8$  and

10 ml 0.9 M  $\text{H}_2\text{SO}_4$ , from which the  $\text{HCO}_3\text{-P}_{\text{total}}$  was determined colourimetrically. The difference between the total and inorganic phosphate gives the  $\text{HCO}_3\text{-P}_o$  (organic P).

#### *1 M HCl extractable P*

After the NaOH supernatant was decanted, 30 ml of 1 M HCl was pipetted to the 0.5 g of the residue left after NaOH extraction, shaken three times, each time for two hours. It was then centrifuged at 4000 rpm for 15 min. A 15 ml aliquote was collected and centrifuged using an ultra-centrifuge for 5 min at 15000 rpm. The solution extract was filtered through a Whatman no.42 filter paper into a clean 50 ml beaker. 5 ml of the filtrate was pipetted into a 50 ml volumetric flask and the 1 M HCl-Pi was determined colourimetrically with the method of Murphy and Riley (1962).

#### *Hot concentrated HCl extractable P*

5 g of the residue from the 1M HCl extracted sludge was digested with 10 ml of concentrated HCl (11.3 M) in a heated water bath at 80° C for 10 min. The sample was removed from the water bath and 5 ml concentrated HCl was added and left at room temperature for one hour. The sample was then centrifuged at 4000 rpm for 15 min followed by ultra-centrifuge of 15 ml aliquot for 5 min at 15000 rpm and decanted into a clean vial. The residue was then washed twice with deionised water, centrifuged at 4000 rpm for 15 min then 15 ml of the aliquot was then centrifuged using an ultra-centrifuge for 5 min at 15000 rpm and the extract was filtered through a Whatman no.42 filter paper into a clean 50 ml beaker. 5 ml aliquot was pipetted into a clean 50 ml volumetric flask and the HCl-Pi (inorganic P) was determined colourimetrically with the method of Murphy and Riley (1962). Another 5 ml aliquot was pipetted into a 50 ml volumetric flask and oxidised with 0.4 g  $\text{K}_2\text{S}_2\text{O}_8$  and 10 ml deionised water to determine the  $\text{NaOH-P}_{\text{total}}$  colourimetrically. The difference between the total and inorganic phosphate represented the organic P (HCl-P<sub>o</sub>).

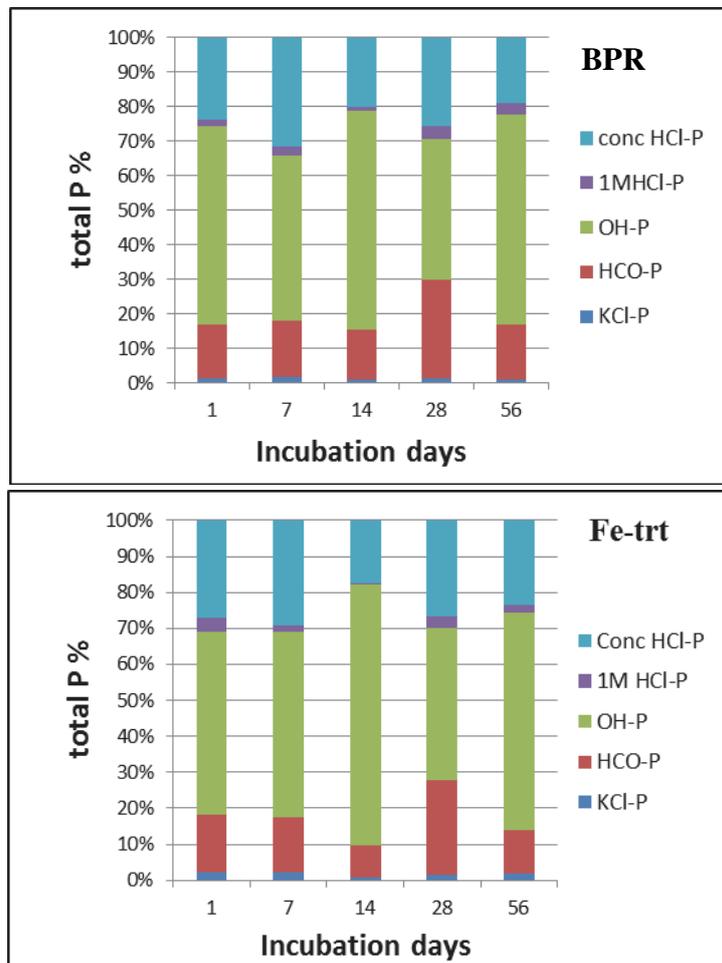
## **5.3 RESULTS AND DISCUSSION**

### **5.3.1 The effect of wastewater P removal methods on Soil P forms**

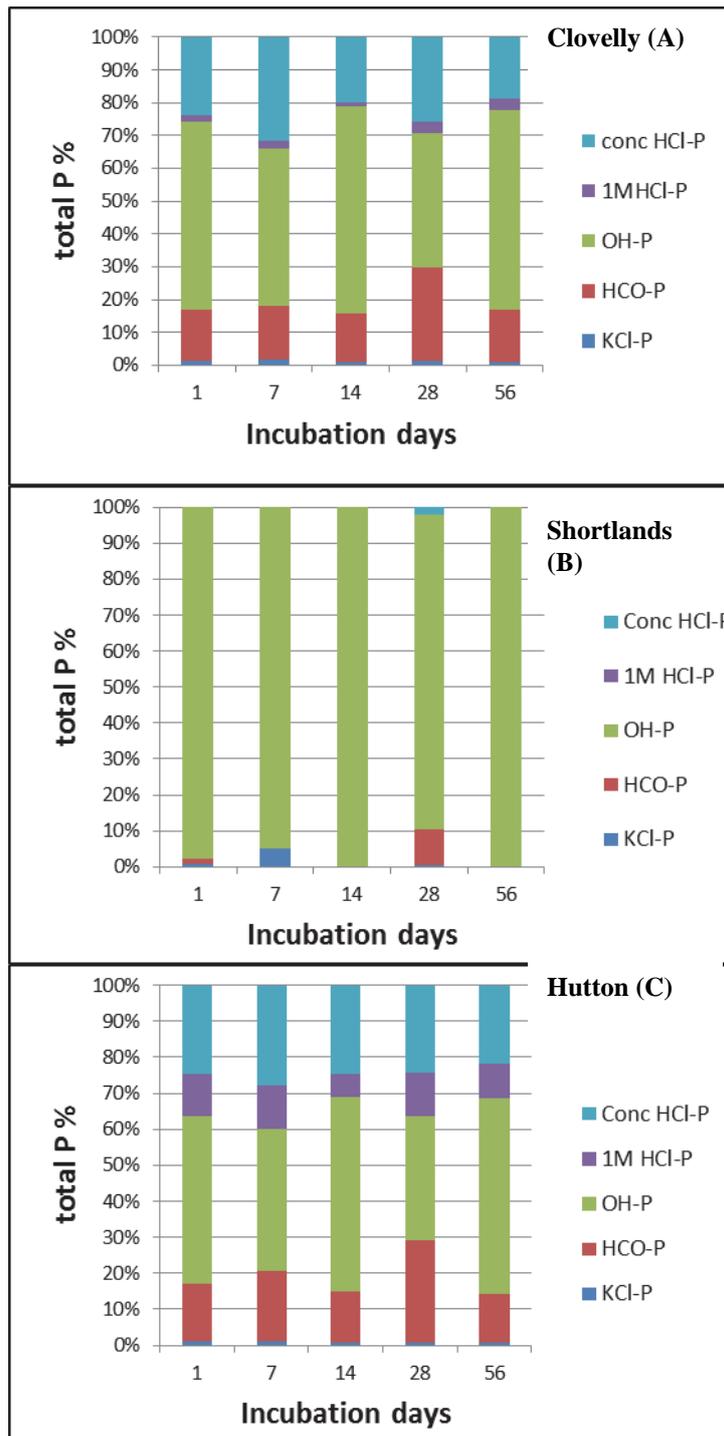
Results from the fractionation study indicate that majority of the P in the Clovelly soil form was alkaline extractable ( $\text{NaHCO}_3$  and NaOH) with the NaOH extractable fraction accounting the most (Fig. 5.3). This is regardless of the wastewater P removal methods. The NaOH extractable fraction of P is mainly bound to Fe and Al and is not available for crop uptake. The Shortland soil form was overwhelmingly dominated by (>90% of the P fraction) NaOH extractable fraction, which is bound to Fe and Al suggesting low availability for crop uptake. It was also apparent that >50% of the phosphorus in all three soil forms amended with BPR was alkaline extractable dominated by NaOH extractable fraction (Fig. 5.4).

It is well known that soils continue to release P into solution over long periods of time and that the size of the easily desorbable pool of soil P will vary with soil properties. P fixation is a simple reaction between  $\text{H}_2\text{PO}_4^-$  ions with dissolved  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Mn}^{3+}$  ions to form insoluble hydroxy phosphate precipitates. In strongly acid soils, enough soluble Al, Fe or freshly precipitated hydroxy phosphates are slightly soluble because they have a great deal of surface area exposed to the soil solution. Therefore, the phosphorus contained in them is, initially expected to be available for crop uptake. However, as time progressed the

precipitated hydroxy phosphate gets less soluble and turns to completely crop unavailable form (Brady and Weil, 2008).



**Figure 5.3 The effect of wastewater P removal method on the dynamics and crop availability of P in sludge amended Clovelly soil**



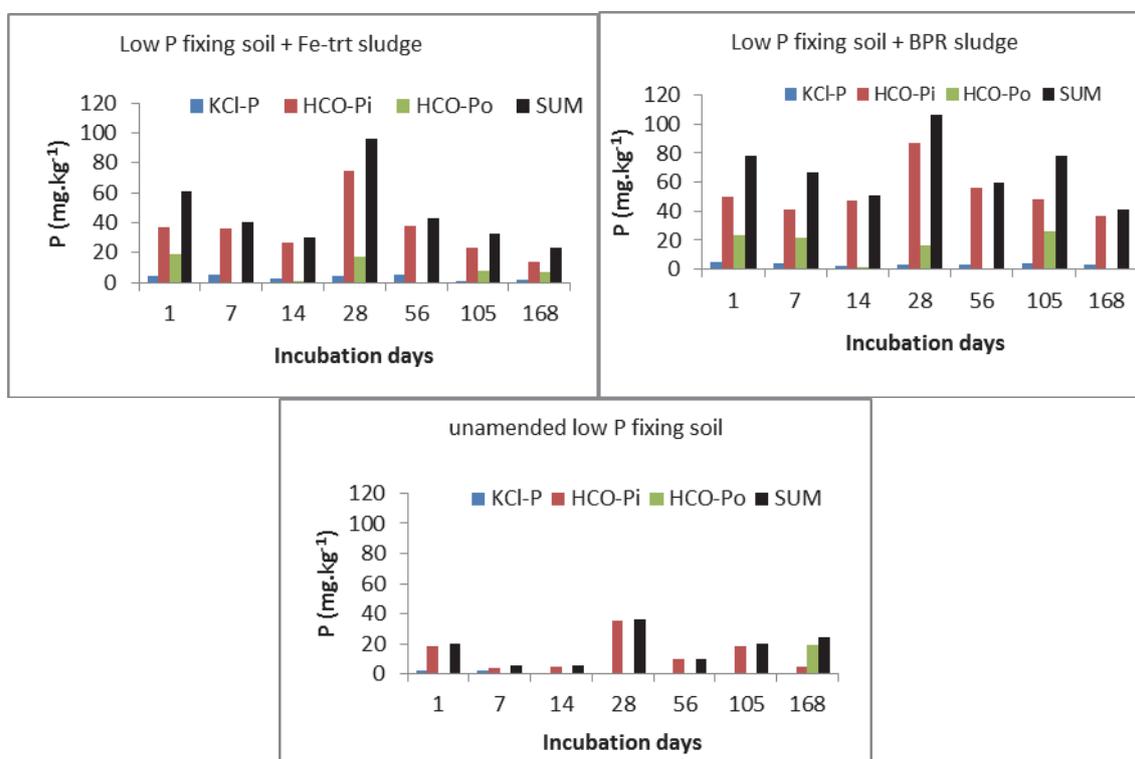
**Figure 5.4 Soil P fraction dynamics in three soil forms (Clovelly, Shortlands, and Hutton soils) amended with BPR sludge**

**5.3.2 Phosphorus release from soils amended with sludges of contrasting P removal methods (biological vs. chemical)**

Generally there was no clear trend in P release dynamics from all three treatments (soil amended with BPR sludge, soil amended with chemical P removal, and zero sludge control) (Fig. 5.5). Plant available P was highest on day 28 for all treatments including the zero

sludge control indicating that the release was most probably the result of desorption from the active pool (OH-P).

It was also apparent that plant available P was relatively higher in soils amended with BPR than soils amended with Fe-treated sludge, which is in agreement with the general literature. For instance O'Connor et al. (2004) and Stratful et al. (1999) reported that sewage sludge that underwent biological P removal has a P fertilizer value, in terms of plant availability, similar to that of manure and inorganic fertilizer. In contrast, chemical P removal methods using Fe and Al salts leads to the precipitation of sparingly soluble aluminium (Al-P) and ferric phosphates (Fe-P) forms, which reduce P water extractability and plant availability. Nonetheless, such reduction in the availability of P for crop uptake reduces the risk to environmental pollution through P leaching and runoff losses (Maguire et al., 2000; Elliot et al., 2002; Hyde and Morris, 2004; Krogstad et al., 2005).



**Figure 5.5 Plant available P dynamics from soils amended with sludges of contrasting P removal methods (chemically (Fe-trt) P removal, biological P removal (BPR)) and a zero sludge control**

The lack of clear trend on the release characteristics of plant available P from sludge amended soils has been one of the key challenges for sludge application rate recommendation based on crop P requirements. Therefore, agronomic sludge application recommendation rates should be done based on crop N requirements. This should be, however, complemented with regular soil monitoring protocols for potential labile P build-up, which could compromise the environment.

## 5.4 CONCLUSION

A large fraction of the P in all sludge amended soils remained NaOH extractable, which is not easily available for crop uptake. The kinetics of P release and transfer between pools in sludge amended soils is influenced to a large extent by the chemical and mineralogical characteristics of soils as well as sludge P removal methods. Nonetheless, the kinetics of P release from this study lacked clear trend across soil types making it challenging to come up with generic P release kinetic equations for modelling purposes. Therefore, it is advisable that agronomic sludge application recommendations be done based on crop N requirements. This should be, however, complemented with regular soil monitoring protocols for potential labile P build-up, which could compromise the environment.

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## **CHAPTER 6 – MOBILITY AND UPTAKE OF ZN, CD, NI AND PB IN SLUDGE-AMENDED SOILS PLANTED TO DRYLAND MAIZE AND IRRIGATED MAIZE-OAT ROTATION**

### **6.1 INTRODUCTION**

The use of sewage sludge for crop production is a well-known practice around the world because of its soil conditioning effect and as a source of low grade fertilizer (Gasco and Lobo, 2007; Herselman, 2010). Sewage sludge, when applied to agricultural soils, can substitute inorganic fertilizers and improve soil physical properties. However, one of the main concerns for sustainable use of municipal sewage sludge on agricultural soils is the long term build-up of trace metals (Smith, 2009). Some trace metals (e.g., Cu and Zn) are essential for plant and animal health. However, concentrations exceeding threshold levels have the potential to cause toxicity to plants and animals (Sterritt and Lester, 1984). Other heavy metals (e.g., Cd and Pb) are not known to be essential to plants and animals. Toxicity, however, occurs when metals are concentrated in the environment above threshold levels.

Finding environmentally acceptable, socially responsible, and economically feasible ways of using municipal sewage sludge has received much attention from both the research community and regulatory agencies, as well as from the general public. Land application provides a means of supplying nutrients, such as nitrogen (N) and phosphorus (P), and organic matter (OM), and can be both agriculturally useful and environmentally responsible. However, application of sludge has led to concerns on how potential contaminants (heavy metals, organic contaminants and pathogens) may pollute the groundwater underlying application areas. Generally the natural background concentration of heavy metals in soils plays a determining role in the level of threat to groundwater pollution from any anthropogenic additions such as through the application of sludge. The background concentration of a soil is defined as the normal chemical composition of an earth material prior to its contamination (Korte, 1999). The background concentration is a function of the parent material and soil formation processes and is therefore highly variable across regions. For instance, in many South African soils, the natural background concentrations of Ni, Zn, and Pb is high (Herselman et al., 2005). Therefore, extreme caution is needed when applying sludge to agricultural soils.

Previous studies have shown that heavy metal uptake by crops increases as sludge application rate increases (Hinesly et al., 1978; Bidwell and Dowdy, 1987; Kiemnec et al., 1990; Logan et al., 1997). Heavy metal uptake by crops is influenced by metal concentration in the soil, as well as soil physical and chemical properties (Merrington, et al., 2003). Other studies report an increase in soil metal concentrations as sludge application rate increased in fields where crops were not planted (Williams et al., 1984). Few studies have investigated the effect of sludge application on crop heavy metal uptake and accumulation in the soil profile (Soon et al., 1980; MacLean et al., 1987; Granato et al., 2004; Fuentes et al., 2006). The movement of heavy metals in sludge amended soils (Emmerich et al., 1982; Yingming and Corey, 1993), mass balance and distribution of sludge-borne trace elements following long-term application of sewage sludge (Baveye et al., 1999), and influence of sewage sludge application on soil properties, distribution and availability of heavy metal fractions (Tsadilas et al., 1995) has also been investigated. However, to our knowledge, there is no

information on the effect of soil water availability (dryland vs. intensive irrigated cropping systems) on the dynamics of metals in the soil-plant system (metal crop uptake and partitioning between plant organs, fate and mobility within the soil system) from class A (U.S. EPA, 1995), or class A1a (South Africa, Snyman and Herselman (2006)) sludge amended soils under controlled short to medium term field experiments. In addition, the unwritten rule of using environmental soil contamination threshold values as phytotoxicity indicators needs to be investigated. Similarly, little is known about the dynamics of these metals with respect to the relationship between total concentration, plant available and water soluble fractions of metals from sludge amended soils under dryland vs. irrigated systems. This study focuses on Zn, Cd, Ni and Pb, which are four of the eight elements of concern listed in the South African agricultural sludge guideline (Snyman and Herselman, 2006). These four are selected because of their potential reactivity, toxicity, mobility and availability in South African soils and sludges.

The objective of the study was to test the hypotheses that in the short to medium term (5-10 years) the application of agricultural quality sludge according to crop nitrogen requirements: i) will not result in a significant increase in the water soluble content of heavy metals in the soil, (ii) mobility and uptake of heavy metals for an irrigated maize-oat rotation will be higher than for dryland maize, and (iii) the concentration of heavy metals in plant tissue could reach phytotoxic levels before the soil reaches environmental threshold levels.

## 6.2 MATERIALS AND METHODS

### 6.2.1 Field Site Description

The study was conducted at the East Rand Water Care Works (ERWAT), Johannesburg, Gauteng, South Africa (26° 01' 01" S; 28° 16' 55" E; altitude 1577 m above sea level). The area has a long term annual average rainfall of 700 mm, mainly from October to March. The soil of the experimental site is a clay loam (Hutton; Soil Classification Working Group, 1991) having a clay content of 36 to 46%, and pH (H<sub>2</sub>O) of 5.3 to 6.1. In the beginning of the study, the cation exchange capacity of the soil (ammonium acetate extract) was 12 cmol<sub>c</sub> kg<sup>-1</sup> and the electrical conductivity of the saturation paste extract ranged from 8 mS m<sup>-1</sup> at 1.2 m depth, to 36 mS m<sup>-1</sup> in the top 0.3 m soil layer. Initial concentration of Zn, Cd, Ni, Pb and other chemical properties of the soil for the study site are provided in Table 6.1.

**Table 6.1 Initial chemical properties and concentration of selected metals in a clay loam Hutton soil.**

Zn	Cd	Ni	Pb	P- Bray1	Exchangeable K	N	Organic matter
mg kg <sup>-1</sup>						%	
10.35	0.018	29.48	14.85	43.9	24.63	0.13	2.98

### 6.2.2 Field Trials and Treatments

Plots of 25 m<sup>2</sup> were arranged in a randomized complete block design comprising four replications of three sludge application rate treatments. The trial was laid out to accommodate widely different levels of bio-solid application to high and low productivity-

cropping systems. It consisted of two farming systems namely: dryland maize and an irrigated maize-oat rotation. The two contrasting cropping systems were selected to represent a dryland (rainfed) farming system on the one hand and an intensive irrigated system on the other hand. This created a range of conditions affecting nutrient and metal mobility and uptake. Maize was selected as test crop because it is one of the most widely cultivated crops across the globe and accounts for 51% of the cultivated land in South Africa (FAO, 2005). Oats were planted as a rotation crop because of its dual benefits: healthy grain for human beings (Peterson, 1992) and a high quality fodder for animals (Schrickel et al., 1992) and can be planted (under irrigation) during winter as rotation crop in the summer rainfall areas or can be alternated with legume crops in summer.

The treatments for dryland maize and irrigated maize-oat rotation consisted of two sludge rates (8 and 16 Mg ha<sup>-1</sup> yr<sup>-1</sup>), and a zero control. The value of 8 Mg ha<sup>-1</sup> yr<sup>-1</sup> represents the annual agricultural upper limit of the 1997 South African sludge guideline (WRC, 1997) which has recently been raised to 10 Mg ha<sup>-1</sup> yr<sup>-1</sup> (Snyman and Herselman, 2006). Sludge rates of 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> represent double the former norm. Sludge was applied since the 2004/05 until the 2011/12 summer season. For the irrigated maize-oat rotation, the annual sludge application was split into two, with half applied to both crops at planting. For dryland maize, however, the entire amount was applied at the beginning of the season before planting. Sludge was broadcast and immediately incorporated into the top soil (0.3 m) with a manually operated, diesel powered rotovator (Agria). After sludge incorporation, the soil was levelled using rakes and maize (CV. PAN 6966) was planted in 0.9 m rows at rates of 80000 seeds per hectare under irrigation and half this rate under dryland conditions. Each plot consisted of 6 rows 5 m in length, with the outer row on either side taken as border rows. After harvesting irrigated maize, sludge was applied accordingly and again incorporated, after which oats were planted. Oats were planted at a rate of 90 kg ha<sup>-1</sup> using a hand-drawn planter with double disk openers. Each oat plot consisted of 15 rows, spaced 0.3 m apart and 5 m in length, with two border rows on either side.

### **6.2.3 Sludge Characteristics**

The sludge used in this study was anaerobically digested and paddy-dried. According to the current South African sludge guideline (Snyman and Herselman, 2006), this sludge is classified as pollutant class “a” because of its low heavy metal content (Table 6.2). Based on the microbiological report from the East Rand Water Care Works (ERWAT) laboratory, the sludge can also be classified as microbiological class “A”. Considering the low odour and vector attraction characteristics of the sludge, it can also be classified as stability class 1.

**Table 6.2 New three-tier system for the classification of South African sludges (Snyman and Herselman, 2006).**

<b>Pollutant Class (mg kg<sup>-1</sup>)</b>			
	<b>A</b>	<b>B</b>	<b>C</b>
Zn	<2800	2800-7500	>7500
Cd	<40	40-85	>85
Ni	<420	420	>420
Pb	<300	300-840	>840
<b>Stability Class</b>			
	<b>1</b>	<b>2</b>	<b>3</b>
	Low odour and vector attraction	Medium attraction	High odour and vector attraction
<b>Microbiological Class</b>			
	<b>a</b>	<b>b</b>	<b>c</b>
Faecal coliform (CFU/g <sub>dry</sub> )	<10 <sup>4</sup>	10 <sup>6</sup> -10 <sup>7</sup>	> 10 <sup>7</sup>
Helminth ova (Viable ova/g <sub>dry</sub> )	<1	1-4	>4

The current South African sludge guideline (Snyman and Herselman, 2006) allows such quality sludges to be utilized in agriculture without restriction, as long as the N applied does not exceed crop demand, with the upper limit set at 10 Mg ha<sup>-1</sup> yr<sup>-1</sup>. Selected chemical characteristics of this class A1a sludge are presented in Table 6.3.

#### **6.2.4 Selection of metals**

This study focuses on Zn, Cd, Ni and Pb because of their potential reactivity, toxicity, mobility and high natural background concentration in most South African soils, as well as high availability in local municipal sludges (Herselman et al., 2005). Cadmium is one of a very small group of metals which the Food and Agriculture Organization/World Health Organization have set a provisional daily intake limit for humans (70 µg Cd/day) (Berglund et al., 1983). Cadmium and lead are considered as the most mobile heavy metals (McLaughlin et al., 2000) and their concentration in plants is highly correlated with that found in soil (Pais and Benton, 1997).

**Table 6.3 Chemical characteristics of anaerobically digested, paddy dried sludge used during the 2004/05-2010/11 growing seasons (Source: Vlakplaas wastewater treatment plant)**

Element	Unit	Year						
		2004/05	2005/06	2006/07	2007/08	2008/09	2009/10	2010/11
<b>N</b>	g kg <sup>-1</sup>	30.3	18.8	22.2	30.9	27.4	22.4	27.5
<b>P</b>	g kg <sup>-1</sup>	19.6	18.4	27.6	22.4	34.3	31.3	42.1
<b>P-Bray1</b>	mg kg <sup>-1</sup>	166	154	40	66	50	80	120
<b>Total C</b>	g kg <sup>-1</sup>	230	200	210	200	212	166	219.6
<b>K</b>	mg kg <sup>-1</sup>	3804	710	689	1356	1720	2530	1850
<b>Ca</b>	mg kg <sup>-1</sup>	25116	13062	17450	10042	26950	23147	28312
<b>Mg</b>	mg kg <sup>-1</sup>	25116	13062	17450	10042	26950	23147	29312
<b>pH</b>	H <sub>2</sub> O	6.01	6.2	6.02	6.08	8.1	5.7	5.6
<b>Cd</b>	mg kg <sup>-1</sup>	1.63	0.07	0.15	18.9	19	12.2	10.75
<b>Hg</b>	mg kg <sup>-1</sup>	1.70	0.02	0.03	1.81	1	1	0.4
<b>Cr</b>	mg kg <sup>-1</sup>	51.93	1.50	2.92	503.8	419	369.7	315.8
<b>As</b>	mg kg <sup>-1</sup>	7.08	0.18	0.23	17.94	6.5	5.88	5.64
<b>Pb</b>	mg kg <sup>-1</sup>	54.46	19.41	61.37	102	75	88.4	66.67
<b>Zn</b>	mg kg <sup>-1</sup>	459.9	40.3	200.8	2325	4920	3459	5755
<b>Ni</b>	mg kg <sup>-1</sup>	23.83	10.37	50.97	144.50	152.00	99.30	103.27
<b>Cu</b>	mg kg <sup>-1</sup>	97.2	3.21	4.59	526.8	681	497.29	544.52

### 6.2.5 Irrigation Scheduling

The irrigated maize-oat rotation experiment was planted under drip irrigation. The lateral spacing between dripper lines was 0.5 m from the summer 2005/06 season, but was reduced to 0.3 m after the 2005 winter season for the rest of the study period. Dripper spacing was 0.3 m in the laterals. The drip system was operated at a pressure of 100 to 150 kPa with an average drip rate of 13.8 mm hr<sup>-1</sup>. In the absence of rainfall, maize was irrigated 10 mm every three days for the first four weeks after planting. In 2005, this was followed by irrigation according to the FAO crop factor method in the Soil Water Balance (SWB) model (Jovanovic and Annandale, 1999) once every five days until harvest in the absence of rainfall. During the growing season from 2007 to 2011, however, maize was irrigated according to neutron probe deficit readings to fill the profile to field capacity once a week in the absence of rainfall. During the winter seasons of each year, oats were irrigated every three days (9 mm in 2005 and 10 mm in 2006 and 2008) for the first four weeks. This was followed by irrigations to field capacity according to a site calibrated neutron water meter (Model 503 DR CPN Hydroprobe, Campbell Pacific Nuclear, California, USA) to a depth of 1.2 m for the rest of the season until harvest, mostly twice a week in 2005 and once a week during the rest of the study period.

### 6.2.6 Plant and Soil Sampling

In the 2010/11 growing season, whole plant (above-ground) samples were collected for heavy metal uptake determination from an area of 0.5 m<sup>2</sup>. Two plants per plot were taken under dryland maize and four under irrigated maize. A hand grab of additional plant samples

of irrigated oats were collected randomly from all plots during the 2010/2011 growing season for heavy metal uptake determination.

After harvest, three soil samples were collected diagonally across each plot of a treatment at 0.3 m depth intervals down to 1.2 m using an auger. The samples were collected from the 0 to 0.3m, 0.3 to 0.6m, 0.6 to 0.9m, and 0.9 to 1.2m layers. The three samples from each layer of a plot were combined and mixed to make a single homogenous composite soil sample per layer (typically 48 soil samples were prepared for each cropping system).

### 6.2.7 Plant and Soil Chemical Analyses

Plant material was washed using distilled water to remove adhered soil particles and subsequently pulverized using a stainless steel shredder. All shredded maize plants (including stems, leaves, cobs and grains) were dried at 80°C for 72 hours and milled using a stainless steel mill. Plant samples (maize and oat stover, and maize grain) were analyzed for heavy metals after wet acid digestion using an inductively coupled plasma optical emission spectrometer (ICP-OES) (SpectroFlame Modula; Spectro, Kleve, Germany), following standard procedures (Non-affiliated Soil Analyses Work Committee, 1990). Plant toxicity level was assessed based on the reference values provided by Jones (2012) (Table 6.4).

**Table 6.4 General phytotoxic and acceptable levels of heavy metals in plant leaf tissue (dry mass) (Jones, 2012).**

Heavy metal	Normal	Toxic	Excessive
	mg kg <sup>-1</sup>		
<b>Zn</b>	10-100	100-150	150-400
<b>Cd</b>	0.05-0.20	0.20-5.0	5-30
<b>Ni</b>	0.50-10.0	10-50	50-100
<b>Pb</b>	5-30	30-100	100-300

Corresponding soil samples were air dried, pulverized and sieved using <2 mm sieves prior to acid digestion and analyzed using aqua regia (75% HCl, 25% HNO<sub>3</sub>) for total metal concentration, and Ammonium Ethylenediaminetetraacetic acid (NH<sub>4</sub>-EDTA) for available heavy metal concentration. Soil samples were also analyzed for pH (H<sub>2</sub>O) and Carbon (C) using a Carlo Erba NA1500 C/N analyser (Carlo Erba Strumentazione, Milan, Italy). The threshold level of selected heavy metals in sludge amended soils was assessed as stipulated in the South African sludge guideline (Table 6.5), and guidelines for maximum permissible metal concentration in agricultural soils from other countries around the globe (Table 6.6).

**Table 6.5 Metal limits for sludge amended soils (Snyman and Herselman, 2006).**

Metal elements	Total Investigative	Total Maximum	Maximum Available
	Level (TIL) (aqua regia)	Threshold (TMT) (aqua regia)	Threshold (MAT) (NH <sub>4</sub> NO <sub>3</sub> )
	mg kg <sup>-1</sup>		
Zn	185	200	5.0
Cd	2	3	0.1
Ni	50	150	1.2
Pb	56	100	3.5

**Table 6.6 Guidelines for maximum permissible metal concentrations in agricultural soil across regions.**

Heavy metal	S.A. Sludge guideline <sup>1</sup>	Europe <sup>2</sup>	USA <sup>3</sup>	Australia & New Zealand <sup>2</sup>
	mg kg <sup>-1</sup>			
Zn	200	150-300	1400	200
Cd	3	1-3	20	3
Ni	150	30-75	210	60
Pb	100	50-300	150	300

<sup>1</sup>Snyman and Herselman (2006)<sup>2</sup>McLaughlin et al. (2000)<sup>3</sup>US EPA (1995)

According to the current South African sludge guideline (Snyman and Herselman, 2006), the risk to the environment is unacceptable when the total metal content of the soil exceeds the total maximum threshold (TMT) level. If the total metal content of the soil is between total investigative level (TIL) and the TMT (Table 5), the mobility of the metals concentration in the soil needs to be assessed. Total investigative level (TIL) is a flag that warrants detailed soil analyses in terms of mobility using NH<sub>4</sub>NO<sub>3</sub> extraction. If the NH<sub>4</sub>NO<sub>3</sub> extractable metal content of the soil exceeds the maximum available threshold (MAT), sludges of pollutant class b may not be applied to this soil. If the NH<sub>4</sub>NO<sub>3</sub> extractable metal content of the soil is lower than the MAT, sludge of pollutant class b can be applied to the soil and the land should be re-assessed two years after sludge application (Snyman and Herselman, 2006). The soluble fraction of soil heavy metals was also analyzed using saturated paste extracts. The saturated pastes were prepared by adding deionized water to 250 g of air-dried samples until it reached a condition of complete saturation, as described by the standard procedures in Non-affiliated Soil Analyses Work Committee (1990). Saturated pastes were allowed to equilibrate for 24 hours in a covered container. An extract from the saturated paste was acquired by filtering the soil paste through Whatman no 50 paper on a Buchner funnel under low suction (20 kPa).

### 6.2.8 Statistical Analyses

Statistical analyses were performed to evaluate the effect of varying sludge application rates on heavy metal uptake by dryland maize, irrigated maize and oat, and concentrations in the soil. The statistical analyses were conducted using Analysis of Variance (ANOVA) and General Linear Model (GLM) procedures of Windows SAS Version 9.3 (SAS Institute, 2010) to determine significant treatment effects on measured response variables. When treatment effects were found to be significant, Fisher's protected LSD test at the 0.05 level was used to separate means.

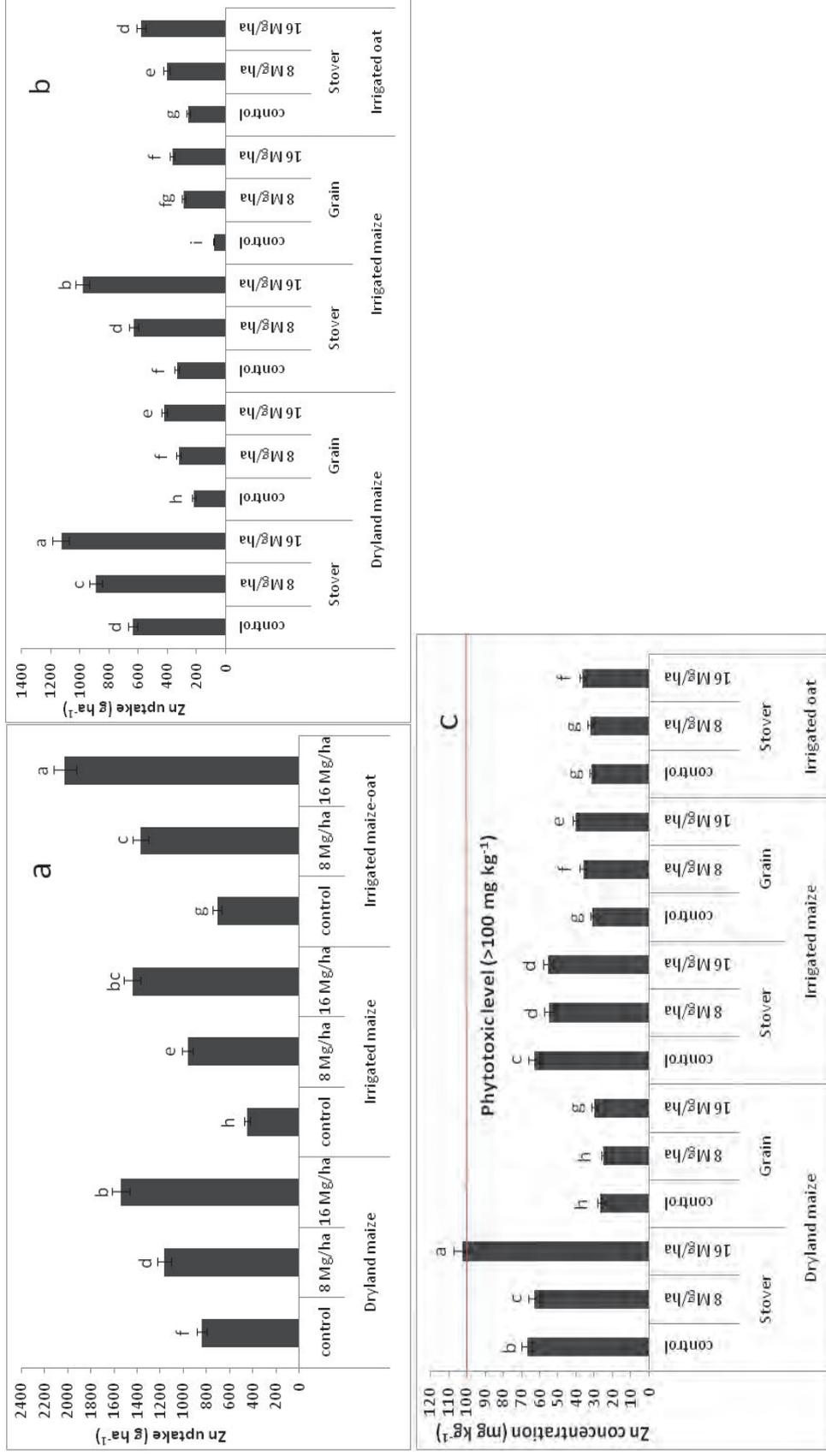
## 6.3 RESULT AND DISCUSSION

### 6.3.1 Heavy Metal Uptake by Crops

#### 6.3.1.1 Zinc (Zn)

Zinc uptake by both dryland maize and the irrigated maize oat-rotation increased significantly as sludge application rate increased (Fig. 6.1a). This is in agreement with previous findings by Hinesly et al. (1978), who reported a significant increase in Zn uptake by maize (20 inbred lines) as sludge application rate increased. Generally Zn uptake was significantly lower for the irrigated maize than for dryland maize treatments receiving similar levels of sludge, except for the 16 Mg ha<sup>-1</sup>yr<sup>-1</sup> treatment, where uptake by dryland maize was relatively higher, although not significantly so. Nonetheless, the annual Zn uptake by the irrigated maize-oat rotation from sludge amended treatments was significantly higher than similar dryland maize treatments. The lower Zn uptake by the irrigated maize is mainly attributed to the reduction in Zn plant availability because of the extra Zn removal by oats (Fig. 1b) during the winter season. The amount of Zn taken up by oats was generally lower than similar irrigated maize treatments (Fig. 1b) despite receiving similar Zn amounts. Such variations in Zn uptake between crops and within cultivars of a specific crop are common (Hinesly et al., 1978; Alloway, 1995).

It was also apparent that Zn stored in the stover (stems and leaves) was significantly higher than that in the grain (Fig. 1b). Previous studies conducted by Hinesly et al. (1978) and Granato et al. (2004) also report similar results. Grain Zn storage accounted for 13 to 19%, 30 to 33%, and 22 to 27% of the total crop aboveground biomass Zn uptake from the 0, 8 and 16 Mg ha<sup>-1</sup> sludge treatments, respectively, by dryland and irrigated maize-oat rotation. The fraction of Zn stored in maize grain from the 8 Mg ha<sup>-1</sup> and 16 Mg ha<sup>-1</sup> treatments were similar to the low-medium (33-36%), and high (26%) sludge application treatments of Bidwell and Dowdy (1987), respectively. Similarly, the fraction of Zn in maize grain from the 8 Mg ha<sup>-1</sup> sludge treatment was closer to the findings of Shivay and Prasad (2014) (34-39%) for maize that received Zn as micro nutrient through foliar and soil applications.



**Figure 6.1. Total aboveground biomass zinc uptake by dryland maize, irrigated maize and irrigated maize-oat rotation (a), and zinc uptake by maize stover vs. grain (b) as well as concentration of zinc in stover and grain of dryland maize and irrigated maize-oat rotation (c) planted to a clay loam Hutton soil treated with municipal sludge at varying rates for seven years.**

The fraction of Zn in maize grain for the control treatment from this study was much lower than the 63% of Bidwell and Dowdy (1987), as well as, the 37% of Shivay and Prasad (2014). This is most probably due to the lower natural background concentration of Zn from this study (0.0155 mg kg<sup>-1</sup>; total) compared with that of Bidwell and Dowdy (1987) (9.10 mg kg<sup>-1</sup>; total) as well as Shivay and Prasad (2014) (0.36 mg kg<sup>-1</sup>; plant available).

The low grain Zn concentration is an indication of low Zn transfer from vegetative biomass to the grain (Fig. 6.1b). Similar to the patterns of total Zn uptake, Zn uptake by stover and grain increased as the sludge application was doubled under both cropping systems but was only significant under dryland (Fig. 6.1b). It was interesting to note that the concentration of Zn in maize stover (Fig. 6.1c) under dryland production, reached phytotoxic levels (103 mg kg<sup>-1</sup>) for the 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> sludge treatment following the reference values provided by Jones (2012) in Table 6.4. This is in contrast to soil Zn concentration (95 mg kg<sup>-1</sup> near the soil surface) which was far below environmental threshold levels (185 mg kg<sup>-1</sup>) stipulated by South African sludge guideline (Table 6.5) as well as other international guidelines for maximum permissible metal concentration in agricultural soils (Table 6.6).

The high dryland maize Zn concentration under the 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> application rate, is most probably attributed to a combination of factors, including relatively low biomass production (Tesfamariam, 2009) and therefore lower crop Zn uptake over the 7 consecutive years of this study compared with the irrigated system, which might have resulted in the build-up of Zn in the soil. This is in agreement with previous findings who reported high Zn uptake at high sludge application rates because of Zn accumulation in the soil (Miller et al., 1995; Kalbitz and Wennrich, 1998; and Merrington et al., 2003). The high Zn uptake observed at high sludge application rates under dryland maize relative to equivalent irrigated maize-oat rotation is mainly attributed to the increase in the amount of Zn added to the soil with the sludge. The observed reduction in soil pH as the sludge application rate increased (Table 6.7) could have also contributed to such increase in Zn uptake. This is in agreement with previous findings of Miller et al. (1995), who reported that, Zn uptake is mainly associated with high metal concentrations in sludges, and/or low soil pH values of 4.5-6.

**Table 6.7 Soil pH (H<sub>2</sub>O) and organic C (%) in the soil profile of both dryland maize and irrigated maize-oat rotation for the growing season of 2010/11.**

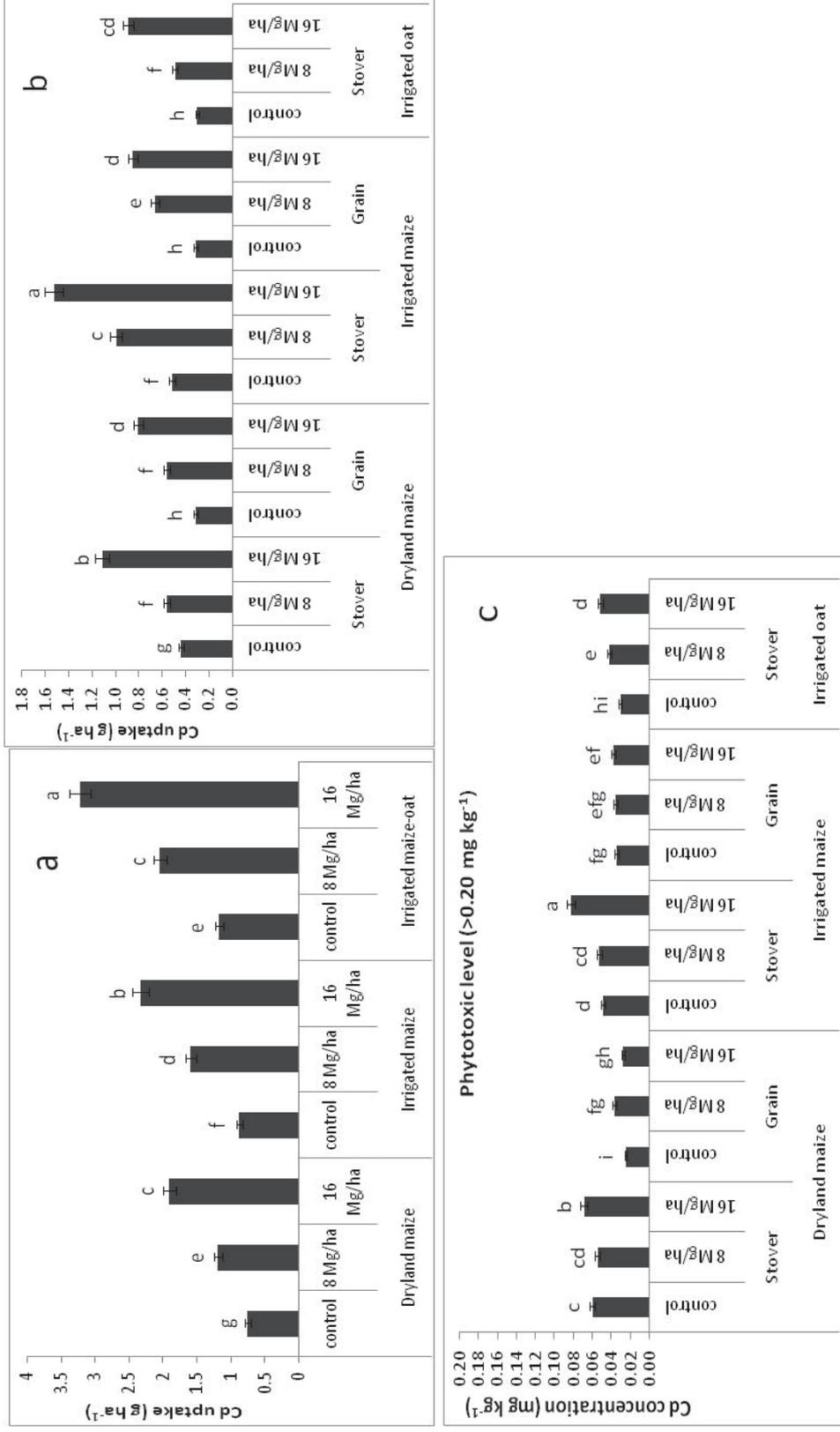
Cropping system	Soil depth (m)	Soil pH (H <sub>2</sub> O)			Soil C (%)		
		Sludge application rates (Mg ha <sup>-1</sup> )					
		0	8	16	0	8	16
Dryland maize	0-0.3	6.54	5.68	5.44	1.37	1.52	1.58
	0.3-0.6	6.27	5.76	6.07	0.8	0.94	0.81
	0.6-0.9	5.89	5.90	5.81	0.39	0.48	0.53
	0.9-1.2	5.81	5.78	5.44	0.28	0.39	0.31
	0-0.3	7.1	6.83	6.00	1.4	1.54	1.64
Irrigated maize-oat rotation	0.3-0.6	6.47	6.72	6.60	0.92	0.94	0.77
	0.6-0.9	6.4	6.44	6.53	0.46	0.58	0.43
	0.9-1.2	6.07	6.03	6.16	0.33	0.42	0.27

The increasing trend in Zn uptake observed in this study strengthens concerns raised by Lotter and Pitman (1997), who point out that uncontrolled utilization of sewage sludge on agricultural lands will lead to accumulation of Zn in the receiving soil, which could lead to a permanent risk to plants, and thereby compromise sustainability.

#### **6.3.1.2 Cadmium (Cd)**

Cadmium uptake by dryland maize and irrigated maize-oats also increased significantly as sludge application rate increased (Fig. 6.2a). Generally, Cd uptake by irrigated maize was higher than for dryland maize treatments (Fig. 6.2a). This is in contrast to Zn uptake, which was relatively lower for equivalent irrigated maize treatments. This indicates that the mobility of Cd from soil to crop is influenced by the availability of soil water. This leads to the acceptance of hypothesis 2 “Uptake of heavy metals under irrigated maize-oat rotation is higher than dryland maize” for Cd. This supports previous findings that the mobility of Cd in the soil-plant system is greater than for Zn (Sauerbeck, 1991; McLaughlin et al., 2000; Legind et al., 2012). Similar to Zn, the amount of Cd stored in stover was significantly higher than the grain under both cropping systems (Fig. 6.2b). It was also interesting to note that Cd uptake by stover and grain significantly increased as the sludge application rate increased. This is attributed to the increase in Cd concentration in the soil at higher sludge levels and is highly correlated to plant uptake (Pais and Benton, 1997). Cadmium in the grain of both cropping systems accounted for 38 to 45% of the total aboveground biomass Cd uptake, indicating the mobility of Cd within the plant system. This is in contrast to the 13 to 33% for Zinc. The fraction of Cd in maize grain relative to the total aboveground biomass Cd uptake from this study was higher than the 3-12% of Bidwell and Dowdy (1987). Such big differences could most probably be because of the genetic differences between the cultivars (Hinesly et al., 1978; Alloway, 1995) among other environmental factors.

The observed increase in Cd uptake by crops as the sludge application rate increased is mainly attributed to increase in the amount of Cd added to soil. The reduction in soil pH at higher sludge application rate (Table 6.7) could have also contributed to the increase in Cd uptake. This is because the bioavailability of Cd and metals in general increases as the soil pH decreases below 7 (Kalbitz and Wennrich, 1998). Despite the highly mobile nature of Cd, the concentration within the plant tissue remained below phytotoxic levels ( $>0.2 \text{ mg kg}^{-1}$ ) (Fig. 6.2c) following seven years of continuous sludge application at varying rates.

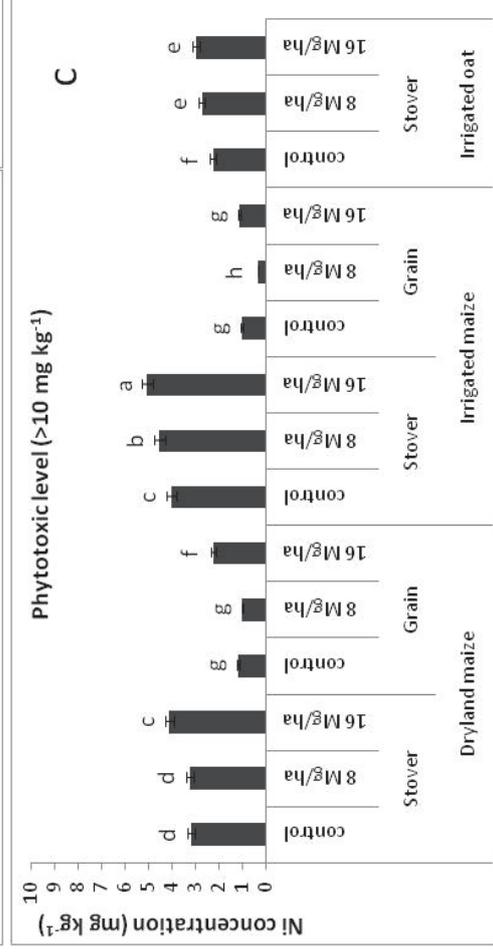
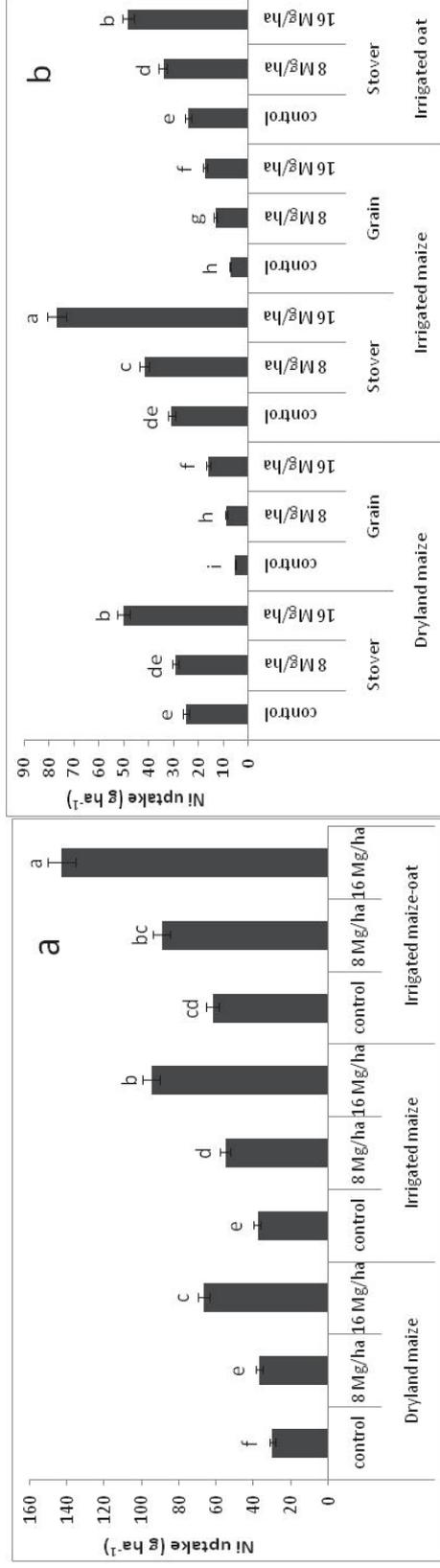


**Figure 6.2** Total aboveground biomass cadmium uptake by dryland maize and irrigated maize-oat rotation (a), and cadmium uptake by maize stover vs. grain (b) as well as concentration of cadmium in stover and grain of dryland maize and irrigated maize-oat rotation (c) planted to a clay loam Hutton soil treated with municipal sludge at varying rates for seven years.

### 6.3.1.3 Nickel (Ni)

Nickel uptake by both cropping systems increased significantly as the sludge application rate increased (Fig. 6.3a). This is mainly attributed to the increase in the amount of Ni added to the soil. The reduction in soil pH as the sludge application rate increased (Table 6.7) could have also contributed to such increase in Ni uptake because bioavailability of metals increases as soil pH decreases (Kalbitz and Wennrich, 1998). Nickel uptake by irrigated maize was significantly higher than for dryland maize treatments (Fig. 6.3a). This is despite the application of only half of the annual sludge application at planting of the irrigated maize, in contrast to the full application for the equivalent dryland maize treatments. Annual Ni uptake of  $16 \text{ Mg ha}^{-1}\text{yr}^{-1}$  under irrigated maize-oat rotation was double that of similar dryland maize treatments. This indicates that Ni is quite soluble and its uptake by maize is influenced by the availability of water. Therefore, hypothesis 2 “Uptake of heavy metals under irrigated maize-oat rotation is higher than dryland maize” was accepted for Ni.

Similar to Zn and Cd, the amount of Ni stored in stover was significantly higher than that in the grain under both cropping systems (Fig. 6.3b). Nickel uptake by stover and grain increased significantly as the sludge application rate increased, except for stover under the  $8 \text{ Mg ha}^{-1} \text{ yr}^{-1}$  dryland maize, which was not significantly different compared with the zero control. The concentrations in the plant tissue, however, remained below phytotoxic levels ( $>10 \text{ mg kg}^{-1}$ ) (Fig. 6.3c). Nickel concentration in the grain accounted for 14 to 22% of uptake at lower sludge application rates of 0 and  $8 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ , and 9 to 14% at  $16 \text{ Mg sludge ha}^{-1}\text{yr}^{-1}$ . This indicates that Ni has relatively lower mobility within the plant system than Zn and Cd.

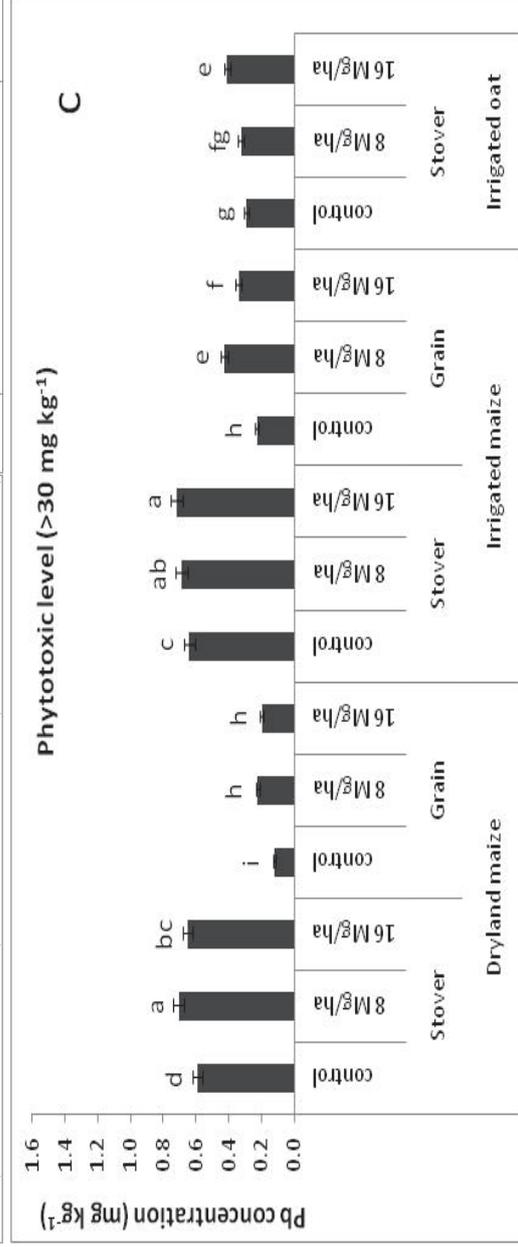
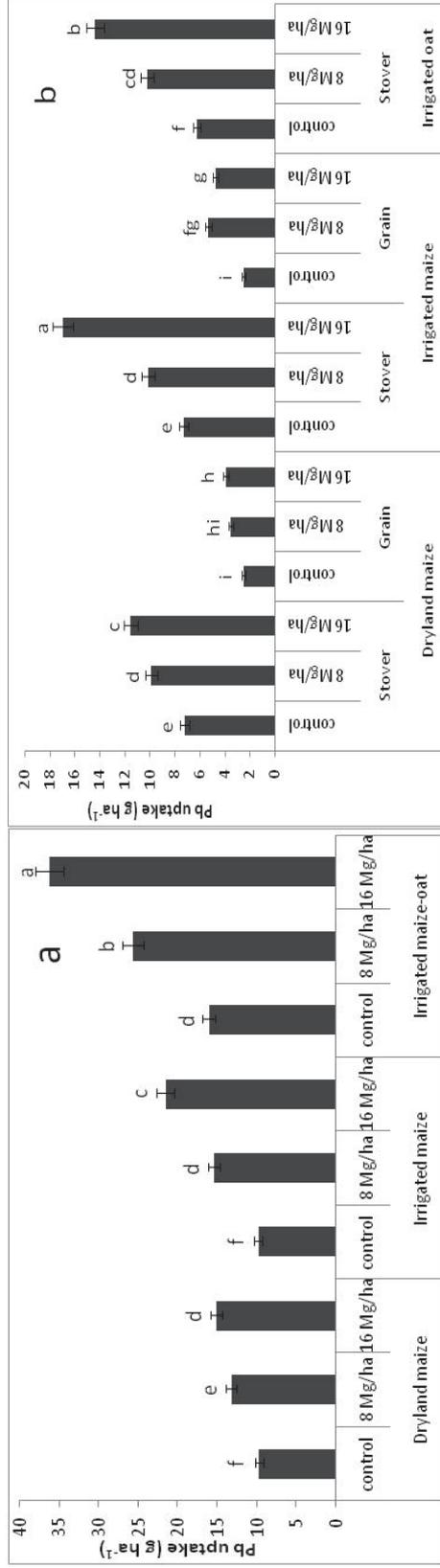


**Figure 6.3 Total crop nickel uptake by dryland maize and irrigated maize and irrigated maize-oat rotation (a), and nickel uptake by maize stover vs. grain (b) as well as concentration of nickel in stover and grain of dryland maize and irrigated maize-oat rotation (c) planted to a clay loam Hutton soil treated with municipal sludge at varying rates for seven years**

#### **6.3.1.4 Lead (Pb)**

Crop uptake of Pb increased significantly as sludge application rate increased (Fig. 6.4a). Similar to Zn, Cd and Ni, this is mainly attributed to the increase in the amount of Pb added to the soil with the sludge. The reduction in soil pH as the sludge application rate increased (Table 6.7) could have also contributed to such increase in Pb uptake because heavy metal availability increases as soil pH drops below 7 (Kalbitz and Wennrich, 1998). It was interesting to note that the annual aboveground biomass Pb uptake by irrigated maize was significantly higher than for dryland maize treatments receiving the same amount of sludge. This is despite the application of only half the annual sludge application at planting of the irrigated maize, in contrast to the full application for dryland maize. The annual crop Pb uptake by the irrigated maize-oat rotation was more than double that of dryland maize. Similar to Ni, the uptake of Pb by maize was influenced by the availability of water. Thus hypothesis 2 was also accepted for Pb. Generally, Pb uptake by stover was significantly higher than grain uptake, both for dryland maize and the irrigated maize-oat rotation (Fig. 6.4b). Similarly, both stover and grain Pb uptake increased significantly as the sludge application rate increased for both cropping systems.

The amount of Pb in the grain accounted for 20 to 29% of the total Pb stored in the aboveground biomass for the treatments that received sludge rates of 8 and 16 Mg ha<sup>-1</sup> yr<sup>-1</sup>. This indicates that Pb has relatively moderate mobility within the plant system. The parallel increase in Pb uptake as the sludge application rate increased is a good indication of the potential accumulation that could lead to phytotoxicity. Nonetheless, the concentration of Pb in plant tissues following 7 years of municipal sludge application was far below phytotoxic levels (>30 mg kg<sup>-1</sup>) (Fig. 6.4c).



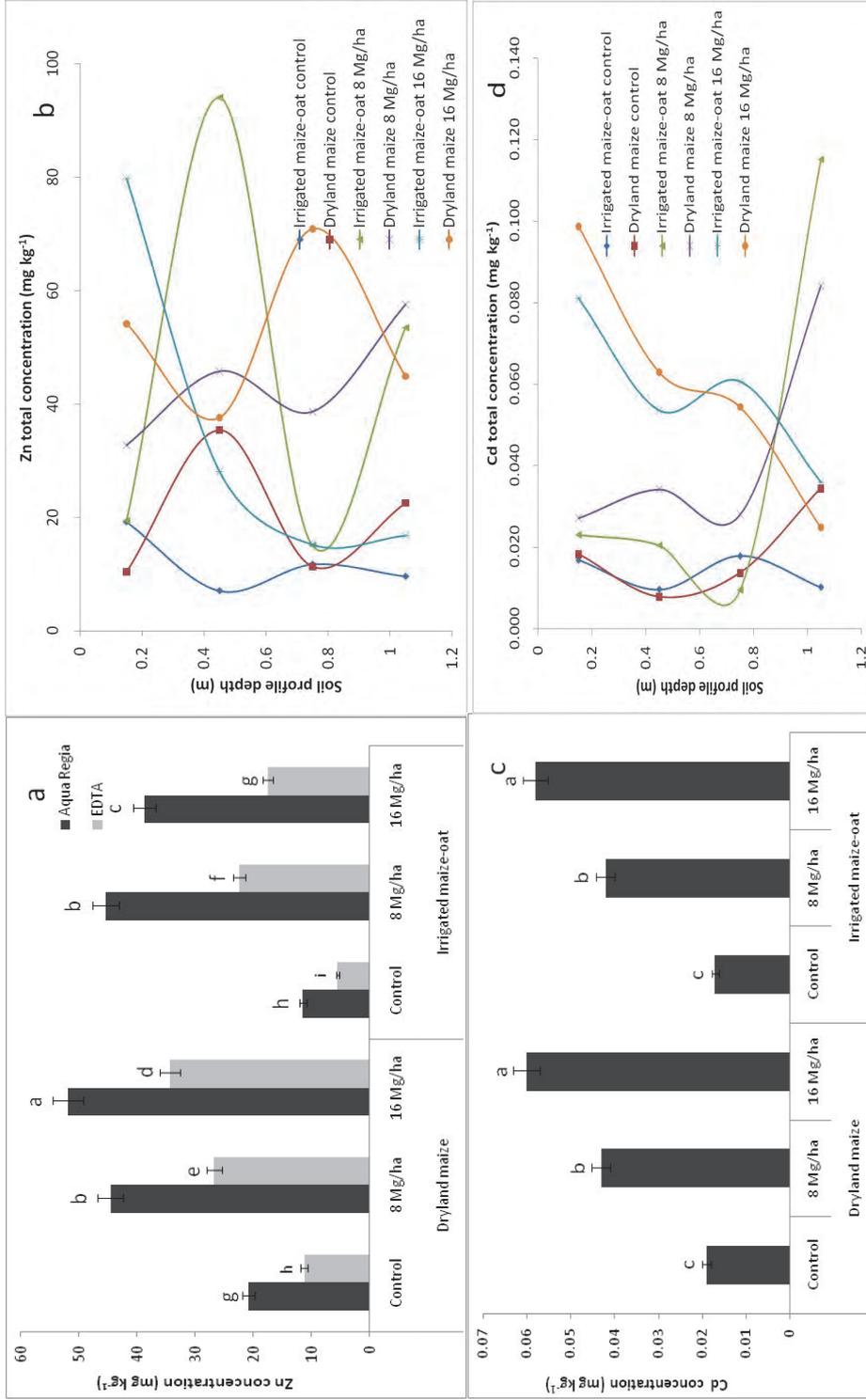
**Figure 6.4** Total crop lead uptake by dryland maize and irrigated maize-oat rotation (a), and lead uptake by maize stover vs. grain (b) as well as concentration of lead in stover and grain of dryland maize and irrigated maize-oat rotation (c) planted to a clay loam Hutton soil treated with municipal sludge at varying rates for seven years.

## 6.3.2 Heavy Metal Accumulation and Mobility in the Root Zone

### 6.3.2.1 Zinc (Zn)

The mean soil profile Zn concentration under dryland maize increased significantly as sludge application rate increased (Fig. 5a). Under irrigated maize-oat, however, the mean soil profile concentration of the 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> was lower than that of 8 Mg ha<sup>-1</sup> yr<sup>-1</sup>. This is most probably because of a higher biomass production from the 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> (20% higher) than for the 8 Mg ha<sup>-1</sup> yr<sup>-1</sup> treatment (Tesfamariam, 2009) during the past six years, which might have resulted in higher plant uptake. Generally there was no clear pattern of Zn translocation (leaching) to deeper layers as a function of sludge application rate, but the general pattern seemed to follow a sinusoidal curve, except for the irrigated 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> treatment, which had a sigmoidal pattern with high concentrations in the top 0.3 m layer (Fig. 6.5b). Nonetheless, there is a clear indication of Zn translocation to lower layers, which increased as sludge application rate increased, except for the irrigated 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> treatment. This is in agreement with previous findings of Hinesly et al. (1978); Boswell (1975); and Sidle and Kardos (1977), who all report the movement of Zn below the depth of incorporation in agricultural lands. In contrast, Ippolito and Barbarick (2008) did not find Zn mobility below 20 cm under dryland wheat production on a plat-ner loam soil, which received sludge at rates of 0, 6.7, 13.4, 26.8 and 40.3 dry Mg ha<sup>-1</sup> every 2 years from 1982 to 2002. The absence of Zn mobility below 20 cm in the Ippolito and Barbarick (2008) study, is most probably attributed to the low rainfall of the study site (350 mm) compared with our study site, which has a long-term annual rainfall of 700 mm. It was apparent that Zn distribution in the soil profile (Fig. 6.5a) seems to have similar patterns to that of soil organic matter (Table 6.7), which agrees with the findings of Antoniadis and Alloway (2002), who report a direct relationship between organic matter and Zn concentration in sludge amended soils.

The overall concentration of Zn in the soil profile of all treatments was still far below the total investigative level (185 mg kg<sup>-1</sup>) of the South African sludge guideline (Table 6.5) and international guidelines for maximum permissible metal concentration in agricultural soils (Table 6.6). However, the increase in Zn concentration by 250% following 7 years of 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> sludge applications indicate the potential for future build up.



**Figure 6.5 Mean soil profile total (Aqua Regia extractable) and plant available (Ethylenediaminetetraacetic acid extractable) concentrations of zinc (a) and cadmium (c) as well as mean soil profile total (Aqua Regia extractable) concentrations of zinc (b) and cadmium (d), distribution in the top 1.2 m layer of a clay loam Hutton soil treated with class A1a sludge for seven years (Plant available (Ethylenediaminetetraacetic acid extractable) fraction of Cadmium was below the method detection limit <1 mg kg<sup>-1</sup>)**

A large fraction of the total Zn for both dryland maize and irrigated maize-oat rotation was EDTA extractable or plant available. The water soluble fraction was, however, well below 1% of the total concentration throughout the profile, indicating that water soluble Zn was not the main contributor to the translocation of heavy metals. Therefore hypothesis 1, “Continuous use of good quality sludge with low heavy metal content will not result in a significant accumulation of water soluble heavy metal fraction in the short term” was accepted.

### 6.3.2.2 Cadmium (Cd)

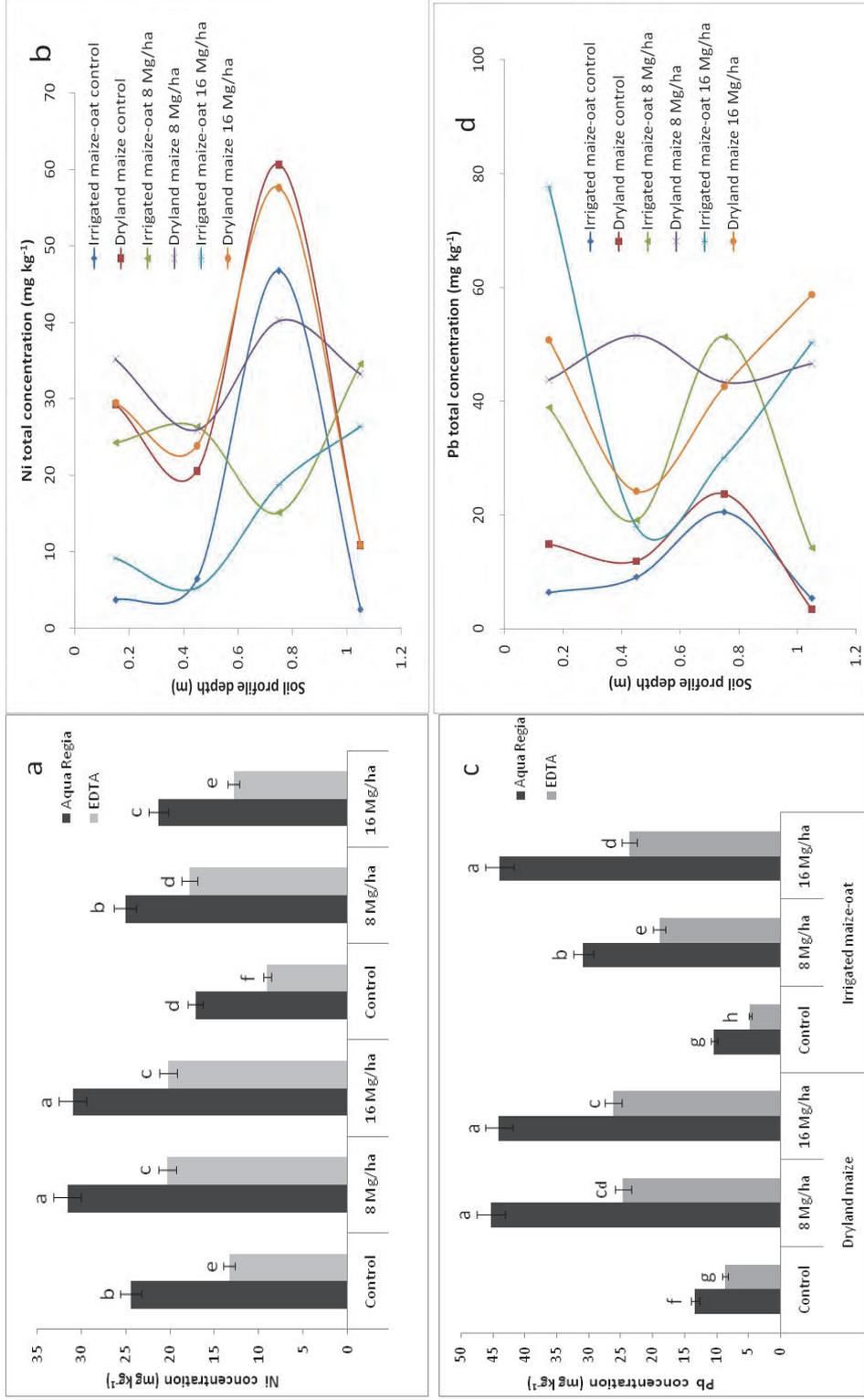
The mean Cd concentration in the soil profile of both dryland maize and the irrigated maize-oat rotation system, increased significantly as the sludge application rate increased (Fig. 6.5c). Similar findings were reported by Baveye et al. (1999) on a liquid sludge treated silt loam soil, where the total concentration of Cd increased as sludge application rate increased. There was, however, no significant difference between dryland maize and irrigated maize-oats that received the same sludge application rates. It was also interesting to note that most of the Cd for the 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> dryland maize and irrigated maize-oat rotation accumulated in the top 60 cm layer and decreased with depth (Fig. 6.5d). This agrees with findings of Baveye et al. (1999), who report Cd mobility to a depth of 75 cm, which also decreased with depth. In contrast, relatively high concentrations of Cd accumulated down to 1 m for the 8 Mg ha<sup>-1</sup> yr<sup>-1</sup> of both cropping systems. The distribution of Cd in the top 0.3 m layer and 0.9-1.2 m soil layer (Fig. 6.5d) followed similar patterns to soil organic C and pH (H<sub>2</sub>O) of the corresponding layers (Table 6.7). This too is in agreement with the findings of Antoniadis and Alloway (2002), who report an increase in the mobility and plant availability of Cd at high sludge application rates because of the increase in dissolved organic matter.

The concentration of Cd in the whole profile of both cropping systems, however, was far below the total investigative level (2 mg kg<sup>-1</sup>) of the South African sludge guideline (Table 6.5), guidelines from other regions of the world (1-20 mg kg<sup>-1</sup>) (Table 6.6), and the global soil mean Cd concentration of 0.6-1.1 mg kg<sup>-1</sup> (Kabata-Pendias and Pendias, 2000). The EDTA extractable and saturated paste extractable (mobile) Cd fraction in the soil profile of both cropping systems was below the method detection limit (<1 mg kg<sup>-1</sup>). This is in contrast to the findings of Baveye et al. (1999), who reported an increase in the DTPA extractable Cd in the top 45 cm soil layer. This indicates that the excess accumulated Cd was complexed either with soil minerals or organic matter within the soil. Therefore, hypothesis 1 was accepted for both cropping systems.

### 6.3.2.3 Nickel (Ni)

Nickel accumulation in the soil profile did not increase with doubling of the 8 Mg ha<sup>-1</sup>yr<sup>-1</sup> norm, both under dryland maize and in the irrigated maize-oat rotation (Fig. 6.6a). This is in contrast with the patterns observed for Zn and Cd. It was also interesting to note that the mean soil profile Ni concentration of dryland maize was significantly higher than the same irrigated treatments. This is most probably because of higher plant uptake (Fig. 6.3a) and potential leaching below 1.2 m under irrigation because Ni in sewage sludge is mainly in soluble form and is readily available for plant uptake as well as leaching (Kabata-Pendias and Pendias, 2000). The concentration of Ni in the whole profile of both cropping systems, however, is far below the total investigative level (50 mg kg<sup>-1</sup>) of the South African sludge guideline (Table 5) as well as other international guidelines (Table 6.6).

The increasing Ni concentration towards the bottom of the soil profile (Fig. 6.6b), under the irrigated 8 and 16 Mg ha<sup>-1</sup> treatments provides evidence for possible leaching below the point of measurement (1.2 m) because of the mobile nature of Ni as reported by Snyman and Van Der Waals (2004). According to Snyman and Van Der Waals (2004) heavy metals such as Ni leached 8 cm below the plough layer in a short time and suggest that there is a risk of these metals moving below the incorporation zone. Unlike Zn and Cd, water-soluble Ni was detected at low concentration levels ( $\leq 1\%$  of the EDTA extractable fraction). Therefore, hypothesis 1 was accepted for Ni. In addition, considering the low soil profile Ni concentration and the increase in Ni concentration with depth under irrigated conditions, hypothesis 2 is also accepted for Ni.



**Figure 6.6 Mean soil profile total (Aqua Regia extractable) and plant available (Ethylenediaminetetraacetic acid extractable) concentrations of nickel (a), and lead (c) as well as mean soil profile total (Aqua Regia extractable) nickel (b) and lead (d) distribution in the top 1.2 m soil profile of a clay loam Hutton soil treated with class A1a sludge for seven years.**

#### 6.3.2.4 Lead (Pb)

Generally the mean Pb concentration in the soil profile of dryland maize was significantly higher than under irrigation, except for the 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> sludge treatment (Fig. 6.6c). Under irrigated system soil profile Pb concentration increased significantly as sludge application rate increased, which was not the case for the dryland system. A large fraction of the Pb in the soil profile (46 to 79%) was plant-available (EDTA extractable), but the water-soluble fraction was below the method detection limit (<1 mg kg<sup>-1</sup>). Consequently, hypothesis 1 was accepted for both dryland and irrigated maize-oat rotation.

Lead concentration in the soil profile of the zero control treatment remained the lowest throughout the profile (Fig. 6.6d), while the irrigated as well as dryland maize production systems that received 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> sludge annually showed an increase in Pb concentration below 0.6 m. This indicates the potential leaching losses that might have occurred during the study period and could probably be the reason for the reported insignificant difference in soil profile concentration between the 8 and 16 Mg ha<sup>-1</sup>yr<sup>-1</sup> treatments under dryland maize production. The distribution of Pb in the top 0.3 m of the soil profile and between 0.6-0.9 m (Fig. 6.6d) followed similar patterns to soil organic C (Table 6.7). Previous studies conducted by Baveye et al. (1999) also report significant mobility of Pb in their case, to a depth of 45 cm. The overall concentration of Pb is, however, below the total investigative level (56 mg kg<sup>-1</sup>) as stipulated in the South African sludge guideline (Table 6.5) as well as those from other countries (Table 6.6).

The mean soil profile Pb concentration of the 16 Mg ha<sup>-1</sup>yr<sup>-1</sup> sludge treatments for dryland maize and irrigated maize-oat rotation increased by 30.56 and 32.06 mg kg<sup>-1</sup>, respectively after 7 consecutive years of sludge application. Assuming negligible leaching and constant sludge heavy metal content, annual sludge application rate of 16 Mg ha<sup>-1</sup> yr<sup>-1</sup> could raise soil Zn concentration of the study site to total maximum threshold levels after 20, 30 and 145 years, according to the South African (Snyman and Herselman, 2006), European (McLaughlin et al., 2000), and USA (US EPA, 1995) guidelines, respectively. Similar application rates would raise soil Cd concentration to TMT levels after 86 years according to South African and European guidelines, and 580 years according to USA guideline. Nickel could reach to TMT levels after 370, 140 and 550 years, and Pb after 330, 1100 and 525 years according to the South African, European, and USA guidelines, respectively. Nevertheless, the potential for leaching observed from this study warrants monitoring protocols that take into account pollutant distribution within a soil profile over time.

#### 6.3.3 Heavy Metal Mass Balance (Supply minus Uptake Mass Balance)

Heavy metal mass balance based on sludge input less crop output is not the full story because there are other sources and sinks for these metals, in particular losses through leaching. Mass balance was calculated by subtracting the metal exported (crop uptake) from the total applied in sludge.

According to a supply minus uptake mass balance of a single year (2010/11), Zn uptake by crops accounted for only 3 to 5% of what was added with sludge (Table 6.8). This indicates that more than 95% of Zn added with sludge should accumulate in the soil profile. This is in agreement with findings of Chang et al. (1984), who report a significant accumulation of Zn in the soil profile of sludge amended soils. The negative mass balance of the zero control

treatment indicates that the crop used Zn from the soil reserve. Similar to Zn, based on the mass balance of Cd applied with sludge less that removed by crop, only 3 to 6% of what was added with the sludge was taken up by the crop under both cropping systems (Table 6.8). This was the reason for the significant build-up of Cd observed in the soil profile as the sludge application rate was doubled (Fig. 6.5c).

Based on the mass balance of Ni added with sludge less uptake (removed) by crop, there was a net positive Ni accumulation in the profile of both dryland maize and irrigated maize-oat rotation (Table 6.8). Of the total Ni added within a year, only 4.5 to 5.5% of the Ni was recovered by the plant. The rest either accumulated in the soil profile or leached below the depth of measurement. Similar to Zn and Cd, the net positive Ni mass balance highlights future potential accumulation in the soil profile and warrants setting monitoring protocols.

Based on the mass balance of Pb added with sludge less uptake by dryland maize and irrigated maize-oats, sludge application resulted in a net positive mass balance indicating a potential build-up of Pb in the soil though at a low rate (Table 8). According to this study, only 2 to 5% of the total Pb added to the soil was taken up by the plant with, the rest mostly accumulating in the soil profile. This provides evidence for possible accumulation or binding of Pb in sludge-amended soils as reported by Planquart et al. (1999). According to Planquart et al. (1999) most of the Pb in sludge amended soil was found as an organic matter bound fraction.

Therefore, it is of utmost importance to have integrated management and monitoring protocols for beneficial agricultural use of sludge in order to minimize potential long-term risks to human health and the environment in general.

**Table 6.8 Mass balances of Zn, Cd, Ni and Pb under dryland maize and irrigated maize-oat rotation for the growing season of 2010/11.**

Element	Sludge application		Metal Uptake		Metal Supply minus uptake	
	Rate	Metal Supply	Dryland	Irrigated	Dryland	Irrigated
	<b>Mg ha<sup>-1</sup></b>		<b>kg ha<sup>-1</sup></b>			
<b>Zn</b>	0	0	0.8482	0.4101	-0.8482	-0.4101
	8	46.04	1.1969	0.9049	44.843	45.135
	16	92.08	1.4861	1.4012	90.593	90.678
<b>Cd</b>	0	0	0.0005	0.0012	-0.0005	-0.0012
	8	0.086	0.0016	0.0017	0.0844	0.0843
	16	0.172	0.0018	0.0029	0.1702	0.1691
<b>Ni</b>	0	0	0.0279	0.0200	-0.0279	-0.0200
	8	0.826	0.0395	0.0370	0.7865	0.789
	16	1.652	0.0788	0.0970	1.5732	1.555
<b>Pb</b>	0	0	0.0085	0.0101	-0.0085	-0.0101
	8	0.533	0.0128	0.0141	0.5202	0.5189
	16	1.067	0.0158	0.0226	1.0512	1.0444

#### 6.4 CONCLUSION

Crop uptake and accumulation in the soil profile of Zn, Cd, Ni and Pb increased as the sludge application rate increased. Concentrations in tissues of the test crop remained well below phytotoxic levels, except for Zn under dryland maize production that received sludge at 16 Mg ha<sup>-1</sup> yr<sup>-1</sup>. Concentrations of the selected pollutants in the soil profile of all sludge treatments remained below threshold levels as stipulated in the South African sludge guideline as well as international guidelines. A large fraction of these metals was EDTA extractable. The saturated paste extractable fractions of Cd and Pb were <1 mg kg<sup>-1</sup>. However, water soluble fractions of Zn and Ni were detected though <1% of the EDTA extractable fraction, indicating the mobile nature of these elements and potential for leaching and groundwater contamination. Consequently, hypotheses 1 and 3 were accepted for the metals studied and hypothesis 2 was rejected for Zn. Therefore, it is of utmost importance to have integrated sludge management practices and rigorous heavy metal monitoring protocols below the top 0.3 m plough layer for sustainable beneficial agricultural use of sludge. Further investigation on metal leaching below the active root zone is recommended.

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## **PART II Computer Modelling**

## CHAPTER 7 – USING THE SWB-SCI MODEL TO GENERATE GENERIC ANNUAL N RELEASE FROM SLUDGE AMENDED SOILS

### 7.1 INTRODUCTION

Beneficial use of sewage sludge on agricultural lands is a very well-known practice around the world. The benefits include; a source of essential crop nutrients (Muse et al., 1991), improvements in soil structure (Ojeda et al., 2007), and minimization of soil erosion and runoff (Muse et al., 1991). A large fraction of the N in sewage sludge is in organic form. Plants, however, utilize N in the form of  $\text{NH}_4$  and  $\text{NO}_3$ . The availability of N for plant uptake primarily depends on the rate of mineralization of the sludge (Kelley et al., 1984) and the subsequent losses through volatilization, denitrification, and leaching. In order to determine the amount of N that will be available for crop uptake from sludge amended soil within a growing season, it is essential to know the N mineralization rate of the sludge.

Nitrogen mineralization is a biological process which involves the transformation of N from its organic state to inorganic forms of  $\text{NH}_4^+$  or  $\text{NH}_3$  by heterotrophic soil organisms (Jansson and Persson, 1982). Therefore, any abiotic factor that influences the microbial activity has a direct effect on N mineralization (Terry et al., 1981; Serna and Pomers, 1992; Jarvis et al., 1993; Guntinas, et al., 2012). The dominant abiotic factors that influence microbial activity and therefore N mineralization include: climatic factors especially rainfall and temperature (Terry et al., 1981; Sierra, 1997; Wang et al., 2003; Van Niekerk et al., 2005), edaphic factors (soil porosity and pH) (Carlyle et al., 1990) and agronomic activities such as tillage (Hernandez et al., 2002; Snyman and Van der Waals, 2004; Zaman and Chang, 2004).

Several models have been developed to quantitatively describe the interactive effects of the various abiotic factors on N mineralization (Manzoni and Porporato, 2009) at various time scales of hourly to decades (Austin et al., 2004; Schwinning and Sala, 2004; Richter and Markewitz, 2001). Some of these models have been tested using field data sets (Smith et al., 1997; Zhang et al., 2008; Moorhead et al., 1999) and used as decision support tools for crop production and investigation of environmental impacts (Li et al., 2009).

The need for decision support tools is becoming quite imminent due to the ever increasing concerns of environmental pollution associated with the use of organic and inorganic fertilizers. Consequently models such as AmaizeN, APSIM, and DSSAT have been used as decision support tools for irrigation scheduling, fertilizer recommendations and environmental impact assessments (Li et al., 2009). Other decision support systems such as MANure Nitrogen Evaluation Routine (MANNER) were developed to take account of manure N analysis, ammonia volatilization, nitrate leaching and mineralization of organic N (MAFF, 1999).

During the late 1990s, a simple Sludge Land-Application Decision-Support Software (SLADS) was developed to provide sludge application recommendation for a range of crops (Water Research Commission, 1997). This simple model helped to set a benchmark. The model, however, used a single annual N mineralization rate for all sludge types across all regions failing to consider the effect of water availability, temperature, cropping intensity, and agronomic management practices on sludge application rate recommendations. Considering the wide annual rainfall distribution across South African agro-ecological zones ranging from

<200mm in the desert to >1000mm in Super humid zone, using a single annual N release rate across agro-ecological zones could compromise crop production, or the environment or both. Therefore, a mechanistic crop and nutrient model was sought in order to investigate the interactive effect across abiotic factors on N mineralization from sludge-amended soils to generate a generic N mineralization rates across a combination of soils and locations within and between agro-ecological zones. Mechanistic models represent our current best understanding of physical, chemical and biological processes and interaction and are a synthesis of knowledge gained from years of research and experience (Ma et al., 2000). The SWB-Sci model, which has been locally tested for various cropping systems planted to municipal sludge amended soils (Tesfamariam, 2009) was considered for this study. The SWB-Sci model is a mechanistic soil-water balance (Annandale et al., 1996), crop growth/irrigation scheduling (Annandale et al., 2000, 2003), N (Tesfamariam, 2009) and P (Van der Laan, 2010) model.

The objective of this study was to investigate if a single annual N percentage release rate could be used across sites within an agro-ecological zone. To achieve this objective the following hypotheses were tested using the SWB-Sci model: under dryland cropping, cumulative annual N mineralization from sludge in sludge amended soils: 1) will vary significantly across agro-ecological zones but not between sites within an agro-ecological zone 2) will not vary significantly between and within seasons at a specific site except for few anomalous seasons, and 3) will not vary significantly across soil textures within a site.

## 7.2 MATERIALS AND METHODS

### 7.2.1 Model Description

The SWB-Sci model is a mechanistic crop growth, irrigation scheduling, salt N and P balance model. It is a one-dimensional, daily time step generic model that uses soil, weather and crop units to mechanistically carry out crop growth, soil water and salt balance as well as nitrogen cycle simulations. Details of the crop growth and irrigation scheduling modules of the SWB-Sci model can be found in Annandale et al. (2000). The Nitrogen module of the SWB-Sci model follows similar approaches to that of the Cropping Systems Simulation Model (CropSyst) (Stöckle et al., 2003). The nitrogen balance in SWB-Sci module includes nitrogen transformation (mineralization, nitrification, denitrification, and ammonia volatilization), ammonium sorption, nitrogen transport and crop nitrogen uptake. SWB-Sci simulates nitrogen mineralization indirectly from C-decomposition using first order kinetics as presented in equation 1. Net N mineralization is then computed using equation 2.

$$\text{Carbon decomposition (kg)} = C_{\text{res}} * CF * [1 - \exp^{(-k * TF)}] * WF \quad (1)$$

Where

$C_{\text{res}}$  – is carbon mass in residue or manure (kg)

CF – is residue or manure contact fraction (from literature)

K – is residue or manure decomposition constant

TF – is soil temperature function

WF – is soil water function

$$\text{Net N mineralization} = (1/\text{CN ratio}_{\text{decomp}} - C_{\text{trans}}/\text{CN ratio}_{\text{pool}}) * C_{\text{decomp}} \quad (2)$$

Where

CN ratio<sub>decomp</sub> – is CN ratio of the decomposition pool

C<sub>trans</sub> – is carbon fraction transferred from the decomposing pool to another pool

CN ratio<sub>pool</sub> – is the CN ratio of the receiving pool

C<sub>decomp</sub> – is carbon decomposition

The model simulates ammonium sorption using the approach presented by Stöckle and Campbell (1989) while symbiotic N fixation is simulated after the approaches of Bouniols et al. (1991). Crop nitrogen uptake is modelled using a modified version of the Godwin and Jones (1991) approach where crop nitrogen uptake is determined as the minimum of crop nitrogen demand and potential nitrogen uptake (Stöckle, 1994). A detailed description of the N module including the major nitrogen transformation processes can be found in Stöckle et al. (2003).

## 7.2.2 Model Parameterization

### 7.2.2.1 Soil

Four major soil textural classes (clay, clay loam, sandy clay loam, and sandy loam) were selected to investigate the effect of soil texture on N mineralization from sludge amended soils. Selected physical and chemical properties of the four soil textural class used for model simulation are presented in Table 7.1.

**Table 7.1 Selected soil physical and chemical characteristics of the four soil textures used for model scenario simulations**

Soil types	Field capacity (m/m)	Permanent wilting point (m/m)	Bulk density (Mg/m <sup>3</sup> )	Sand (%)	Clay (%)	Organic matter (%)
Clay	0.479	0.348	1.207	20	60	2.8
Clay loam	0.328	0.189	1.314	32	34	2.5
Sandy clay loam	0.255	0.159	1.401	60	27	1.6
Sandy loam	0.196	0.089	1.557	65	10	1.5

### 7.2.2.2 Sludge

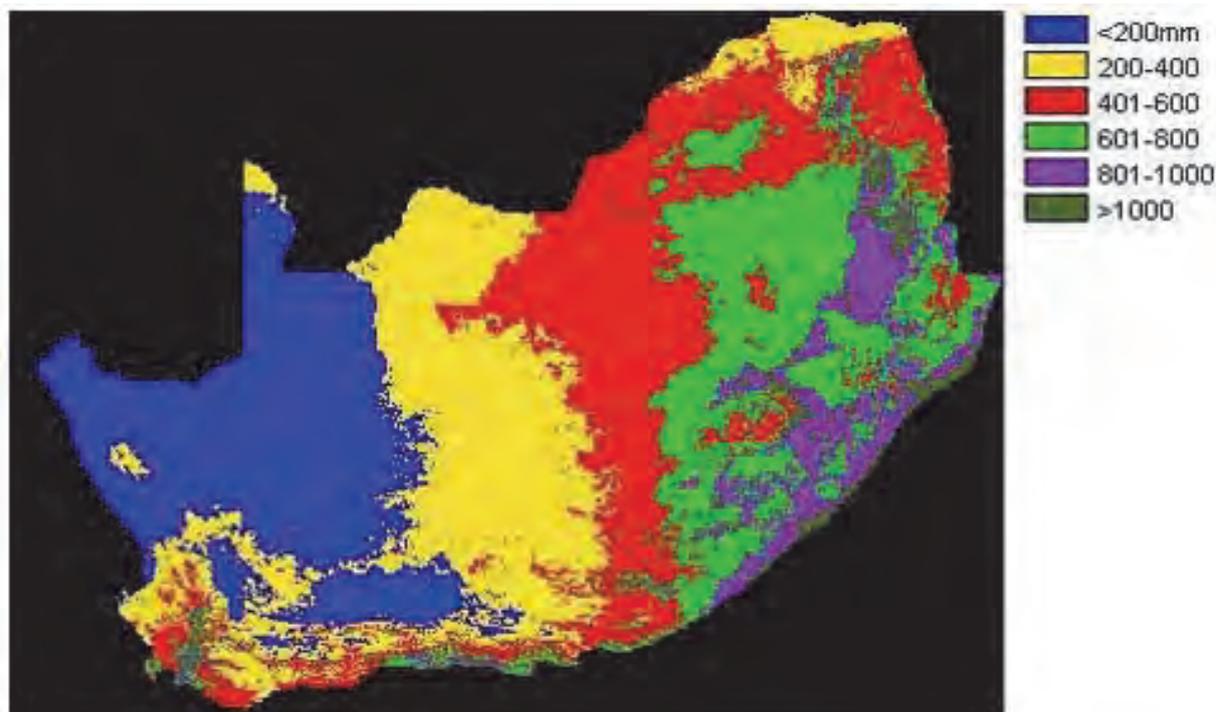
The sludge used for simulation in this study was anaerobically digested sludge, and dried on conventional concrete beds. The sludge was digested to 33% VSS destruction under mesophilic conditions. The retention time was 15 days in the primary and 2 days in the secondary digesters. Sludge properties required for model parameterization to run scenario simulations are presented in Table 7.2. The amount of sludge used as input for the SWB-Sci model to run scenario simulations was 10 t ha<sup>-1</sup>.

**Table 7.2 Selected properties of the anaerobically digested sludge used for model parameterization**

Sludge parameter	Units	Value
C	%	17
Total N	%	2.81
NH <sub>4</sub>	%	0.264
NO <sub>3</sub>	%	0.051
P	%	3.02
pH (H <sub>2</sub> O)	NA	5.86
Water content	%	30
Fast cycling fraction	kg kg <sup>-1</sup>	0.3
Slow cycling fraction	kg kg <sup>-1</sup>	0.3
Fast cycling half-life	Days	3
Slow cycling half-life	Days	60
C:N ratio	kg kg <sup>-1</sup>	8

### 7.2.2.3 Study site

Scenario simulations were run using the SWB-Sci model for five (arid, semi-arid, sub-humid, humid, super-humid) of the six major agro-ecological zones of South Africa (Fig. 7.1) (Table 7.3) to establish a generic N release rate. The sixth agro-ecological, desert, was excluded because water is limiting for crop production. Depending on the availability of weather data three representative cities were selected from each agro-ecological zone, except for arid (two cities) and super humid (one city). A long-term measured weather record for the selected sites within an agro-ecological zone were obtained from the South African Weather Bureau for the year 1993-2013 except for two cities, Nelspruit and Port Alfred, where data was only available for the years 2002-2013. The annual rainfall amount (1993-2013) of the selected sites for the five agro-ecological zones are presented in Table 7.4.



**Figure 7.1 Agro ecological zones of South Africa (Source: ARC-ISCW, 2004)**

**Table 7.3 The six agro-ecological zones of South Africa with typical representative cities (ARC-ISCW, 2004).**

Agro-ecological zone	Annual rainfall (mm)	Selected sites
Desert	< 200	Upington, Hopetown
Arid	200-400	Springbok, and Kimberley
Semi-arid	401-600	Bloemfontein, Rustenburg, and Polokwane
Sub-humid	601-800	Johannesburg, Port Alfred, and Bethlehem
Humid	801-1000	Durban, East London, and Cape town
Super-humid	>1000	Nelspruit

**Table 7.4 Twenty year (1993-2013) measured annual rainfall (mm) of selected sites in South Africa.**

Zone	Site	93	94	95	96	97	98	99	00	01	02	03	04	05	06	07	08	09	10	11	12	13
Arid	Kimberley	298	340	310	287	298	356	370	310	320	236	196	280	170	392	340	390	247	286	320	340	298
	Springbok	245	280	221	240	198	208	260	212	225	193	131	138	245	304	283	256	251	122	214	248	198
Semi-arid	Polokwane	296	401	487	401	346	401	298	386	272	478	223	388	341	513	341	420	389	480	481	421	457
	Rustenburg	496	520	440	521	489	521	389	491	435	585	405	440	435	585	305	440	474	490	398	480	443
Sub-humid	Bloemfontein	520	581	430	490	501	321	398	473	505	477	440	510	440	390	400	510	580	510	512	583	482
	Bethlehem	696	646	701	709	687	698	723	781	791	659	677	634	755	705	577	763	773	886	812	790	778
Humid	Johannesburg	740	748	798	810	830	801	890	910	840	666	539	861	619	726	688	800	958	981	890	910	878
	Port Alfred	-	-	-	-	-	-	-	-	-	636	749	671	574	696	638	944	901	890	689	795	897
Super-humid	Durban	980	864	926	993	920	826	980	946	885	880	620	1004	1049	997	924	896	587	980	876	898	986
	Cape town	712	689	812	765	681	694	745	619	785	844	615	844	917	980	829	926	548	866	709	827	801
	East London	895	864	896	775	793	812	932	873	927	948	627	863	959	918	880	1136	797	789	701	789	811
	Neilspruit	-	-	-	-	-	-	-	-	-	1026	903	964	941	1023	948	1253	977	1029	993	981	1001

### **7.2.3 Model calibration and validation**

The N subroutine of SWB-Sci model was adapted from the CropSyst model. Nitrogen mineralization prediction by CropSyst in response to changes in temperature and water was tested and validated previously by Stöckle and Nelson (1996) and Stöckle and Debaeke (1996). The SWB-Sci model was previously successfully calibrated and validated for N uptake by maize, oats and weeping love grass from municipal sludge amended soils at plot scale (Tesfamariam et al., 2009).

#### **7.2.3.1 Simulated annual Rainfall**

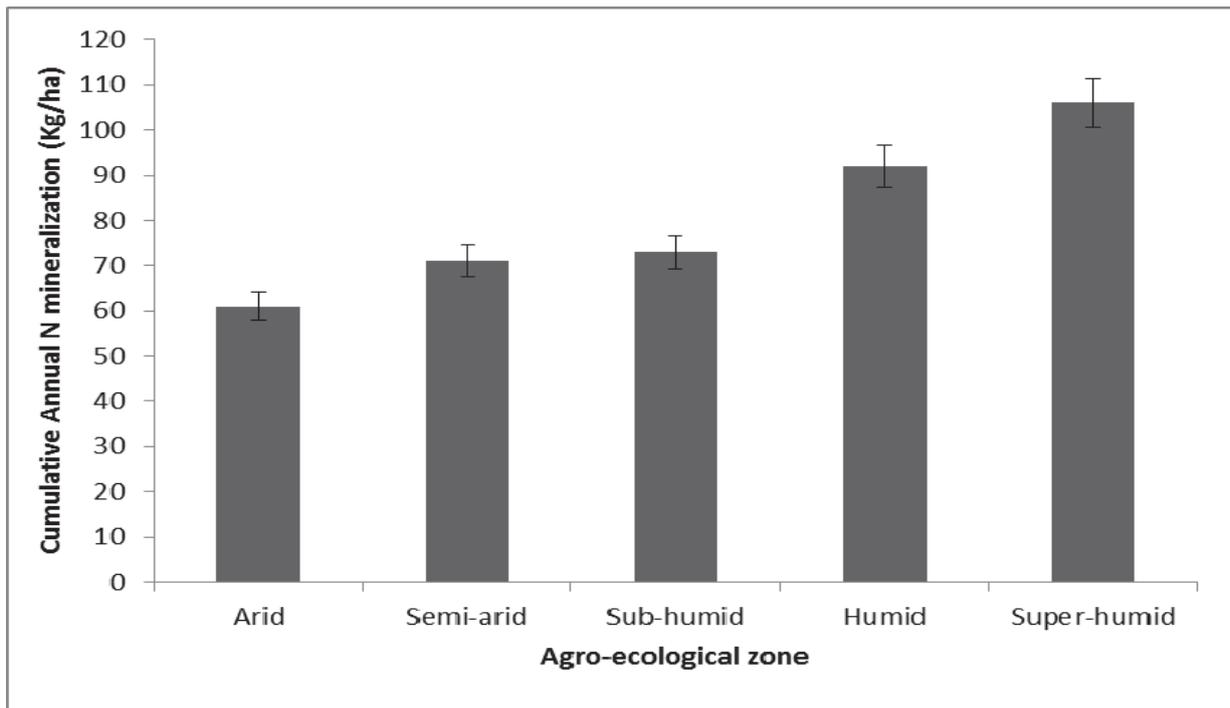
To simulate the effect of rainfall distribution on cumulative annual N mineralization, the measured annual rainfall for selected sites was equally distributed on a weekly basis for the whole rainy season. Model simulations of N mineralization from measured rainfall data was then compared against predictions from simulated rainfall.

### **7.2.4 Simulation and Statistical analysis conducted**

Simulations of more than 40 scenarios were done based on fully factorial combinations of 5 agro-ecological zones, 3 sites per agro-ecological zone (in two zones 2 sites and one zone 1 site), and 4 soil textures. Each scenario was run for 20 years of simulation time. Forty treatment combinations were used having agro-ecological zones, sites, and soil textures as the main effects. The number of years were used as replications except in testing hypothesis 2 (between seasons), where the number of years were used as the main effect. Statistical analyses were done using Analysis of Variance (ANOVA) and General Linear Model (GLM) procedures of Windows SAS version 9.3 (SAS Institute, 2010) on model simulated mineralization values for factorial combinations of 5 zones, 3 sites and 4 soil textures.

## **7.3 RESULTS AND DISCUSSION**

It was apparent from the model simulations that N mineralization from sludge varied significantly across the 5 major South African agro-ecological zones with highest decomposition recorded in the wet regions and lowest in the dry arid areas (Fig. 7.2). Sludge mineralization was relatively higher under super-humid as compared to all the other agro-ecological zones with the annual release rate of 106 kg N ha<sup>-1</sup> within the first year of sludge application.



**Figure 7.2 Model scenario simulations of N mineralization from sludge applied at a rate of 10 Mg ha<sup>-1</sup> per annum to a five agro-ecological zones (values presented are mean of the mineralization from clay, clay loam, sandy clay loam and sandy loam soils).**

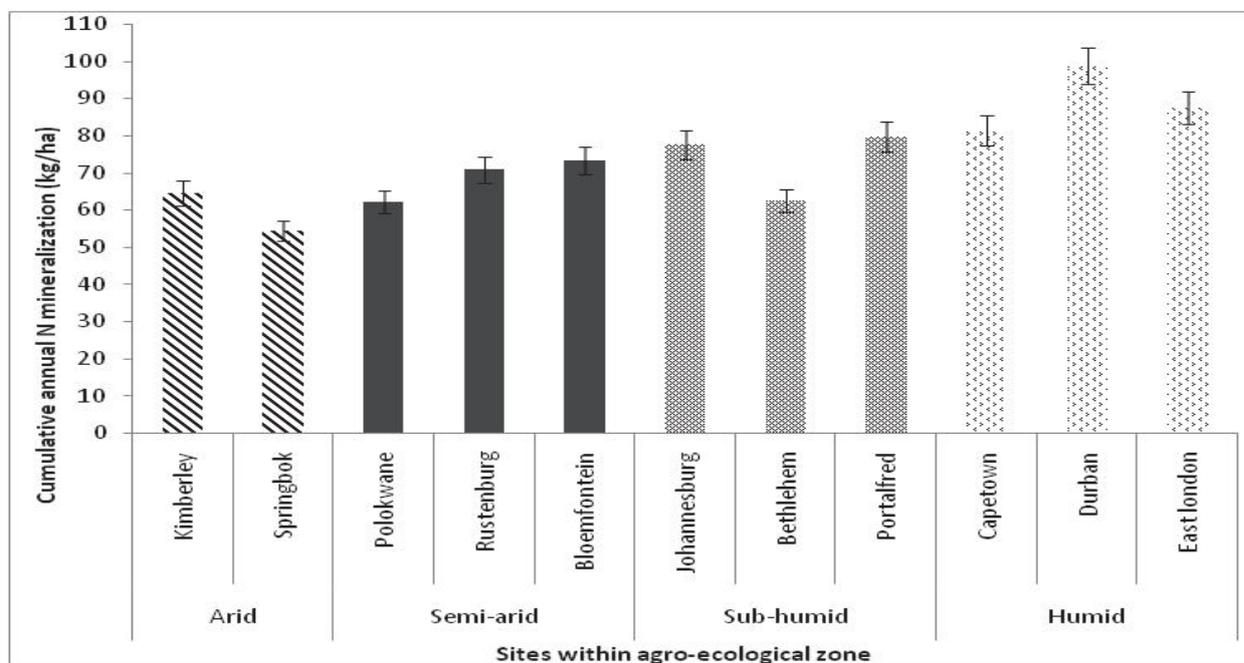
It was apparent from the model simulations that cumulative annual N mineralization during the first year of sludge application varied significantly ( $P < 0.05$ ) between the wet and dry agro-ecological zones of South Africa. This significant variation between the agro-ecological zones was mainly attributed to the variation in rainfall (Table 7.4) because the mean annual rainfall in the wet super-humid zone was 1023 mm while in the dry arid zone was 263 mm rain. This is in contrast to the similarity in the mean annual air temperature (22°C) between these two sites. This indicates that rainfall was the main cause for the variation in N mineralization between these two contrasting sites. This is in agreement with previous findings (Terry et al., 1981; Paul et al., 2003; Nobela, 2011) who reported a direct relationship between N mineralization and soil water availability. The mean cumulative annual N mineralization during the first year of application accounted for 24%, 28%, 29%, 37% and 42% of the organic N applied to arid, semi-arid, sub-humid, humid, and super-humid agro-ecological zones, respectively.

Despite a 69% and 189% increase in annual rainfall under semi-arid and sub-humid zones compared to arid, the cumulative annual N mineralization increased only by 4% and 5%, respectively. This poor response of N mineralization to an increase in rainfall was attributed to a 4-5°C lower temperature in the semi-arid and sub-humid zones, respectively. In contrast, an increase in annual rainfall by 10% (humid compared with sub-humid) and 17% (super-humid compared with humid) resulted in an 8% and 5% increase in N mineralization, respectively. The comparatively higher N mineralization response per rainfall increment in the latter case was mainly attributed to a 3°C and 2°C increase in temperature, respectively. This is in line with previous findings of Tejeda et al (2002) and Guntiñas et al. (2012), who reported a direct relationship between soil temperature and N mineralization.

The highest annual N release rate was recorded under super-humid agro-ecological zone of Nelspruit (42% of organic N applied) was almost double to that of arid (24% of organic N applied). Such variation in N mineralization between agro-ecological zones will have negative implications to the environment or finance, or agricultural production or to all three if fixed annual N release rates are used across agro-ecological zones. For instance, if the commonly recommended 25% release during the first year of application is used in super-humid agro-ecological zone, the amount of sludge needed to satisfy crop N demand will be over-estimated by 200%. The implications are high transport cost, increased nitrate leaching potential, and P build up in the soil profile.

Model simulations of N mineralization from sludge applied at rates of 10 Mg ha<sup>-1</sup> yr<sup>-1</sup> varied significantly across sites within an agro-ecological zone (Fig. 7.3). Under the humid agro-ecological zone, N mineralization within the first year of sludge application varied significantly across sites with the lowest mineralization recorded in Cape Town (29.5%) and highest in Durban (36%). Cumulative annual N mineralization during the first year of sludge application in the sub humid region of Bethlehem and Johannesburg ranged 22% and 28% of the organic N applied, respectively (Fig. 7.3).

Model simulations of N mineralization from sludge applied at the rate of 10 Mg ha<sup>-1</sup> yr<sup>-1</sup> varied significantly across sites within an agro-ecological zone. Such variation was attributed to the difference in rainfall or temperature or both between sites within an agro-ecological zone. For instance, cumulative annual N mineralization was 4% higher in Kimberly than Springbok because rainfall in Kimberly is 82 mm higher. This is despite the mean annual temperature in Springbok being 4°C higher than that of Kimberly.



**Figure 7.3 Model scenario simulations of N mineralization across selected sites within five agro-ecological zones of sludge application at the rate of 10 Mg ha<sup>-1</sup> per annum on a sandy clay loam soil.**

In a similar manner, under the semi-arid agro-ecological zone, cumulative annual N mineralization in Rustenburg was 3% higher than in Polokwane despite similar mean annual air temperature. The difference was mainly attributed to a 75 mm higher rainfall in Rustenburg compared with Polokwane. These findings agree with the findings of Li et al. (2014). According to Li. et al. (2014), N mineralization increased significantly as the water filled porosity increased from 20% to 40%. These authors further reported that further increase in the water filled porosity from 40% to 60% also increased N mineralization, though not statistically significant. Other studies conducted by Guntinas et al (2012) also reported an increase in N mineralization as the soil moisture level increased from 40% to 100% of field capacity.

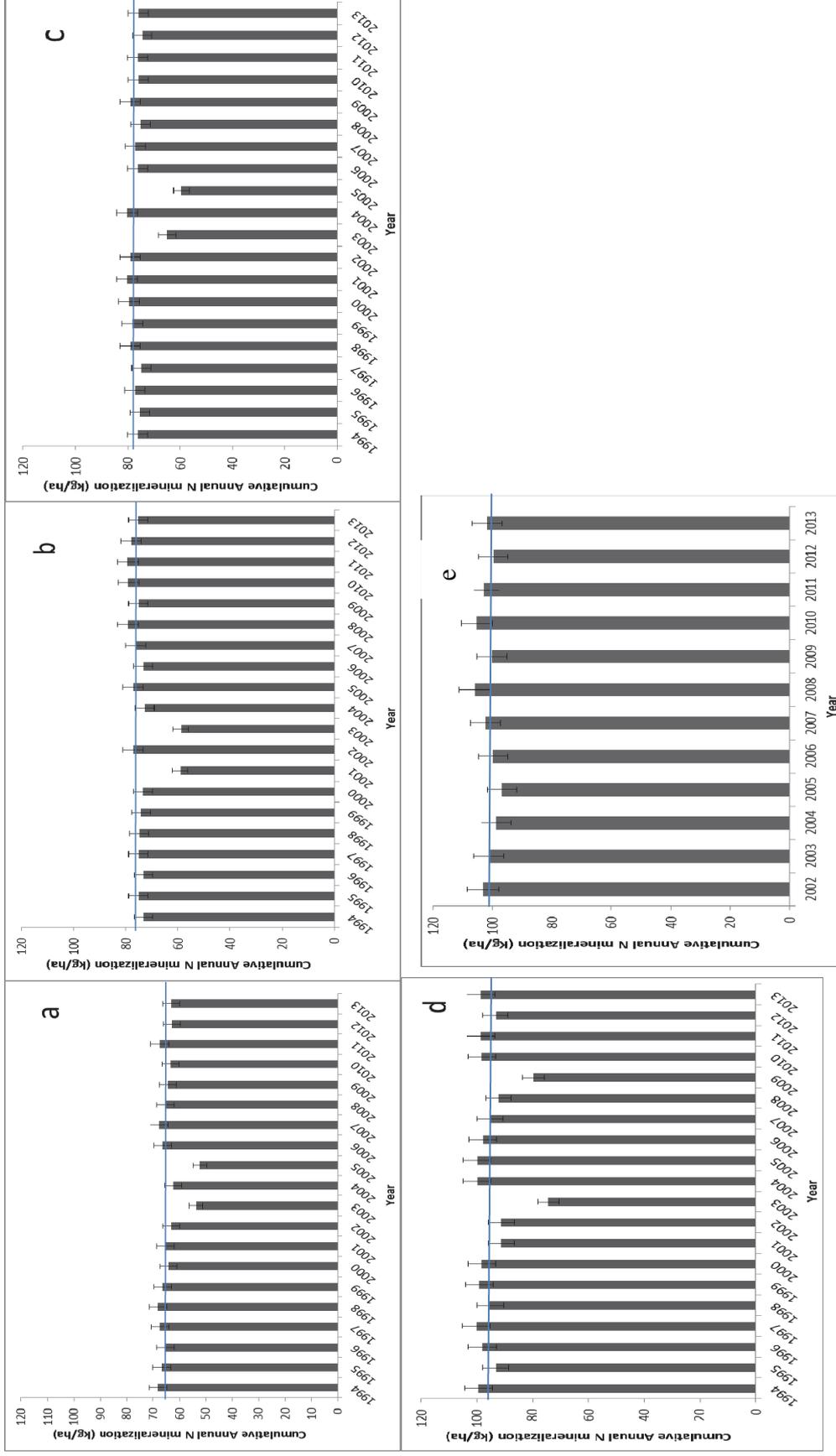
On the other hand, the dominance of temperature on cumulative annual N mineralization was more prevalent in the sub-humid zone between Bethlehem and Port Alfred. Cumulative annual N mineralization in Port Alfred was 7% higher than in Bethlehem though the difference in mean annual rainfall between the two sites was only 31 mm. The difference in cumulative annual N mineralization is thus mainly attributed to the higher mean annual air temperature in Port Alfred (20°C) compared to that of Bethlehem (13°C). The dominance of soil temperature over soil moisture on N mineralization has been well investigated by Sierra (1997). Sierra (1997) reported that N mineralization was more responsive to temperature than it was to soil water content at certain temperature and water content ranges.

There were also events, where the effect of both temperature and rainfall on cumulative annual N mineralization was vivid. For instance the cumulative annual N mineralization from the humid zone of Cape Town was 7% lower than Durban, which is located in the same agro-ecological zone. This was because the long-term cumulative mean annual rainfall and mean annual temperature of Cape Town was 134 mm and 5°C lower than Durban. Such interactive effects of both water and temperature on N mineralization are well documented in the broad literature (Sierra, 1997; Wang et al., 2006; Leiros et al., 1999).

Therefore, the hypothesis “cumulative annual N mineralization from sludge amended soils will not vary significantly between sites within an agro-ecological zone” is not accepted. Consequently, a single annual N mineralization rate cannot be used across sites within an agro-ecological zone.

Model simulation of N mineralization from a sludge applied at a rate of 10 Mg ha<sup>-1</sup> per annum was similar across seasons within a site, except for very few anomalous low rainfall seasons (Fig. 7.4). The long-term mean cumulative annual N mineralization during the first year of application from anaerobically digested sludge dried in conventional concrete beds was 25%, 28%, 29, 39%, and 42% in Kimberly, Polokwane, Johannesburg, Durban, and Nelspruit, respectively. In the super-humid zone of Nelspruit, there was no significant difference in the cumulative annual N mineralization between years.

Cumulative annual N mineralization from sludge applied at a rate of 10 Mg ha<sup>-1</sup> on a yearly basis did not differ significantly in 18 of the 20 years in the arid, semi-arid, sub-humid, and humid agro-ecological zones despite a 156 mm, 217 mm, 315 mm, and 223 mm annual rainfall variation between seasons, respectively.

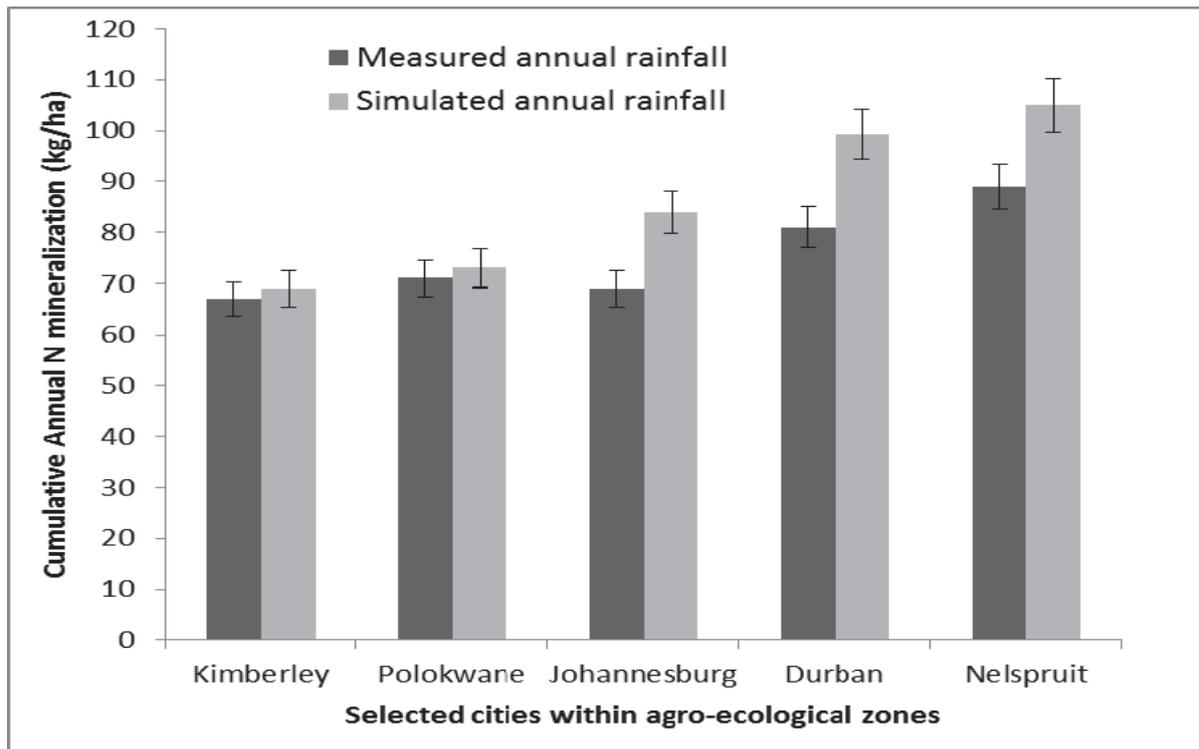


**Figure 7.4 Model predictions of mean nitrogen mineralization from anaerobically digested sludge dried in concrete beds during the first year of land application at a rate of 10 Mg ha<sup>-1</sup> in Kimberley (arid) (a), Polokwane (semi-arid) (b), Johannesburg (sub-humid) (c), Durban (humid) (d), and super humid (Nelspruit) (e) (results are mean values from clay, clay loam, sandy clay loam and sandy loam soils)**

The significant difference ( $P < 0.05$ ) in N mineralization observed in two of the 20 years took place as the difference between the maximum and the minimum rainfall exceeded 196 mm, 241 mm, 362 mm, and 429 mm in the arid, semi-arid, sub-humid and humid agro-ecological zones, respectively. The absence of significant difference in N mineralization despite substantial differences in annual rainfall ranging from 156 mm in the arid to 315 mm in the sub-humid zones is in line with recent findings of Li et al. (2014). Li et al. (2014) reported that N mineralization did not differ significantly despite an increase in water filled porosity from 40% to 60%. On the other hand, his findings showed that an increase in water filled porosity from 20% to 40% resulted in significant increase in N mineralization. Therefore the hypothesis “cumulative annual N mineralization from sludge amended soils will not vary significantly between seasons at a specific site except for few anomalous seasons” is not rejected.

Cumulative annual N mineralization varied significantly ( $P < 0.05$ ) within a season in the sub-humid, humid, and super humid sites as the rainfall distribution changed, despite the cumulative annual rainfall being similar (Fig. 7.5). In contrast, in the arid and semi-arid sites the distribution of rainfall did not alter cumulative annual N mineralization significantly ( $P < 0.05$ ).

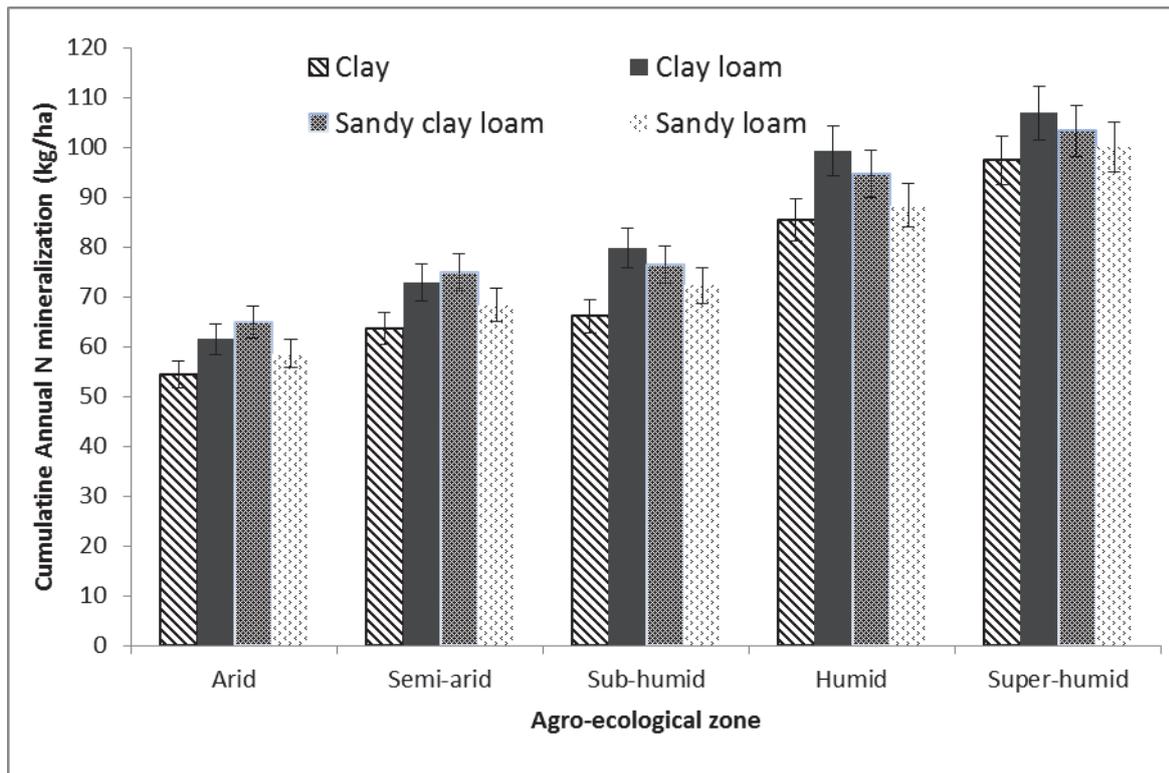
Model simulation of cumulative annual N mineralization from sludge amended soils under measured (natural distribution of rainfall) and simulated (similar rainfall amount as measured but evenly distributed) varied significantly across agro-ecological zones. Model simulations showed that in arid and semi-arid agro-ecological zones, cumulative annual N mineralization did not vary significantly ( $P < 0.05$ ) between simulated and measured rainfall distribution patterns. This implies that, in these agro-ecological zones, the main limiting factor for N mineralization is rainfall amount and not rainfall distribution. In contrast, cumulative annual N mineralization response to rainfall distribution was significant ( $P < 0.05$ ) in the sub-humid, humid, and super-humid agro-ecological zones of South Africa. The implications are, in these three agro-ecological zones, rainfall distribution is responsible for the limiting factor for potential N mineralization under the given rainfall amount. Previous reports by Broken and Matzner (2009) discussed the cause for such differences in N mineralization between places as the interactive effects between intensity and duration of drying, the amount and distribution of precipitation among other factors. Therefore, the hypothesis “cumulative annual N mineralization from sludge amended soils will not vary significantly within a season due to variation in distribution of rainfall was not rejected for arid and semi-arid zones but humid and super-humid agro-ecological zones.



**Figure 7.5 Cumulative annual N mineralization from anaerobically digested sludge applied at a rate of 10 Mg ha<sup>-1</sup> per annum in selected cities of the five South African agro-ecological zones as affected by rainfall distribution within a season.**

It was apparent that cumulative annual N mineralization was significantly ( $P < 0.05$ ) lower from clay than clay loam and sandy clay loam in all but the super-humid agro-ecological zone (Fig. 7.6). Cumulative annual N mineralization from clay loam and sandy clay loam did not differ significantly ( $P < 0.05$ ) in all agro-ecological zones. Similarly the difference in N mineralization between sandy clay loam and sandy loam was not statistically significant ( $P < 0.05$ ) in all agro-ecological zones.

Cumulative annual N mineralization varied significantly ( $P < 0.05$ ) between textures in all but the super-humid agro-ecological zone. The study also showed that N mineralization was lowest from clay soil. The low N mineralization from clay soils and higher N release from sand dominated loam soils is in agreement with previous findings (Cartroux et al., 1987; Ladd et al., 1990; Hassink et al., 1990; Verberne et al., 1990). According to Verberne et al. (1990), the low N mineralization from clay soils is to a larger extent due to the physical protection of soil organic matter and microbial biomass. Therefore, the hypothesis “cumulative annual N mineralization from sludge amended soils will not vary significantly across soil textures within a site is not accepted. Consequently, a single N mineralization rate cannot be used cross soil textures within a site.



**Figure 7.6 Cumulative annual N mineralization across agro-ecological zones as affected by soil texture**

#### 7.4 CONCLUSIONS

It was apparent from model simulations that N mineralization rates during the first year of sludge application varied significantly ( $P < 0.05$ ) across agro-ecological zones with highest rates of 42% recorded in super-humid and lowest rates of 24% in arid zones. Annual mineralization rates varied significantly between sites within an agro-ecological zone as well as between soil textures within a specific site. Nonetheless, N mineralization rates did not differ significantly between seasons within a specific site. Consequently, hypothesis 1 “N mineralization will not vary between sites within agro-ecological zone” and hypothesis 3 “N mineralization will not vary across soil textures within a site” were not accepted. Hypothesis 2 “N mineralization will not vary significantly between seasons at a specific site” was, accepted. Therefore, a single annual N mineralization rate cannot be used across sites within an agro-ecological zone. However, a single N mineralization rate could be used within a specific site but should be adjusted for each soil texture.

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## CHAPTER 8 – SIMPLE SLUDGE APPLICATION RATE ADVISOR DATA-BASE MODEL

### 8.1 SLUDGE APPLICATION RATE ADVISOR (SARA) MODEL

The sludge application rate advisor is a simple user-friendly database model developed with an aim to aid wastewater care works: a) classify their sludge according to the current South African Sludge Guideline, b) as decision support tool for sludge application rate recommendations across South African agro-ecological zones and selected crops, c) as decision support tool for simple cost-benefit analyses, d) as decision support tool on long-term potential heavy metal accumulation using a simple mass balance method.

### 8.2 INTRODUCTION TO THE SARA MODEL GRAPHICAL USER INTERFACE

The main window of the SARA graphical user interface including its two main components **Sludge classification** and **Sludge application rate advisor** are presented in Fig. 8.1.

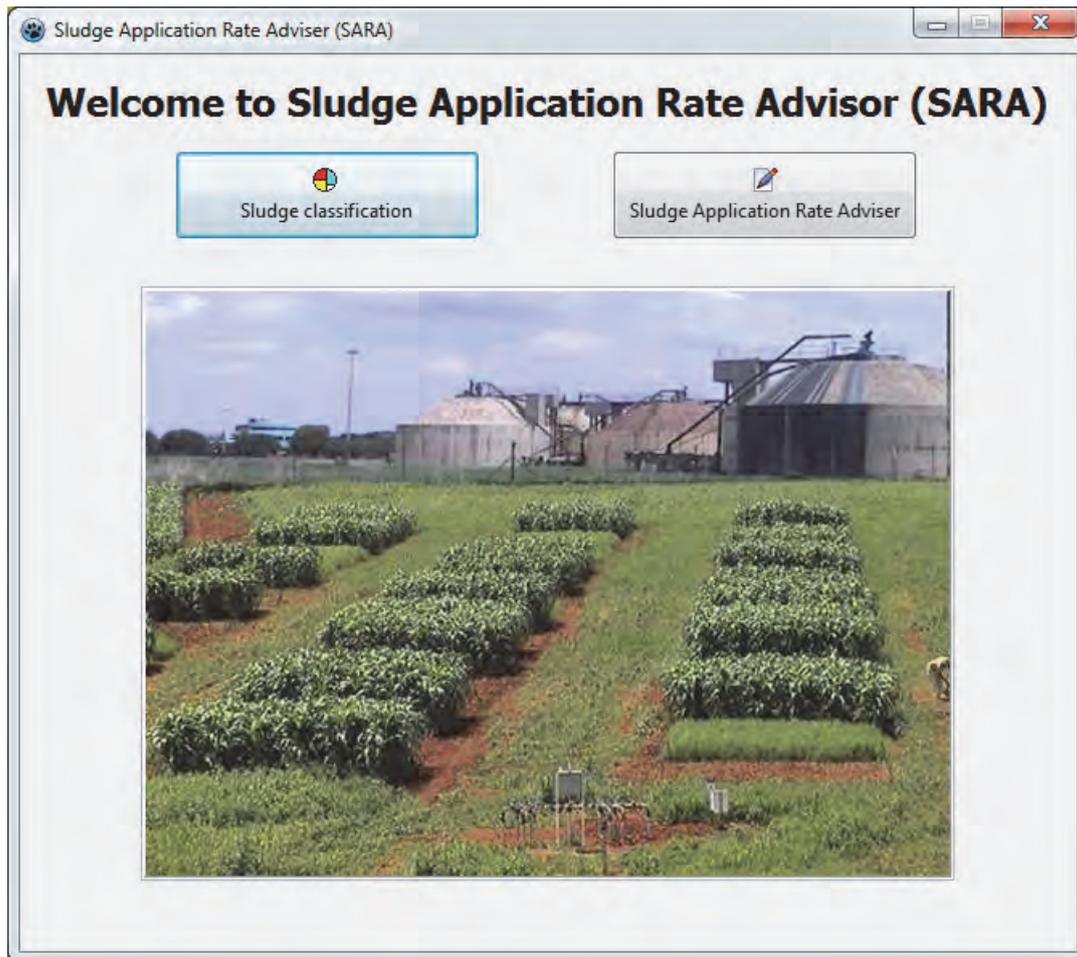
#### 8.2.1 Sludge classification graphical user interface

Work for sludge classification should begin by opening the **Sludge classification**. Figure 8.2 shows **Sludge classification** graphical user interface, including its main components: the **Microbial class**, **Pollutant class**, and the **Stability class**. The text below provides a detailed description of all major components of the graphical user interface.

In the dialogue window that a user encounters after opening the **Sludge classification** graphical user interface, he/she needs to populate the **Microbial class** and **Pollutant class**. The user should also select the **Stability class** based on the 10 criteria that fits best.

The variables that need to be populated in the **Microbial** and **Pollutant** classes are presented below:

Microbial class: a) Faecal coliforms                      b) Helminth ova  
Pollutant class: a) As    b) Cd    c) Cr    d) Cu    e) Pb    f) Hg    g) Ni    h) Zn



**Figure 8.1 Interface of the beta version of Sludge Application Rate Adviser (SARA) model**

The microbial, pollutant and stability class for each sludge is predicted based on the manual “Guidelines for the utilization and disposal of wastewater sludge volume 1 of 5” (Snyman and Herselman, 2006) and is displayed at the bottom of the **Sludge classification** dialogue window (Fig. 8.2).

Sludge classification

Microbial class

Faecal coliforms 100

Helminth ova 0.2

Pollutant class

As 35 Cr 1000 Pb 250 Ni 400

Cd 35 Cu 1400 Hg 10 Zn 2500

Stability class

1 2 3

Comply with one of the options listed below on a 90 percentile basis

Comply with one of the options listed below on a 75 percentile basis

No stabilisation or vector attraction reduction options

Option 1: Reduce the mass of volatile solids by a minimum of 38 percent

Option 2: Demonstrate vector attraction reduction with additional anaerobic digestion in a bench-scale unit

Option 3: Demonstrate vector attraction reduction with additional aerobic digestion in a bench-scale unit

Option 4: Meet a specific oxygen uptake rate for aerobically treated sludge

Option 5: Use aerobic processes at a temperature greater than 40 C (average temperature 45 C) for 14 days or longer (eg during sludge composting)

Option 6: Add alkaline material to raise the pH under specific conditions

Option 7: Reduce moisture content of sludge that do not contain unstabilised solids (from treatment processes other than primary treatment) to at least 75 percent solids

Option 8: Reduce moisture content of sludge with unstabilised solids to at least 90 percent solids

Option 9: Inject sludge beneath the soil surface within a specified time, depending on the level of pathogen treatment

Option 10: Incorporate sludge applied to or placed on the surface of the land within specified time periods after application to or placement on the surface of the land

Sludge class

**A1b**

Figure 8.2 Sludge classification dialog Window

### 8.2.2 Sludge application rate advisor graphical user interface

Work for sludge application rate recommendation, cost benefit analyses, and trace metal accumulation should start by opening the **Sludge Application Rate Advisor**. The sludge application rate advisor graphical user interface (Fig. 8.3) is the place where the list of farms and the input and output data is located. In the first dialog window that a user encounters after opening the **Sludge Application Rate Advisor** user interface he/she will find two Tabs **Fields** and **Sludge**, on the left side just above the grids.

#### 8.2.2.1 Fields Tab

The **Fields** Tab is the default Tab in which the user needs to either select from the list of available farms or creates a new farm by selecting the **Insert** command at the top of the dialogue window (Fig. 8.3). When the **insert** command is selected, a new dialogue window **Insert** opens up (Fig. 8.4) with two Tabs **Farm** and **Soil**. Under the **Farm** Tab the following list of information about the farm need to be populated:

- Field id (Each field's identification code within a farm)
- Province
- City (nearest city)
- Farmer's name

- e) Farm size (ha)
- f) Crop type
- g) Target yield (t/ha)
- h) Cropping system (dryland/irrigated)
- i) Sludge application method (surface applied/incorporated)

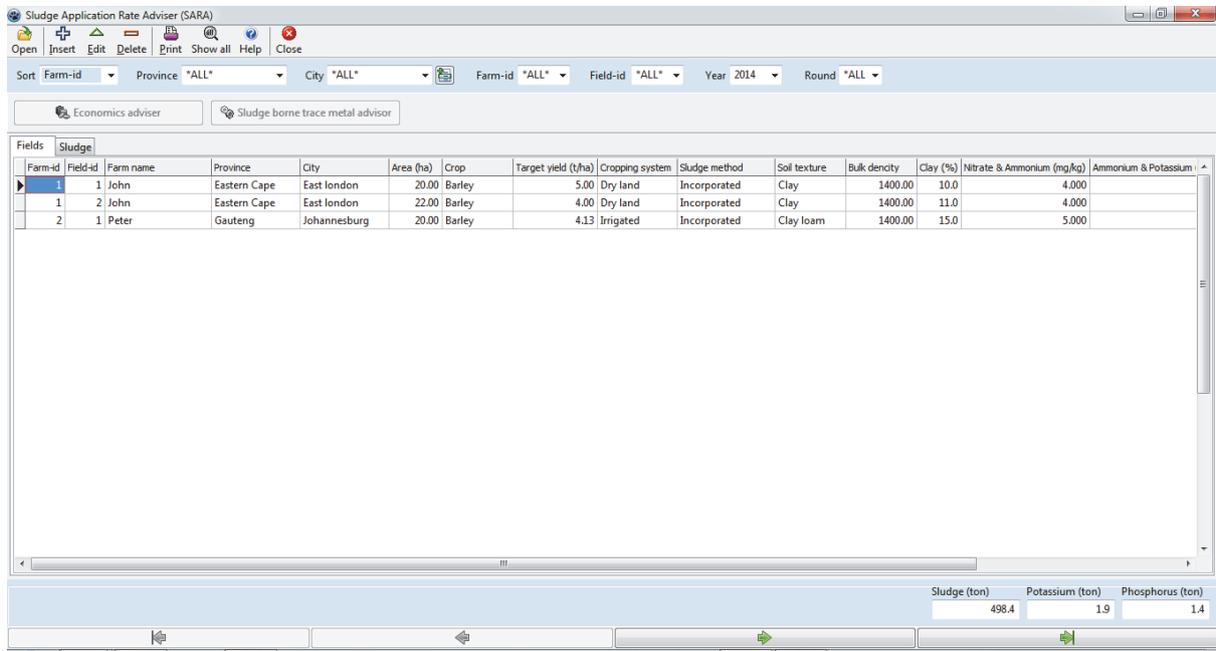


Figure 8.3 SARA model “Sludge Application Rate Advisor” dialogue window

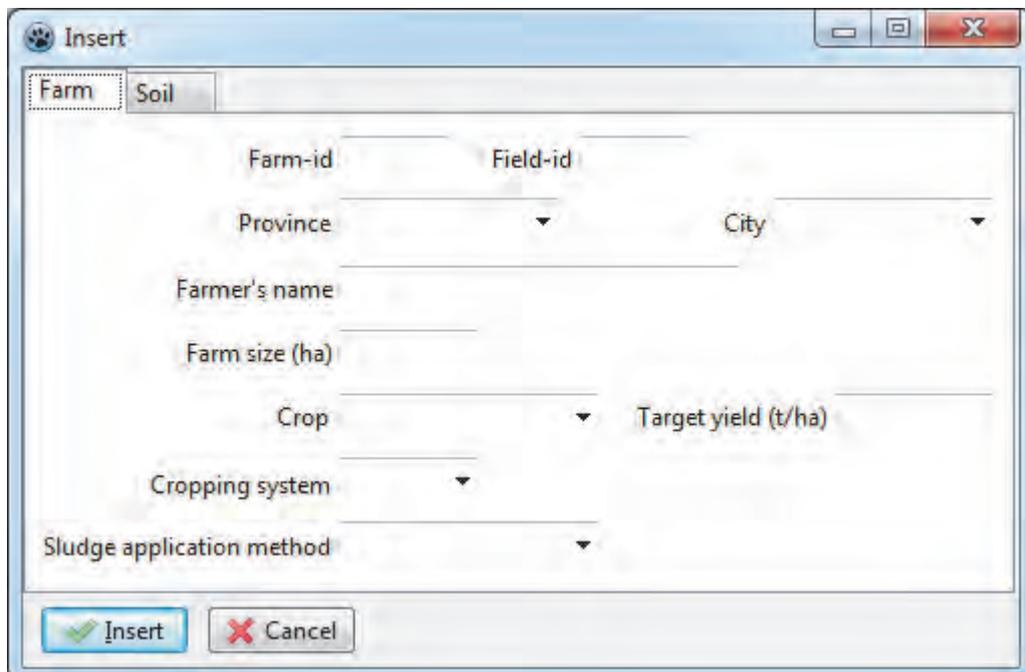


Figure 8.4 Sludge Application Rate Advisor (SARA) model insert new farm dialogue window

Once the **Farm** Tab is populated, soil characteristics of each field within the farm under investigation need to be populated under the **Soil** Tab (Fig. 8.5). Soil characteristics required by the model are listed below.

- a) Soil textural class
- b) Bulk density
- c) Clay (%)
- d) Soil nitrate and ammonium ( $\text{mg kg}^{-1}$ )
- e) Ammonium acetate extractable potassium ( $\text{mg kg}^{-1}$ )
- f) Soil plant available phosphorus ( $\text{mg kg}^{-1}$ )
- g) Analytical method (Bray-1, Ambic Citric acid, Mehlic, Olsen, Bray)

The soil plant available phosphorus is mainly presented to help as a monitoring protocol for environmental pollution and not for fertiliser recommendation because sludge is applied based on crop N requirements.

**Figure 8.5 Sludge Application Rate Advisor (SARA) model soil characteristics of new farm inserted dialogue window**

Information under **Farm** and **Soil** Tabs presented within the **Fields** main Tab can be edited by selecting the **Edit** command, third from left at the top of the **Sludge Application Rate Advisor** Window dialogue box interface (Fig. 8.3).

### 8.2.2.2 Sludge Tab

The **Sludge** Tab is the place where the type of sludge and selected parameters for the sludge are entered (Fig. 8.6). The list of sludge parameters required by the model are presented below: Sludge application round

- a) Sludge type
- b) Sludge moisture content
- c) Sludge total nitrogen content
- d) Sludge nitrate content
- e) Sludge ammonium content
- f) Sludge phosphorus content
- g) Sludge potassium content

The image shows a software dialog box titled "Insert". It contains several input fields and dropdown menus. The fields are: Farm-id, Field-id, Application year (set to 2015), Application round (set to 1st year), Type, Moisture content (%), Total Nitrogen content (%), Nitrate content (mg/kg), Ammonium content (mg/kg), Phosphorus content (%), and Potassium content (%). At the bottom of the dialog, there are two buttons: "Insert" with a green checkmark icon and "Cancel" with a red X icon.

**Figure 8.6 Sludge Application Rate Advisor (SARA) model sludge chemical characteristics input dialogue window**

The **Economics advisor** and **Sludge borne trace metal advisor** buttons are activated when the **sludge** Tab is activated.

### 8.2.2.3 Economics advisor interface

The **Economics advisor** module of SARA model (Fig. 8.7) is the section where the cost benefit analyses on the fertilizer value of sludge is computed. The dialogue window of the Economics advisor consists of three sections: 1) Transport related information section, 2) commercial inorganic fertilizer price related information, and 3) Cost benefit analyses section. Details of the input parameters for each of the three sections are presented below.

#### a) Transportation

- a. Farm distance from wastewater treatment plant (km)
- b. Transport cost per km

#### b) Commercial inorganic fertilizer price information

- a) Nitrogen fertilizer price per ton
- b) Nitrogen content of fertilizer (%)
- c) Phosphorus price per ton
- d) Phosphorus content of fertilizer (%)
- e) Potassium price per ton
- f) Potassium content of fertilizer (%)

#### c) Cost-benefit analyses

- a) Total cost of commercial fertilizer (fertilizer + transport cost)
- b) Transport cost of municipal sludge
- c) Net margin

The following assumptions have been considered during the computation of net margin:

1. Crop N, P, and K requirement was estimated based on the South African Fertilizer Handbook.
2. Sludge application rate recommendation is decided based on crop nitrogen requirement.
3. The P fertilizer value of the sludge applied according to crop N requirement is equal to the crop P requirement.
4. The cost of sludge distribution on the farm was assumed to be equal to the cost of inorganic fertilizer spreading in splits (twice under dryland and four times under irrigation).

**Figure 8.7 Economics adviser dialogue window for Sludge Application Rate Advisor (SARA) model**

#### 8.2.2.4 Sludge borne trace metal advisor

In the **Sludge borne trace metal advisor** dialogue window (Fig. 8.8), users specify the concentration of the 8 trace elements in the sludge as well as receiving soil. This module estimates:

- a) The element that will reach environmental threshold level first,
- b) The duration to reach environmental threshold level (years)

During the computation of the above mentioned outputs, the model assumes:

- minimal leaching of metals to the lower layers below the plough depth, and
- homogenous distribution of trace elements within the plough layer

The module requires the following input variables to generate the above mentioned outputs:

- 1) Trace metal content of sludge and receiving soil (Cu, Zn, Hg, Pb, Cd, Ni, Cr, and As)
- 2) Sludge application method
- 3) Plough depth
- 4) Sludge application rate

Heavy metal balance adviser

Heavy metal accumulation

	Sludge (mg/kg)	Soil (mg/kg)	
Cu	336.37	0.103	Application method: Incorporated
Zn	2451	1.006	Plough depth (m): 0.5
Hg	0.85	0.154	Sludge application rate (t/ha): 11.31
Pb	66.76	0.015	
Cd	8.96	0.029	
Ni	81.11	0.743	
Cr	237.81	0.012	
As	6.21	0.004	

Duration to reach environmental threshold level

Element that will reach environmental threshold level before others:

Time to reach environmental threshold level (years):

Calculate

Figure 8.8 Trace element dialogue window for Sludge Application Rate Advisor (SARA) model

## CHAPTER 9 CONCLUSION AND RECOMMENDATION

### 9.1 CONCLUSION

Drying sludge in drying beds in thick layers seems to reduce the nitrogen and carbon contents while increasing the lignified fraction. Sludge fractionation studies using the Van Soest method indicated that sludge dried in thin layers of less than 10 cm layer thickness both anaerobically digested and activated sludge had the highest total nitrogen (4.95-5.2%) compared with thermally hydrolysed sludge (3.13%), anaerobically digested sludge dried in thick layers of more than 20 cm in concrete and earth paddy (2.81%). The inorganic N fraction accounted for less than 10% of the total N for all sludge types. A large fraction (>60%) of the organic C in all sludge types was soluble compounds with the thermally hydrolysed sludge having the highest (90%). Sludges dried in thin layers were characterised by low lignin fraction (<3% of the total organic C) but largest hemicelluloses fraction (>20%).

Sewage sludge organic matter decomposition and N mineralization was influenced by the biochemical composition of the sludge. Net nitrogen mineralization was negatively co-related with the lignin composition of sludge and positively co-related with the soluble compounds. The nitrogen fertilizer value of activated sludge was higher than thermally hydrolysed and anaerobically digested sludges dried in thick layers. This was mainly due to a higher initial total N (5.2% by mass for activated sludge compared with 2.8 -3% for other sludge types) and higher decomposable organic N (77 g N kg<sup>-1</sup> organic carbon applied) for activated sludge compared with thermally hydrolysed sludge (57 g kg<sup>-1</sup>) and anaerobically digested sludge dried in thick layers (57-73 g kg<sup>-1</sup>).

The expected rate of Nitrogen (N) mineralization is key to sludge application rate recommendations to agricultural lands. The presence of a combination of factors (biotic and abiotic) that contribute to the variation in N release make it difficult to come up with simple sludge application rate recommendations. Despite this, the use of a single annual N mineralization rate across sites and agro-ecological zones is a common practice around the world. Model simulations from this study showed that annual N mineralization rates varied significantly ( $P<0.05$ ) across agro-ecological zones ranging from 25% in arid to 42% in super-humid agro-ecological zones. Similarly, annual N mineralization rates varied significantly between sites within an agro-ecological zone. Annual N mineralization rates, however, did not differ significantly ( $P<0.05$ ) between seasons within an agro-ecological zones. Nitrogen mineralization varied significantly between soil textures within a site. Therefore, a single annual N mineralization rate cannot be used across sites within an agro-ecological zone. Nonetheless, a single N mineralization rate could be used within a specific site but should be adjusted for each soil texture.

Sludge application to agricultural lands is often limited, mainly because of concerns about metal accumulation in soils and uptake by crops. A large fraction of the Zn, Ni, and Pb in the soil profile was EDTA extractable (46 to 79%). Saturated paste extractable fractions of Cd and Pb were <1 mg kg<sup>-1</sup>. Plant uptake of Cd, Pb and Ni under irrigation was double that for dryland systems. Concentrations of the metals considered in plant tissue of both cropping systems remained well below phytotoxic levels, except for Zn under dryland maize that received 16 Mg sludge ha<sup>-1</sup> yr<sup>-1</sup>. Metal concentrations in the soil remained far below total

maximum threshold levels. Therefore, in the short to medium term (5-10 years) the application of good-quality sludge according to crop N requirement will not lead to significant accumulation of water-soluble metal fractions in soil.

## **9.2 RECOMMENDATIONS**

The following research topics need further investigation:

1. The effect of post wastewater treatment dewatering techniques (drying depth and time) on:
  - a. Sludge organic constituents,
  - b. Sludge N composition,
  - c. Nitrogen decomposition rate,
  - d. Sludge fertilizer value, and
  - e. Phosphorus fertilizer value.
2. Water, salt, and nitrogen balances of agricultural lands receiving liquid sludge.
3. Further investigation on trace metal leaching below the active root zone from sludge amended agricultural soils is recommended.