Soil Health Improvement Technologies to Enhance Drought and Nutrient Resilience in Urban Agroecosystems in Zimbabwe

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Declaration

The work in this thesis is based on research carried out at Domboshava Training Centre in Zimbabwe through the University of Zimbabwe's Department of Soil Science and Environment, Stellenbosch University in South Africa and Department of Engineering, University of Durham, United Kingdom. The work was financially supported through Durham University Global Challenges Research Fund. No part of this thesis has been submitted elsewhere for any other degree or qualification, and it is the sole work of the author unless where referenced in the text.

Some of the work presented in this thesis has been published in journals and conference proceedings - the relevant publications are listed below.

Journal Articles

1. **Gwandu, T**., Lukashe, N.S., Rurinda, J., Stone, W., Chivasa, S., Clarke, C.E., Nezomba, H., Mtambanengwe, F., Mapfumo, P., Steytler, J. G. & Johnson, K.L. (2023). Co-application of water treatment residual and compost for increased phosphorus availability in arable sandy soils. Journal of Sustainable Agriculture and Environment. https://doi.org/10.10002/sae2.12039 (Chapter 6)

2. Johnson, K.L., Stone, W., Dominelli, L., Chivasa, S., Clarke, C.E., **Gwandu, T** & Appleby, J. (2023). Boosting soil literacy in schools can help improve understanding of soil/human health linkages in Generation Z. Front. Environ. Sci. 10:1028839. doi: 10.3389/fenvs.2022.1028839 (Thesis)

3. **Gwandu, T**., Blake, L. I., Nezomba, H., Rurinda, J., Chivasa, S., Mtambanengwe, F., & Johnson, K. L. (2022). Waste to resource: use of water treatment residual for increased maize productivity and micronutrient content. *Environmental Geochemistry and Health*, 1-18. (Chapter 5)

4. Johnson, K. L., Gray, N. D., Stone, W., Kelly, B. F., Fitzsimons, M. F., Clarke, C., ... & **Gwandu, T**. (2022). A nation that rebuilds its soils rebuilds itself-an engineer's perspective. *Soil Security*, *7*, 100060. (Thesis)

5. Stone, W., Lukashe, N. S., Blake, L.I., **Gwandu, T.**, Hardie, A.G., Quinton, J., Johnson, K., & Clarke, C.E (2021). The microbiology of rebuilding soils with water treatment residual co-amendments: Risks and benefits. J Environ Qual. 50(6):1381-1394. (Chapter 7)

Conference Proceedings

1. **Gwandu, T**., Nezomba, H., Mtambanengwe, F., Chivasa, S., Dobson,K., Lark, M. & Johnson, K. (2020). From a waste to a valuable resource: Combined application of water treatment residual and compost improves maize productivity. Goldschmidt 2020.

Impact of Covid-19 global pandemic

The period for completion of my studies were extended by six months due the impact of the Covid-19 global pandemic.

Abstract

Soil degradation which is linked to poor soil organic matter management remains a significant barrier to sustained crop production in smallholder urban agriculture (UA) in sub-Saharan Africa (SSA). While organic nutrient resources are often used in UA to complement inorganic fertilisers in soil fertility management, they are usually scarce and of poor quality to provide optimum nutrients for crop uptake. Alternative soil nutrient management options are required. Aluminium-water treatment residual (Al-WTR), a by-product of the drinking water treatment process is an alternative organo-mineral resource that can be used to complement mineral and organic nutrient resources in urban agroecosystems. Although previous research has revealed the transformative effects of Al-WTR on soil physicochemical properties, there is still some inconsistency about the effects of Al-WTR on relations between plant yield and nutrients, particularly phosphorus (P). The aim of this study was to evaluate the impact of co-applying Al-WTR in combination with other organic nutrient resources (compost, cattle manure and maize stover) as 'co-amendments' on soil physical, biological, and chemical properties, P sorption and maize productivity in UA in Zimbabwe. The study employed field, greenhouse, and laboratory approaches to test different Al-WTR-based options for improved soil health. The main treatments included single amendments of Al-WTR, compost (C), cattle manure (CM), maize stover (MS) or their co-amendments as Al-WTR + CM, Al-WTR + MS or Al-WTR + C; an unamended control and standard NPK. A field experiment to determine the influence of Al-WTR co-amendments on soil organic carbon (SOC) and selected soil physical properties showed higher accumulation of SOC and lower soil bulk density; higher soil structural stability, water holding capacity and higher maize grain yields in the co-amendments compared to the unamended soils. The co-amendment of Al-WTR and cattle manure (Al-WTR + CM) accumulated higher (4.96 g. kg^{-1}) concentration of SOC and the lowest (1.30 g cm^{-3}) bulk density, whilst the unamended control recorded the least (4.55 g. kg^{-1}) in SOC and the highest (1.35 g. cm^{-3}) bulk density. The co-amendment, Al-WTR + CM also exhibited greater soil structural stability, recording an average of 121.64 g. kg^{-1} water-stable aggregates (WSA) and 0.17 mm in mean weighted diameter (MWD), equating to an increase of 393% (WSA) and 141% (MWD), relative to the unamended control. The co-amendment, Al-WTR + CM also resulted in increments of at least 0.02 cm^3 cm^{-3} in readily available water, whilst also retaining > 10% more water at field capacity relative to the control. Both co-amendments, Al-WTR + CM and Al-WTR and maize stover (Al-WTR + MS) in turn yielded four times more maize grain yield compared to the unamended control. Results also showed a higher biological activity in the co-amendments, suggestive of a high turnover potential of the co-amendments in restoring soil health. The co-amendment of Al-WTR + CM attained the highest microbial biomass carbon (190 ± 1.14 mg C kg^{-1}) and microbial biomass nitrogen (35.80 ± 0.51 mg N kg^{-1}) at 6 weeks after planting maize, whereas the least (120 ± 1.58 mg C kg^{-1} and 18.72 ± 0.35 mg N kg^{-1}) were recorded for the unamended control. Soil basal respiration (CO_2-C emission) was higher in Al-WTR + MS, which gave the highest CO_2-C emission of 167 ± 3.44 mg CO_2-C kg^{-1} soil. The unamended control on the other hand recorded a higher metabolic quotient, releasing > 0.10 mg CO_2-C microbial C day^{-1} more, compared to the co-amendments, suggesting more available carbon in the co-amendments and therefore less microbial strain compared to the unamended soil. Results of a short-term greenhouse experiment to evaluate the benefits of applying Al-WTR in combination with compost and inorganic P fertiliser, on soil chemical properties, and maize (*Zea mays* L.) productivity and nutrient uptake showed higher (3.92 ± 0.16 g) maize shoot biomass at 5 weeks after emergence in the co-amendment of 10% C + 10% Al-WTR, significantly ($p < 0.05$) out-yielding the unamended control which yielded 1.33 ± 0.17 g. The addition of inorganic P fertiliser to the co-amendment (10% C + 10% Al-WTR + P) further increased maize shoot yield by about six-fold (7.23 ± 0.07 g), showing the important role of inorganic P fertilisers in crop production. The co-amendment, 10% Al-WTR + 10% C + P increased maize uptake of the micronutrients Zinc (Zn), Copper (Cu) and Manganese (Mn) by 13.63-, 1.08- and 0.79- mg kg^{-1}, respectively, compared with the single amendment of 10% C + P. The enhanced micronutrient uptake can potentially improve maize grain quality and subsequently human nutrition for the urban population in SSA. A laboratory experiment to understand P sorption characteristics of a sandy soil co-amended with different ratios of Al-WTR and compost under varying levels of pH, particle size and P concentration showed higher maximum P sorption in the single amendment of Al-WTR compared to the co-amendments. The co-amendments in turn showed a reduction in crop inorganic P fertiliser requirements by ranges of 30 - 70% in the co-amendments compared to the single amendment of Al-WTR. Overall, results from this study showed that Al-WTR co-amendments can be used to re-build soil heath, enhance maize productivity, and improve human nutrition in smallholder urban agro-systems of Southern Africa and partly contribute to the United Nations Sustainable Development Goals (UN SDGs) linked to both soil and human health.

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Dedication

To Ashley, Tavonga and Miss Charlotte!

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List of acronyms and abbreviations

AAS	Atomic Absorption Spectrophotometer
Al	Aluminium
Al-WTR	Aluminium-Water Treatment Residual
ANOVA	Analysis of Variance
As	Arsenic
Ba	Barium
C	Carbon
Ca	Calcium
Cd	Cadmium
CEC	Cation Exchange Capacity
Cu	Copper
FC	Field Capacity
Fe	Iron
GHG	Greenhouse Gas
GY	Grain Yield
HI	Harvest index
K	Potassium
MBC	Microbial Biomass Carbon
MBN	Microbial Biomass Nitrogen
Mg	Magnesium
Mn	Manganese
N	Nitrogen

Ni	Nickel
OC	Organic Carbon
OM	Organic Matter
P	Phosphorus
Pb	Lead
PFRs	Phosphorus Fertiliser Requirements
RAW	Readily Available Water
SBR	Soil Basal Respiration
SDGs	Sustainable Development Goals
SITs	Soil Improvement Technologies
SMB	Soil Microbial Biomass
SOC	Soil Organic Carbon
SSA	sub–Saharan Africa
TCLP	Toxicity Characteristic Leaching Procedure
TN	Total Nitrogen
UA	Urban Agriculture
UK	United Kingdom
WAP	Weeks After Planting
WTP	Water Treatment Plant
WTR	Water Treatment Residual
Zn	Zinc

Chapter 1

1.0 General Introduction

1.1 Background

Soil degradation coupled with climate change if unabated will continue to drive food and nutrition insecurity in sub-Saharan Africa (SSA), particularly in smallholder farming households who depend mainly on subsistence agriculture for survival (FAO and ECA, 2018). This is a major burden for national governments who must rely on importing food with considerable amount foreign currency to feed their population (AGRA, 2022). For instance, it is anticipated that by 2030, the cost of food imports into Africa will have doubled, demanding an estimated USD 110 billion in public and private sector funding to maintain food production on the continent (https://www.scidev.net/sub-saharan-africa/news/africas-food-imports-bill-could-double-by-2030/). Yet the production of major food crops including maize is anticipated to decline by more than 30% by 2050 due to rising temperatures and changing rainfall patterns (Lobell *et al*., 2011; Rurinda *et al*., 2015; Mulungu and Ng'ombe, 2019). More than two-thirds of agricultural land in SSA is estimated to be severely degraded (UNCCD, 2013; Ussiri and Lal, 2019) and without innovative solutions, the United Nations Sustainable Development Goals (UN SDGs), most of which are underpinned by soil health (www.fao.org/news/story/en/item/1148732/icode/ ; Keesstra *et al*., 2016; Lal *et al*., 2021), and in particular goal number two of eradicating hunger by 2030, will unlikely be achieved, especially in SSA where about 230 million people are currently facing serious food shortages and hidden hunger (Joy *et al*., 2015; Kihara *et al*, 2020b).

The food deficits and hidden hunger will further worsen in urban areas, due to the increased demand for food as the urban population is projected to double from 298 to 595 million by 2030 (Cockx *et al*., 2018; FAO *et al*., 2018; Lal, 2020a). Yet also the economic growth in many developing countries has not been keeping pace with population growth, especially in urban areas leading to high rates of unemployment (Fox *et al*., 2016; Awad, 2019). Consequently, many people including young men and women in urban areas in SSA have been forced to resort to agriculture for their livelihoods (Takavarasha, 2003; Kutiwa *et al*., 2010). Urban agriculture (UA) accounts for 15-20% of the world's food production (FAO, 2012; Diehl *et al*., 2019). It has also been associated with many benefits such as production of fresh food and generation of income as well as recycling of urban wastes, creation of green belts and strengthening of cities' resilience to climate change (FAO, 2012; Lal, 2020a; Salomon and Cavagnaro, 2022). Despite the increasing importance of UA for supporting livelihoods, it has been argued that most urban farmers are not producing sufficient food to meet their household needs (Frayne *et al*., 2014; Davies *et al*., 2021), due to various challenges. First, crop production in UA is mainly constrained by poor soil health, insufficient soil organic nutrient resources, inappropriate farming methods and insufficient income to buy the necessary inputs (De bon *et al*., 2010; Bonilla Cedrez *et al*., 2020). Second, lack of extension support, supportive policies and institutions have also been major constrains for UA in SSA (Nyagumbo and Rurinda, 2012; Cilliers *et al*., 2020).

The rise in urbanisation in SSA (UN-Habitat, 2014) has caused a strain on existing food systems, leading to widespread conversion of marginal lands into croplands and hence land degradation (Oliveira *et al*., 2015; Wang and Dong, 2019). To increase output on the increasingly fragile soils, it is urgently necessary to halt and reverse soil degradation without expanding on the current crop land which could lead to a further loss of soil organic matter (SOM), thus increase greenhouse gas (GHG) emission (van Ittersum *et al*., 2016).

However, there are various technologies and practices that have been developed to improve crop productivity and protect the environment. These include conservation agriculture (Rusinamhodzi *et al*., 2011; Masvaya *et al*., 2017), agroforestry (Chikowo *et al*., 2004; Mafongoya *et al*., 2006), integrated soil fertility management (Mapfumo *et al*., 2008; Gram *et al*., 2020) and climate smart technologies (Lipper *et al*., 2014; Taylor, 2018). The agronomic and economic benefits of most of these technologies have been tested in farmers' fields mainly in rural communities (Gwandu *et al*., 2014; Kafesu *et al*., 2018). Little research has been done on UA, which is an emerging source of food security and livelihoods in Africa. Few agronomic technologies have been evaluated for their usefulness in urban areas in SSA (Nyamasoka *et al*., 2015; Shumba *et al*., 2020). For example, the influence of biological (sewage) sludge use on heavy metal accumulation in soils and their bioaccumulation in plant tissue (Gwenzi *et al*., 2016; Kumar *et al*., 2017), has been relatively well studied.

Although soil fertility management has been identified as one way in which farmers can sustain crop productivity (Rurinda *et al*., 2020; Lal *et al*., 2021), while minimising land degradation (Lal, 2015; Nezomba *et al*., 2018) and the negative impacts of climate change (Mapfumo *et al*., 2013; Smith *et al*., 2020), the focus of these studies have mainly been on rural-based smallholder farming systems. UA soils, like many other soils in SSA are severely degraded (Nyamangara *et al*., 2000; Muchena *et al*., 2005) and prone to drought. To enhance soil fertility and stimulate productivity in UA soils as well as protect the environment, there is need to improve such parameters as the soils' water holding capacity and SOM content. SOM plays a central role in nutrient retention and recycling, soil structure improvement, aeration, and the sustenance of microbial life, in addition to enhancing the soils' water retention capacity (Oldfield *et al*., 2018). Furthermore, soil carbon (C) storage in soil through organic matter (OM) additions has also been reported to contribute to climate change mitigation (Minasny *et al*., 2017; Lal, 2020b). In the wake of climate change, rising temperatures, changed rainfall patterns coupled with high frequency of droughts anticipated for southern Africa, soil C turnover is likely to be amplified (Knorr *et al*., 2005; Powlson, 2005), increasing pressure on water resources and causing reduction in soil water available for plant uptake. Therefore, integrated approaches that contribute to a more balanced built-up of soil C, improving both soil fertility and water management within urban agroecosystems will be fundamental in response to land degradation for building resilience to climate change and for improved food and nutritional security needed for stable economic growth.

Some studies have explored use of a by-product of clean water treatment, water treatment residual (WTR) as a soil amendment (e.g., Mahdy *et al*., 2007; Clarke *et al*., 2019; Gwandu *et al*., 2022). WTR is organo-mineral, containing Aluminium (Al) and / or Iron (Fe) oxides (depending on coagulant used), activated C and flocculated material from reservoirs, including clay particles and organic matter (Matilainen *et al*., 2010; Turner *et al*., 2019). Soil amendment with WTR can improve soil physicochemical properties (Basta, 2000; Ribeiro *et al*., 2022) and maize yield at certain threshold application levels (Rengasamy *et al*., 1980; Mahdy *et al*., 2007). However, there are concerns about using WTR as a soil improvement technology as it can reduce phosphorus (P) availability (Jonasson, 1996; Cox *et al*., 1997). Nevertheless, recent work in southern Africa (Clarke *et al.,* 2019; Gwandu *et al*., 2022) has shown that when WTR is used in combination with organic matter (OM) based amendments, crop productivity significantly ($p < 0.05$) improved by 33 to 50% at 1:1 ratio of WTR to compost compared with WTR sole application levels of between 5% to 20%, respectively (Clarke *et al*., 2019; Gwandu *et al*., 2022). Knowledge of whether WTR with or without OM can restore degraded soils is still scarce especially for developing countries like Zimbabwe, which are now faced with increased urban waste production due to rapid population growth and urbanisation. No field trials have been conducted, particularly in urban agroecosystems in Zimbabwe to evaluate the influence of soil improvement technologies (SITs) which include Al-WTR on plant growth, soil nutrient and water holding capacity. Thus, this study focuses on exploring the potential to use Al-WTR as a SIT to increase soil fertility and crop production and nutritional quality.

1.2. Rationale

UA in Zimbabwe encompasses the cultivation of maize (*Zea mays L.*) as the staple crop, vegetables, and grain legumes such as cowpea (*Vigna unguiculata* (L.) Walp) to supplement dietary proteins (Ngwerume and Mvere, 2003). It is a low-input and rain-fed system, except for fields located along streams where wastewater is used for vegetable production (Mapanda *et al*., 2007). Due to farmers' limited resources, UA in Zimbabwe, just as rural smallholder farming systems, is affected by poor soil fertility and lack of soil nutrient resources (Nyamangara *et al*., 2000; Mtambanengwe and Mapfumo, 2006). Periodic droughts and the increasingly unreliable rainfall patterns, intensified by climate change (Rurinda *et al*., 2014) have compounded the situation. Restoring productivity of soils within urban agroecosystems is not only key for increased crop yields, income, and nutritional security, but also improved ecosystem functions and enhanced resilience of these agroecosystems to global environmental changes.

In Zimbabwe, 70% of arable land supporting the country's agricultural productivity consists of granite-derived coarse sandy soils (Grant, 1981; Mapfumo and Giller, 2001), which are characterised by low OM content, poor nutrient and water holding capacity (Zingore *et al*., 2007), and poor soil structure to support crop production, and are prone to degradation if not properly managed (Nezomba *et al*., 2015). Although the application of inorganic fertilisers on the dominantly sandy soils in Zimbabwe is known to increase crop productivity (Mtambanengwe *et al*., 2007; Kafesu *et al*., 2018), their high cost makes them unaffordable to many UA farmers. For example, a 50 kg bag of fertiliser costs around US $38, a figure beyond the reach of many farmers who survive on less than US$2 per day (Makombe, 2021). UA farmers therefore depend heavily on a range of locally derived organic nutrient sources to sustain soil and crop productivity. These include livestock and poultry (from backyard chicken rearing) manure, and to a limited extent sewage sludge (Katanda *et al*., 2007), which is readily and freely available from wastewater treatment systems. However, high levels of pathogens (Lewis and Gattie, 2002) and heavy metals (Mapanda *et al*., 2007) in sewage sludge pose significant public health and environmental risks, likewise it is not 'socially accepted' by many farmers and consumers alike in Zimbabwe. Organic nutrient sources are also insufficient to sustain crop production as their use is often compromised by low application rates and poor nutrient content (Mapfumo and Giller, 2001). In addition, many urban farmers prefer to burn crop residues prior to tilling their land, a practice that reduces labile SOM (Blanco-Canqui and Lal, 2009; Sarkar *et al*., 2020). Low SOM is associated with low biochemical functions and such soils often show little or no response to fertiliser additions (Tittonell *et al*., 2012; Nezomba *et al*., 2015). Thus, the need to build SOM levels amidst challenges of limited organic nutrient sources requires interventions in exploring additional organic matter-based technologies to rehabilitate such degraded soils and restore soil ecosystem functions.

The water industry is interested in exploring low-cost alternative means of waste disposal for their WTR, allowing them to move towards zero waste. The use of WTR is therefore of interest not only to improve soil and crop productivity, but also to help society move to a circular economy (SDG 12). This study hypothesised that SITs comprising of WTR in combination with other OM nutrient resources enhance crop productivity due to improved soil structure, soil biological functions, and nutrient cycling. The impact of this study lies in using locally available mineral and organic "wastes" as SITs to improve nutrient and water use efficiency, and thus enhance drought and nutrient resilience in soils.

1.3 Research Approach and Methods

This study investigates the impact of WTR, in combination with various types of organic nutrient resources, on maize productivity, and on soil physicochemical and biological properties, under both greenhouse and field conditions. While previous research has revealed the transformative effects of WTR on soil physicochemical properties, there is still some inconsistency about the effects of WTR on relations between plant yield and nutrients, particularly P. Emerging evidence has revealed the synergistic effect of integrating WTR and other organic nutrient sources on nutrient supply and the ensuing plant growth. Yet also, the influence of WTR on soil physicochemical properties may directly influence plant growth, as well as have possible effects on soil microbiology and how these soil-microbial interactions may drive plant growth have not been extensively explored.

1.4. Hypotheses

The study was guided by the following hypotheses:

1. Use of aluminium-based water treatment residual (Al-WTR) in combination with other organic nutrient resources as a soil amendment improves soil structure (i.e., soil bulk density, aggregate stability and water holding capacity).
2. Addition of Al-WTR in combination with organic nutrient resources as a soil amendment improves soil health as measured by soil microbial biomass, basal respiration, and metabolic quotient.
3. Use of Al-WTR in combination with other organic nutrient resources improves soil chemical properties, nutrient uptake, maize (*Zea mays L.*) productivity and maize grain nutritional quality.

1.5 Main objective

The main objective of the study was to evaluate the impact of applying Al-WTR in combination with other organic nutrient resources (compost, cattle manure and maize stover) as 'co-amendments' on soil physical, biological, and chemical properties, and maize (*Zea mays* L.) productivity in urban agriculture in Zimbabwe.

1.6 Specific objectives

1. To evaluate the impact of Al-WTR in combination with organic nutrient resources as a soil amendment on soil bulk density, soil aggregate stability and soil water holding capacity.
2. To assess the effects of co-applying Al-WTR and other organic nutrient resources as a soil amendment on soil chemical properties, nutrient uptake, and maize productivity and nutritional quality.
3. To investigate the phosphorus (P) sorption characteristics and crop P fertiliser requirements of a sandy soil co-amended with Al-WTR and compost.
4. To evaluate the impact of combining Al-WTR with organic nutrient resources on the concentration of soil carbon and nitrogen, microbial biomass, basal respiration, and metabolic quotient.

1.7 Definition of important terms

Soil resilience refers to the ability of soil to resist or recover its structural and functional integrity after an anthropogenic or natural perturbation (Seybold *et al*., 1999; Herrick, 2000). In this study, **drought resilience** refers to the ability of soils and plants to adapt or withstand prolonged dry periods, which can be enhanced through improved soil water holding capacity. **Nutrient resilience** means building the ability of soils to recover their **healthy state of supplying plant food** (nutrients). **Soil health** is defined as the ability of a soil to deliver essential **ecosystem services,** a subset of which includes food security and climate change adaptation and mitigation (e.g., Johnson *et al*., 2022).

1.8 Thesis structure

Chapter 1 provides background information on the role of soil degradation and climate change in driving food insecurity in urban areas in Zimbabwe and SSA and outlines how the use of WTR can be used as an entry point in restoring soil health for improved crop productivity in urban agroecosystems. Chapter 2 provides a detailed literature review on urban agriculture (global overview and Zimbabwean context), soil degradation and current options for managing soil degradation in urban croplands in Zimbabwe and similar environments across the globe. A detailed study on water treatment residual (production and properties, constraints, and opportunities for its use) as a potential option for improving soil nutrients and enhance soil water holding capacity is also given in Chapter 2. Chapter 3 gives an overview of study sites, general research methodology and the general analytical methods employed during the study. Chapter 4 presents findings on the influence of Al-WTR co-amendments on selected soil physical characteristics and the subsequent maize grain yields. Chapter 5 presents findings based on greenhouse and field experiments on the influence of different organic amendments on soil chemical properties, nutrient uptake, and maize productivity. Laboratory-based evidence on how Al-WTR co-amendments can reduce P sorption and ultimately the crop P fertiliser requirements in Al-WTR amended soils is given in Chapter 6. Chapter 7 explores the influence of different organic amendments on soil microbial activities and soil health. Overall study findings, conclusions and recommendations are provided in Chapter 8.

Chapter 2

2.0. Literature Review

2.1. General overview of urban agriculture: benefits and risks

Urban agriculture (UA) refers to all forms of agricultural production (food and non-food) within and around cities (FAO, 2012; Wagstaff and Wortmann, 2015). Although, animal production is also a significant part of UA, it is beyond the scope of this study. At a global scale, UA is estimated to provide 10 to 20% of the world's food supply (Schnitzler *et al*., 1998; FAO, 2012; Lal, 2020a). Apart from providing nutritious food and extra income (Bryld, 2003), UA has emerged as a key strategy for reducing cities' ecological footprint (Nelson, 1996), recycling urban 'wastes' (Kutiwa *et al*., 2010), greening the city and reducing pollution (Mougeot, 2006). Urban agriculture also aids in containing urban sprawl that threatens food security through taking up agricultural land (Gu *et al*., 2019); protecting biodiversity, building resilience to climate change, and reducing dependency on the global food market (FAO, 2012; Lal, 2020a).

However, UA can be associated with health and environmental risks as many urban soils are often degraded and polluted (Adimalla, 2019) (detailed information on this is given in section 2.3). For example., application of large amounts of soil fertility amendments such as raw household and municipal wastes and sewage may lead to potential contamination of crops with faecal coliforms of human and animal origin (Keraita and Drechsel, 2002; Nyamasoka *et al*., 2015). Environmental pollution due to nutrient leakages may also result in ground and surface water pollution (Nyamangara *et al*., 2013), as well as from overuse of pesticides and ignorance of latency periods, especially for leafy vegetable production (Drechsel *et al*., 2000; Sonou, 2001). Uncontrolled UA practices may also proliferate into marginal areas such as steep slopes, gullies, and floodplains, which are prone to land degradation. Thus, due attention is necessary to ensure that urban farming employs techniques and technologies that will safeguard human and environmental health (Birley and Lock, 1998; McDoughall *et al*., 2019).

2.2 Food insecurity and poverty as key drivers of urban agriculture in Zimbabwe

Like the rest of SSA, urban Agriculture in Zimbabwe evolved along with the rising challenges of increased food insecurity and poverty due to lack of livelihood alternatives (Kutiwa *et al*., 2010; Chaminuka and Dube, 2017). By 2030, Africa's urban population is expected to rise to 55.5% of the total population because of high urban growth rates (4.58% per year) compared to other regions (UN-HABITAT, 2006). Urban population in Zimbabwe is currently estimated at 38.6% of the total population (ZimSTAT, 2022), and yet economic growth has stagnated since the early 1990s resulting in high poverty and unemployment (Coltart, 2008; Manjengwa *et al*., 2016; Mhazo and Thebe, 2021). As such, most urban-poor households survive on less than USD $2 per day (Makombe, 2021) and have resorted to practicing UA to supplement their food and incomes (Hungwe, 2006; ZimVAC, 2019). Although this has resulted in high demand for agricultural land and the utilisation of open spaces to grow crops (Musosa *et al*., 2022); the low incomes mean farmers cannot afford to invest in soil improvement technologies to better sustain soils for good crop yields (see section 2.5).

Urban agriculture practices in Zimbabwe are neither planned for nor supported by urban planners and managers in urban land use programs (Mbiba, 1994; Marongwe, 2003). As a result, in many cities in Zimbabwe, agriculture is practised in areas designated for other uses, such as undeveloped residential and industrial stands, open spaces along public roads, railway and power lines, dumpsites, wetlands and catchment areas (Mudzengerere, 2012; Taru and

Basure, 2013; Musosa *et al*., 2022). Although the Harare Combination Master Plan and the Bulawayo Master Plan for 2000-2005 had provisions for urban agriculture to be practised on designated zones (City of Harare, 1992; Bulawayo City Council, 2000), these were never formulated into by-laws. Further to that, the Nyanga Declaration on UA in Zimbabwe (Taru and Basure, 2013) and the Harare Declaration by Ministers of Local Government in Eastern and Southern Africa acknowledged the immense contribution of UA to urban food security, poverty reduction, economic development, and sustainable urban development (Hungwe, 2006), the policies were never formulated into by-laws. This contrasts with other cities in SSA, such as Kampala (Uganda), Cape Town (South Africa), Addis Ababa (Ethiopia) and Nairobi (Kenya), which have administrative units to deal with Food and Agriculture in their local governments (City of Cape Town, 2007; Lee-Smith and Lamba, 2015). As such, UA in Zimbabwe is still regarded as illegal due to lack of relevant supporting institutional frameworks (Taru and Basure, 2013; Chaminuka and Dube, 2017). Thus, there are always conflicts amongst urban farmers and between urban farmers and the local authorities (Mushayavanhu, 2003), hampering efforts towards sustainable urban agriculture practices (**Figure 2.1**).

Insert A

Council to slash maize fields

Emmanuel Kafe

HARARE City Council plans to slash maize planted on undesignated land amid concerns chemicals from fertilisers used by farmers are contaminating the city's water sources.

There are also fears over alleged crimes taking place under the cover of the maize fields.

City of Harare's public relations manager Mr Michael Chideme warned residents last week that "the law will take its course".

Most of the crop planted late last year, has reached tasseling stage and will be ready for harvesting soon.

City by-laws prohibit planting crops on undesignated land.

"The law will take its course on people who are growing crops on undesignated areas in the city," said Mr Chideme.

He could not divulge when the exercise, which is likely to be controversial, would begin. An official in the city's urban planning department told *The Sunday Mail* that there were growing concerns over the environmental damage caused by haphazard urban agriculture.

"There were deliberations within council and it was agreed that all maize planted in areas which are not designated for agriculture must be removed," said the official, who elected to remain anonymous.

"Council is now concerned with the environmental degradation caused by haphazard urban agriculture."

Harare Residents Trust (HRT) director Mr Precious Shumba said the city should clamp down on urban agriculture before planting begins.

"If the City of Harare did not approve of urban agriculture in undesignated places, they should have deployed sufficient manpower to warn residents against tillage in those areas," said Mr Shumba.

"They should not have allowed the crop to reach maturity stage.

"The city should just leave the crop as it is because it is contributing to household food security for struggling urban families.

"Harare should develop a clear programme of support to smallholder farmers and designate land for urban farming."

Environmentalist Mr Kindness Maridza of Conserve Africa said urban farming has resulted in contamination of raw water sources.

"There is increased siltation of our rivers or raw water sources, in particular Lake Chivero, Seke and Harava dams, thereby reducing their capacity," said Mr Maridza.

"This is mainly caused by urban agriculture.

"Some residents are using fertilisers, which affect water treatment processes, making water production more expensive."

Urban farming is major a source of food security for some households in cities around the country.

Children walk past a maize crop growing on garbage dumped on the roadside in Budiriro, Harare. — Picture: Believe Nyakudjara

Insert B

Figure 2.1: Local newspaper extracts showing escalation of council-urban farmer conflicts. Insert A shows a thriving maize crop grown behind the signage prohibiting urban cultivation in Harare, Zimbabwe. Photo adopted from the Sunday Mail dated 07 February 2021(https://www.sundaymail.co.zw), Insert B shows an article where the Harare city council was proposing to slash down maize crops in Harare. Article adopted from The Herald, 13 November 2013 (https://www.herald.co.zw/council-to-slash-maize/).

2.3 General status of soils in urban agroecosystems

Urban environments are heterogenous and largely differ from other agroecosystems e.g., rural smallholder-farming systems, as they often exhibit altered physical, chemical, and biological characteristics in comparison to local non-urbanised soils (Kaye *et al*., 2006). Many urban soils are often associated with degraded and possibly polluted soils (Meuser, 2010; Adimalla, 2019), low soil Organic Carbon (SOC) (Craul, 1999; Bradley *et al*., 2005) and biological activity (Lorenz and Kandeler, 2005; Scharenbroch *et al*., 2005) compared to non-urban soils in forests or croplands. The physical properties of urban soils are mainly influenced by compaction because of engineering works to transform land into urban areas. Such soils often have high bulk densities (Short *et al*., 1986; Jim, 1998). Urbanisation also results in alteration of the soil chemical characteristics (Groffman *et al*., 1995), resulting in elevated levels of toxic heavy metals such as lead (Pb), arsenic (As) and cadmium (Cd), particularly in soils irrigated with sewage waste (Mapanda *et al*., 2005; Balkhair and Ashraf, 2016). Soil contamination by organic residues such as polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethans (DDTs) and phthalate esthers (PAEs) due to persistent pesticide residues and irrigation by wastewater from biological industrial effluents have also been reported (Chen *et al*., 2005; Cai *et al*., 2008; Menefee and Hettiarachichi, 2018). Alterations in the physical and chemical properties of these soils have a net effect on the soil biological environment (Steinberg *et al*., 1997; Pavao-Zuckermann and Coleman, 2007), ultimately shifting ecosystem functions and processes related to biogeochemical cycling (Pavao-Zuckerman and Coleman, 2005; Kaye *et al*., 2006). In densely built areas, alterations in hydrological regimes because of the heat island effect, can strongly affect soil microclimates, the availability of water, and activity of soil organisms (Oke, 1995; Brazel *et al*., 2000). For these reasons, disturbed urban soils are generally considered to have a low physical and chemical quality, regarded not suitable for crop production (Jim, 1998). However, remediation can be done by adding soil amendments like compost, mulch, and engineered media that can reduce the bioavailability of some heavy metals and organic pollutants while improving soil health and microbial biodiversity (Lal, 2020a). Nevertheless, urban wastes, which can be significant environmental hazards and sources of pollution, can become resources (Lal, 2020a; Gwandu *et al*., 2022), thereby developing a cyclical economy in line with UN Sustainable Development Goal number 12 that relates to responsible production and consumption. For example, Water Treatment Residual (WTR), a waste-product from clean water treatment is an essential amendment to restore soil health, enhance productivity, and improve the nutritional quality of food grown in urban agriculture systems (Gwandu *et al*., 2022). By improving soil health, the use of WTRs indirectly impacts on all SDGs linked to soil health (Keestra *et al*., 2016) and this is discussed in detail in chapter 8 section 8.3.

2.4 Soil degradation and soil resilience

Soil degradation is the loss of the intrinsic physical, chemical, and /or biological qualities of soil either by natural or anthropogenic processes, which result in the diminished capacity of soil to perform its important **ecosystem services** (Nunes *et al*., 2020). Soil **ecosystem services** include but not limited to the soils' provision of food, fuel, and fibre (Pozza and Field, 2020); nutrient cycling, OM decomposition, pollutants degradation, pathogen control; water storage and purification (Pereira *et al*., 2018; Pozza and Field, 2020). On the other hand, **soil health** is defined as the ability of soil to deliver essential ecosystem services a subset of which includes food security and climate change adaptation and mitigation (e.g., Johnson *et al*., 2022).

The impact of soil degradation is most severe in SSA (arguably because the soils are so old and lack micronutrients), with greater than two thirds of the land area classified as degraded (Nezomba *et al*., 2015; Stewart *et al*., 2020). Extractive farming practices are the major driver of soil degradation in SSA (Vlek *et al*., 2010; Zingore *et al*., 2021), with climate change e.g., floods and droughts, also contributing (Climate Change Impacts Review Group, 1991). In Zimbabwe, population density and land tenure have also been cited as causes of soil degradation, with physical factors (rainfall characteristics, soil types, and terrain) being of lesser significance (Whitlow and Campbell, 1989). Other anthropogenic causes of soil degradation include inappropriate tillage practices, overgrazing, deforestation, pollution and poor soil and water conservation measures (Diagana, 2003; Titonell and Giller, 2013). Soil degradation can take many forms with four main processes being: physical, chemical, biological, and ecological (Eswaran *et al*., 2019).

- **Physical degradatio**n is distinguishable by changes in the natural composition and structure of the soil (Guto *et al*., 2011; Lal, 2015). Rainfall, surface runoff, floods, wind erosion, tillage, and mass movements are the major causative agents resulting in loss of fertile topsoil thereby declining soil quality. Wind and water erosion contributes to 22% and 25% respectively, of the total share of soil degradation in SSA (Reich *et al*., 2001; Muchena *et al*., 2005), and this is exacerbated by tillage which enhance soil structure deterioration and soil redistribution hence accelerated erosion (Van Oost *et al*., 2006). Mouldboard ploughing and hand hoeing, commonly used forms of tillage in smallholder urban farming systems in SSA are often associated with land degradation and excessive loss of nutrients (Fowler and Rockstrom, 2001; Knowler and Bradshaw, 2007).

- **Chemical degradation** in the broadest sense, involves depletion of essential nutrients for plant growth, accumulation of salts and heavy metals in toxic amounts, reduced cation exchange capacity (CEC), pH, increased aluminium (Al) or manganese (Mn) toxicities, calcium (Ca) or magnesium (Mg) deficiencies and leaching of nitrates (NO_3-N) (Lal, 2015). These chemical factors may bring forth irreversible loss of soil nutrients and loss of productivity.
- **Biological degradation** includes depletion of the soil organic C (SOC) pool, which in turn leads to decline in population, diversity and activity of flora and fauna, a reduction in soil C sink capacity, and increased greenhouse gas (GHG) emissions from soil into the atmosphere (Lal, 2015), contributing to global warming. Also, the overuse of chemical pesticides, herbicides and fertilisers results in alteration of the soil microbiome (Johnson *et al*., 2022).
- **Ecological degradation** on the other hand, reflects a combination of the other three, and leads to disruption in ecosystem functions such as elemental cycling, water infiltration and purification, perturbations of the hydrological cycle, and a decline in net biome productivity (Lal, 2015).

As soil structure underpins all the degradative processes (Lal, 1997), there is need for targeted efforts towards soil structure improvement (Johnson *et al.*, 2022) to avert degradation and enhance soil productivity. This study seeks to enhance soil structure built up through additions of water treatment residual (which is organo-mineral) in combination with locally available organic resources and inorganic fertiliser. Taking cognisance that wind and water erosion leads to loss of not only soil OM but also minerals, this study seeks to build new soil by adding both OM and minerals (Saidy *et al*., 2012; Johnson *et al*., 2015). Increased use of inorganic fertiliser and balanced nutrient management in combination with various organic matter inputs collectively termed integrated soil fertility management (Mapfumo, 2009; Vanlauwe *et al*., 2010), offer the best prospects to reverse soil degradation in SSA (Nezomba *et al*., 2015; Zingore *et al*., 2015) which may proffer **soil resilience**.

Under favourable conditions, a resilient soil can restore its life support processes although this is dependent on soil type, topography, vegetation, climate, land use, technological innovations, and input management (Herrick *et al*., 1996; Lal, 1997). As **soil resilience** is affected by both inherent and dynamic soil characteristics, it varies substantially from one area to another (MacEwan, 1997), e.g., under similar climatic conditions, clayey soils are more resilient than sandy soils (Prasad and Power, 1997; Neal *et al*., 2020). Likewise, the drier the climate, the less resilient soil systems are following various disturbances (Lal, 1997). If a soil is degraded beyond some critical level, its life support processes are grossly impaired, with loss of resilience (Tittonell *et al*., 2012). However, appropriate land use and judicious crop management have a favourable effect on **soil resilience** and can restore **soil ecosystem** functions such as productivity and nutrient cycling (Zingore *et al*., 2008; Nezomba *et al*., 2015).

2.5 Current soil fertility management practices in urban agroecosystems in Zimbabwe: an entry point for using water treatment residual.

As in most parts of Zimbabwe, many of the soils in urban agroecosystems are derived from granitic rocks with inherent deficiency in key essential nutrients (Nyamangara *et al*., 2000). In addition, maize mono-cropping which is commonly practised result in nutrient mining as crop residues are rarely returned to the soil. This means that nutrients need to be added in the form of organic and /or inorganic fertilisers to maintain the soil fertility. Maize farmers apply inorganic fertiliser at a rate of < 110 kg ha^{-1}, against a blanket recommendation of 300 kg ha^{-1} resulting in very low yields of < 1 t ha^{-1} (Nyamasoka *et al*., 2015). Most farmers have cited high costs of mineral fertilisers as the major reason for its low use. For instance, a 50 kg bag of compound D fertiliser is often pegged at US$38, a figure beyond the reach of many farmers who survive on less than US$2 per day (Makombe, 2021; https://www.worldbank.org/en/country/zimbabwe/overview#1). Some farmers within urban areas in Zimbabwe use a range of organic nutrient sources including poultry manure, composts, domestic sewage sludge and cattle manure (Shumba *et al*., 2014). However, farmers are often faced with challenges of getting sufficient quality organic inputs (Mapfumo and Giller, 2001; Shumba *et al*., 2014) and often apply no more than 5 t ha^{-1}. $year^{-1}$ (Zingore *et al*., 2007). This has resulted in a decline in soil organic matter (SOM) content endangering soil fertility and enhancing erosion. Marondedze and Schütt (2020) predicted soil losses of 13.2 t ha^{-1} yr^{-1} between 1984 and 2008 in Epworth, a residential area located in the South-eastern part of the capital city, Harare. This figure is anticipated to have increased over the years with increase in urban agriculture practices. Accordingly, identifying other organic nutrient sources could be key to sustain these soils.

A promising solution to this problem, and problems related to the growing production of wastes in urban areas, might be the utilisation of urban wastes as soil amendments (De Bon *et al*., 2010; Gwandu *et al*., 2022). One such candidate is aluminium-water treatment residual (Al-WTR), a by-product of clean water treatment. The use of Al-WTR for soil improvement is increasingly becoming an important alternative disposal route (Dassanayake *et al*., 2015; Turner *et al*., 2019). This could be an advantage for African urban settings, firstly, because the generation of Al-WTR in most African cities is set to increase due to the increased demand for clean water as urban population grows (Saghir and Santoro, 2018), guaranteeing continued supply of Al-WTR. Secondly, urban agriculture practices are on the rise as urban dwellers tackle food insecurity and unemployment (Nkrumah, 2019), creating a potential niche for the Al-WTR to counteract shortages of organic nutrient sources (Mapfumo and Giller, 2001; Gwandu *et al*., 2022). In addition, Al-WTR is organo-mineral and the additions both organic and mineral components to the soil can stabilise OM (Saidy *et al*., 2012; Johnson *et al*., 2022), with potential to enhance the soils' drought and nutrient resilience. The reclamation of Al-WTR for use as a soil improvement technology (SIT) will enable re-use of nutrients loaded into water bodies for soil fertility and soil structural improvement (Titshall and Hughes, 2005), at the same time enabling water treatment plants to get rid of this waste-product in a sustainable manner.

2.6 Water Treatment Residual

Water treatment residual (WTR), in this instance Al-WTR, which is depicted in **Figure 2.2**, is a by-product of the coagulation-flocculation-sedimentation process of drinking water treatment (Turner *et al*., 2019). During the purification process of drinking water, coagulants are added to aid in settling suspended particles from raw water resulting in the formation of the WTR. Substances commonly added as coagulants include aluminium sulphate [$Al_2\ (SO_4)_3 \bullet 14H_2O$] or iron salts (e.g., $FeCl_3.6H_2O$, $FeCl_2$, $FeSO_4.7H_2O$) and organic polymers for the raw water flocculation (Sales *et al*., 2011; Turner *et al*., 2019), with the resultant waste sludge denoted as Al-WTR, Fe-WTR, or organic polymer-WTR, respectively (Heil and Barbarick, 1989). Additionally, activated charcoal is added for odour control, silica for taste improvement, lime for pH correction and chlorine gas or ozone for water purification (Hyde and Morris, 2000; Matilainen *et al*., 2010). Among the coagulants, aluminium sulphate (also referred to as alum) is the commonly used coagulant for water pre-treatment process due to its availability, effectiveness, easy to use and cheap cost supply (Zhao *et al*., 2011; Maiden *et al*., 2015), making Al-WTR the most extensive by-product of water industries globally including in Zimbabwe. Apart from coagulant residues, WTR contains flocculated material from reservoirs, including clay, sand, silt, OM, and mineral particles (Matilainen *et al*., 2010; Dassanayake *et al*., 2015). Humic substances if present in the water, impart turbidity and colour (Titshall *et al*., 2007), with heavy metals often present in some instances (Titshall and Hughes, 2005). If present however, these heavy metals are not readily bioavailable (Elliot *et al*., 1990; Titshall and Hughes, 2005) due to being tightly bound to mineral surfaces.

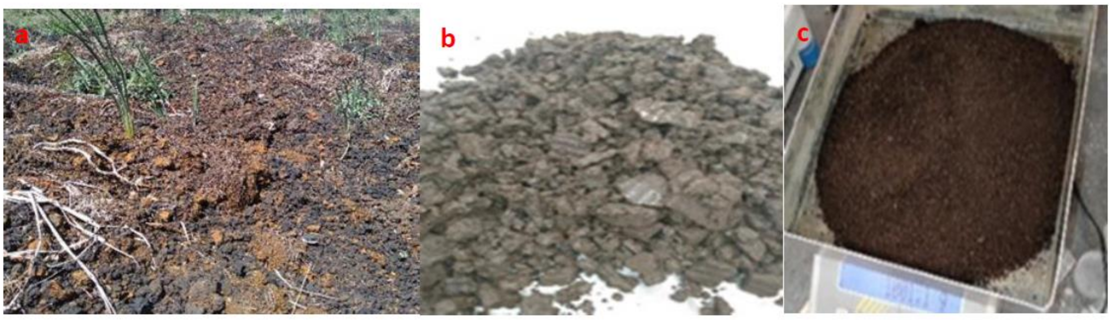

Figure 2.2: Physical appearance of Al-WTR (sampled from Prince Edward Water Treatment Plant, Zimbabwe) under different storage or processing conditions. a- Al-WTR in landfill, b-wet Al-WTR after dewatering, c-dried and ground Al-WTR.

2.6.1 Production trends of water treatment residuals

Water treatment plants (WTP) the world over produce various amounts of WTRs depending on demand, local standards, and water quality. Information on the amount of WTRs generated from water treatment plants is generally scarce and not well documented due to varying reporting requirements in different countries. Data shown in **Figure 2.3** is drawn from a few selected countries with publicly available data on WTR production trends.

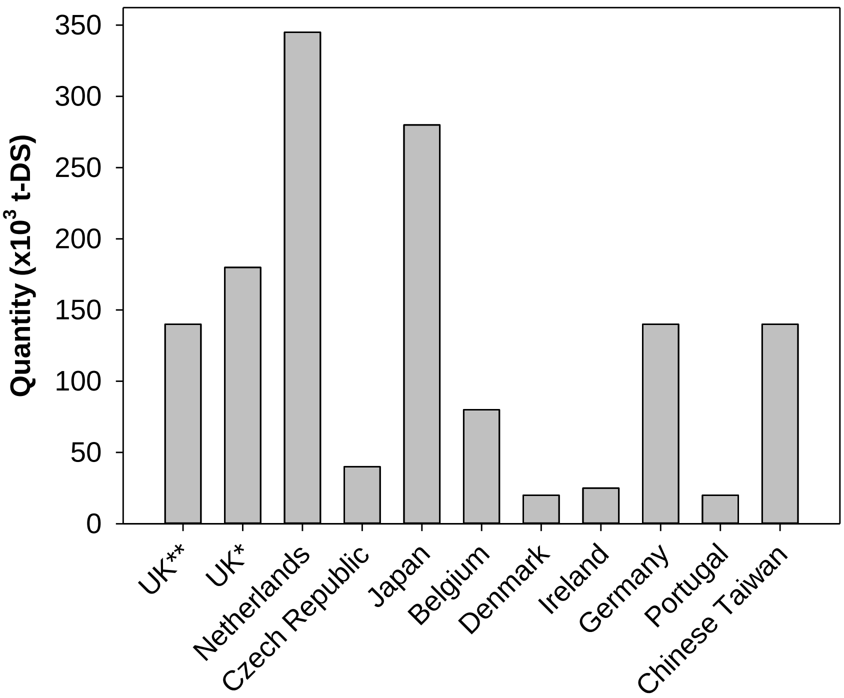

Figure 2.3: Annual water treatment residual production figures (dry matter basis) from selected countries. Figure re-drawn from Turner et al. (2019). *2003, **2013 data.

Even though literature estimates global water treatment residual production rates from standard WTPs to be over 10 000 t day^{-1} (Gibbons and Gagnon, 2011; Ahmad *et al.*, 2016), this figure is likely to have been surpassed. Future production trends are anticipated to increase due to industrial development, regulatory changes, and the increasingly variable raw water quality associated with climatic changes (Delpla *et al.*, 2009). Even though WTR production trends from SSA including Zimbabwe are missing, they are expected to rise due to population increases and urbanisation, which will likely increase the demand for domestic water, hence an increase in WTR production.

However, the disposal of WTRs has become a concern due to the controversy surrounding their disposal into water sources and the limited area available for their disposal into landfills (Elliott *et al*., 1990; Maiden *et al*., 2015) as well as the high costs associated with their disposal. In the Netherlands cost of disposal was estimated to be around £30–£40 million per year (Evuti and Lawal, 2011) whilst in Australia disposal costs were estimated at Aus $130 per ton culminating to an approximate total cost of over $6.2 million per annum (Maiden *et al*., 2015) and about £5.5 million annually in the United Kingdom (Keeley *et al*., 2014). Beneficial reuse of WTR through land application may thus reduce costs associated with its disposal, in addition to rebuilding soil health.

2.6.2 Physical characteristics of Al-WTR

The physical characteristics described herein are based on general trends due to the inherent variability of WTR characteristics caused by its provenance being dependent on geological, environmental, and anthropogenic factors. A comprehensive review of a range of Al-WTR physico-chemical properties was adopted from Dassanayake et al. (2015) and is shown in **Table 2.1**. The characteristic nature of WTR (both physical and chemical) is generally dependent on the source water quality, coagulant type and the additional chemicals dosed for water treatment (Dassanayake *et al*., 2015; Ahmad *et al*., 2016; Turner *et al*., 2019), and these differ from time to time even within the same treatment plant (Lin and Green, 1987).

Studies of WTRs using scanning electron microscopes have revealed that they are very porous and have a range of particle sizes (Ippollito *et al*., 2011; Dassayanake *et al*., 2015). The particle size distribution of previously analysed WTRs is variable (**Table 2.1**), partly is because of the difficulty in analysing organo-minerals using traditional particle size analysis techniques. The sand content was recorded within the range 60-69%, with silt occupying the median ranges of between 17 and 23%, while clay ranged from 14 to 16%. The moisture content of the wet sludge is generally above 80% (w/w ratio) (Tantawy *et al*., 2015) before the dewatering process whilst, particle densities of most WTRs are in the ranges between 2 to 2.4 g.cm^3 (Titshall and Hughes, 2005). Most WTRs are amorphous in nature due to lack of a crystalline structure. However, X-ray diffraction studies of WTRs have confirmed the presence of individual minerals including quartz, feldspar, calcite, illite, kaolinite and others (Ahmad *et al*., 2018; Turner *et al*., 2019). Particle size distribution and mineralogy is dependent on the geology of the catchment as well as treatment process effects. The WTRs also have a large surface area 100 to 120 m^2.g^{-1} (Markris *et al*., 2005), enabling them to absorb and immobilise various trace elements and macronutrients such as P (Makris *et al*., 2005; Babatunde *et al*., 2008; Bai *et al*., 2014).

2.6.3 Chemical characteristics of Al-WTR

The pH of Al-WTR show variation from values as low as pH 5.1 up to higher values of pH 8.0 (**Table 2.1**). The Zimbabwean Al-WTR used in this study was recorded at pH 5.7 (Gwandu *et al*., 2022). This range of pH values is generally suitable for plant growth (McCauley *et al*., 2009). For example, Maize (*Zea Mays* L.) which is commonly grown in Zimbabwe optimally thrives at pH 5.5. Hastings and Dawson (2012) have affirmed that WTRs with pH > 6 favourably modify soil pH, creating favourable conditions for microbial and plant growth.

The electrical conductivity values (0.36-1.66 mS cm^{-1}) of WTR are reported to be well below the threshold values for salt sensitive crops. The critical conductivity levels in which salt sensitive crops can grow well is estimated at 4.0 mS cm^{-1} (Brady and Weil, 2002). The Al-WTRs also contain a significant amount of carbon (C) and organic matter (OM), which can boost soil physico-chemical properties. Total C around 30 g kg^{-1} in WTR, can contribute to good aggregation and water holding capacity in WTR-amended soils (Kerr *et al*., 2022).

Titshall and Hughes (2005) reported total nitrogen (N) levels of up to 10 g kg^{-1}, while P levels are typically low, ranging between 3.13-3.5 g kg^{-1} (Dassayanake *et al*., 2015). However, the elevated cation exchange capacity (CEC) of 13 to 56 cmol kg^{-1} compared to soils' typical range of 3.5 to 35.6 cmol kg^{-1} (Dassayanake *et al*., 2015) in the WTRs defines its potency to supply cationic nutrients i.e., calcium (Ca), magnesium (Mg) and potassium (K) for plant growth and development (Dayton and Basta, 2001). Aluminium (Al), which is the primary metal constituent in Al-WTR ranged from 27 – 153 g kg^{-1} (**Table 2.1**). Most heavy metal levels reported in literature for WTRs were significantly lower than that of the regulatory levels for the toxicity characteristic leaching procedure (TCLP) (USEPA, 1993) and the European Community guidelines (Tóth *et al*., 2016) (see Chapter 5, section 5.4). The TCLP guidelines are widely used to differentiate municipal and industrial solid waste as hazardous or non-hazardous for landfilling. Dayton and Basta (2001), Elliot et al. (1990) and Wang et al. (2014) also affirmed these findings in similar studies investigating the average level of metals such as cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), arsenic (As) and barium (Ba) found in waterworks residues.

Table 2.1: Summary of average physicho-chemical characteristics of alum sludge as presented by Dassayanake et al. (2015).

Parameter	Range	ASCE 1996	Regulatory limit[a] (mg.kg^{-1})
pH	5.12-8.0	7.0-8.8	
EC (mS.cm^{-1})	0.36-1.66	0.6	
CEC (cmol.kg^{-1})	13.6-56.5	ND	
Sand (%)	60.4-69	ND	
Silt (%)	17-23	ND	
Clay (%)	14-16.6	ND	
Total Carbon (g.kg^{-1})	127-188	ND	
Organic matter (g.kg^{-1})	63-144	ND	
Total N (g.kg^{-1})	4.0-4.8	4.95	
NH4-N (g.kg^{-1})	0.022-0.263	0.16	
NO3-N (g.kg^{-1})	0.035-0.298	0.003	
Total P (g.kg^{-1})	3.13-3.5	ND	
Total Al (g.kg^{-1})	27-153	60	Not defined
Total Fe (g.kg^{-1})	4.87-372.2-11.7	52.75	Not defined
Total Ca (g.kg^{-1})	2.4-7.9	20.82	Not defined
Total Mg (g.kg^{-1})	0.8-2.99	ND	Not defined
Total Mn (g.kg^{-1})	53.3-160	0.385	Not defined
Total Zn (mg.kg^{-1})	35-624	1050	2800
Total Cu (mg.kg^{-1})	10.9-60	270	1500
Total Ni (mg.kg^{-1})	2.5-69	38	420
Total Pb (mg.kg^{-1})	19.1-81	80	300
Total Cr (mg.kg^{-1})	0.12	50	1200
Total Cd (mg.kg^{-1})	0.02-0.46	5.15	39
Total Hg (mg.kg^{-1})	15.89-16.41	1.5	17
Cl^- (mg.kg^{-1})	8.57-9.73	ND	Not defined
SO_4^{2-} (mg.kg^{-1})	8.57-9.73	ND	Not defined

ASCE-American Society of Civil Engineering, ND-Not Determined; [a]USEPA-Pollutant limits for meeting land exceptional quality criteria (USEPA, 1993)

2.7 Use of Al-WTR as a soil amendment in crop production: opportunities and constraints

According to some, as WTRs predominantly contain sediment and humic substances from the raw water, they are similar to fine-textured soils and may be suitable for use as soil substitutes (Elliott *et al*., 1990; Dayton and Basta, 2001). However, the production chlorine or similar treatment processes mean that WTR has little or no in situ microbiome (Titshall and Hughes, 2005; Stone *et al*., 2021) and the Al or Fe hydroxide content means that the OC in WTRs is largely recalcitrant. According to British standards BS 3882, WTRs are classified as 'economy grade-high clay content' soil indicating their possible use as soil or in soil making materials (Owen, 2002). Apart from its soil like nature, WTR contains residual mineral particles of Al or Fe oxides depending on the type of coagulant used. Al or Fe oxides aid in soil structural rearrangement by proffering cementing effect, which contributes to soil aggregation (Elliot *et al*., 1990; Xue *et al*., 2019). It is also documented that the oppositely charged Al and Fe oxide colloidal particles tend to flocculate the soil silicate particles, and upon dehydration, the Al and Fe hydroxides act as cementing agents between soil particles (Elliot *et al*., 1990; Elliot and Dempsey,1991). This imparts favourable structural properties to soils such as reduced swelling, water retention, aeration and increased aggregate stability (Elliot and Dempsey, 1991; Kim *et al*., 2002). Furthermore, some studies have shown that WTRs favourably modify the pH of soils creating favourable conditions for microbial and plant growth (Hastings and Dawson, 2012; Gwandu *et al*., 2022). The potential to increase plant available nitrogen (N), total organic C, Calcium (Ca), magnesium (Mg), zinc (Zn), copper (Cu) and iron (Fe) due to WTR land application is well-documented (Clarke *et al*., 2019; Gwandu *et al*., 2022) and has been highlighted in section 2.5.2. These properties provide an incentive to harness WTR as a Soil Improvement Technology (SIT) particularly for nutrient-poor soils in SSA where organic materials are in short supply.

The major setback highlighted for soil application of WTRs which are rich in amorphous Al or Fe oxides, is their potential to adsorb labile P, making it unavailable for plant uptake. Results from P fractionation experiments showed that the addition of WTRs to soil resulted in a decreased labile P fraction and an increased less-soluble chemisorbed Al- and Fe-bound P fraction (Jonasson, 1996; Cox *et al*., 1997). The mechanism underpinning this is that P becomes fixed to Al-OH groups through inner-sphere complexation, which occurs when phosphate attaches to the surface of alum sludge and becomes directly bound to the surface via an oxygen atom as opposed to through a hydroxyl group. As a result, phosphate is adsorbed via a strong chemical bond (precipitation) reaction with the Al ions, as explained by Equation (2.1) (Makris *et al*., 2005; Babatunde *et al*., 2008; Bai *et al*., 2014) and is described in detail in section 2.8.2.

$$2 \equiv \mathrm{Al} - \mathrm{OH} + \mathrm{H_2PO_4^-} \rightleftharpoons (\equiv \mathrm{Al})_2\ \mathrm{HPO_4} + \mathrm{H_2O} + \mathrm{OH^-} \qquad (2.1)$$

Dayton and Basta (2001) and Hsu and Hseu (2011) confirmed reduced soil P availability at high application rates of Al-WTRs (> 10%), causing P deficiency in plants. Heil and Barbarick (1989) also noted severe P-deficiency symptoms in *Sorghum bicolor (L.) Moench* associated with single additions of 2.5% Al-WTR. Nonetheless, they managed to increase the production of the Sorghum by increasing the rate of P fertiliser application. In accord with this, Hyde and Morris (2004) stated that co application of Al-WTR and fertiliser P to agricultural soil may eliminate the problem of P deficiencies for plant growth. However, some studies (Tay *et al*., 2017; Gwandu *et al*., 2022) noted poor plant growth and low biomass in soils amended with > 10% Al-WTR despite P fertiliser addition, highlighting the possibility that high Al-WTR rates can render the soils less ideal for plant growth. Alternatively, co-additions of Al-WTR and compost or other organic amendments such as manure or maize stover residues may help to alleviate this problem (Clarke *et al*., 2019; Gwandu *et al*., 2022, 2023). Clarke et al. (2019) hypothesised that organic amendments may serve as a source of available P, whilst Al-WTR may provide the mineral components to stabilise soil and to improve soil water retention (Hardwick, 2019; Kerr *et al*., 2022). No research has been done on the concept of coapplication of Al-WTR with locally available organic soil amendments such as manure or plant residues in Zimbabwe.

Even though, observations of negative plant responses in sole Al-WTR amended soils have been widely reported, positive plant growth responses are also documented. For example, Elliot and Singer (1988) reported growth of tomatoes (*Lycopersicon esculentum*) in a WTR amended soil. Rengasamy et al. (1980) and Mahdy et al. (2009) have also reported improved soil properties and dry matter yields of *Zea mays* (corn) in fertilised and unfertilised pots amended with WTRs. Although positive plant growth occurred up to certain threshold limits of WTR application in both studies, i.e., threshold WTR application rates of 10 g kg^{-1} (Rengasamy *et al*., 1980) and 30 g kg^{-1} (Mahdy *et al*., 2007) but that also differed with soil type (see Mahdy *et al*., 2007). Alternately, results from field experiments with trees have shown that WTR applications had no effect on P uptake and plant growth (Grabarek and Krug, 1987; Geertsema *et al*., 1994). Based on these findings, it could conversely mean that the effects of soil amendment with Al-WTR seem to vary according to plant species, soil characteristics, and amendment rate. Moreover, most reports on Al-WTR application on different crops were conducted for short-term periods or pot trials in green houses. Therefore, extensive research on Al-WTR field applications is an urgent need to comprehensively establish the effects of utilising Al-WTR as a soil amendment for crop production.

2.7.1 Potential phosphorus transformation in Al-WTR amended soils.

Phosphorus retention in soils occur by three main mechanisms (i) precipitation by Al and Fe oxides, (ii) anion exchange on the surface of Al or Fe oxides in clays and (iii) through formation of inner sphere complex with Al oxides (Ippolito *et al*., 2003; Bai *et al*., 2014; Penn and Camberato, 2019). Under low pH conditions, Fe and Al oxides result in P retention in soils by adsorption and precipitation reactions (Bai *et al*., 2014; Johan *et al*., 2021). The P adsorption mechanism where P ions are mostly adsorbed onto the surfaces of more crystalline clay compounds, sesqui-oxides (Al_2O_3), or carbonates is more dominant when the solution P concentration is low. In contrast, when P concentration is high, soluble P precipitates with metal cations to form Fe and Al phosphates in acidic conditions and Ca and Mg phosphates in alkaline soils (Plante, 2007; Johan *et al*., 2021). The typical reaction between Al and PO_4^{2}- is shown in **Figure 2.4**:

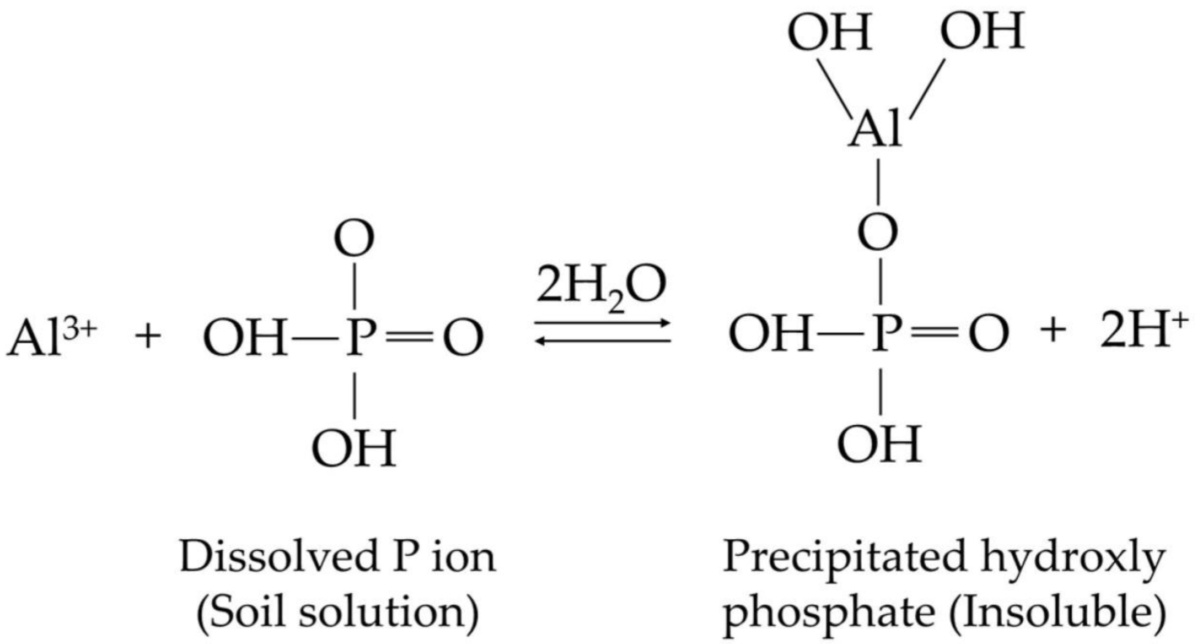

Figure 2.4: Precipitation reaction in the phosphorus fixation process (Johan *et al.*, 2021).

The precipitated hydroxyl phosphates are insoluble; thus, their P content becomes unavailable to plants (Penn and Camberato, 2019; Mahmoud *et al*., 2021). In turn, the anion exchange reaction occurs when negatively charged orthophosphate ions are attracted to positive charges that develop under low-pH conditions on the surfaces of Al or Fe oxides and the broken edges of clay particles (Johan *et al*., 2021) (**Figure 2.5**). Outer sphere complexes are formed through this process. These complexes are formed using weak reversible electrostatic bond because the bonding consists of a water molecule located between the anion and surface (Penn and Camberato, 2019).

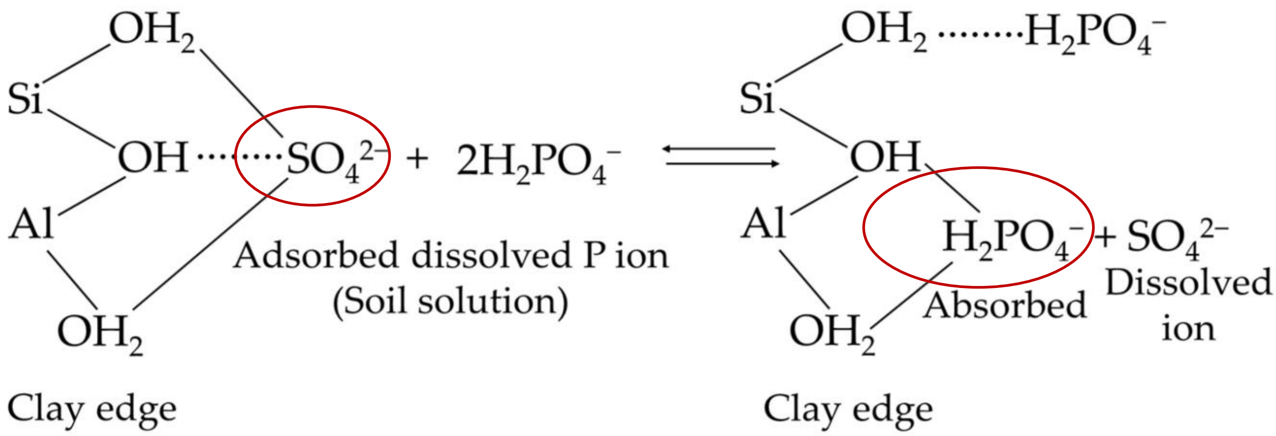

Figure 2.5: Anion exchange reaction in the phosphorus fixation process. Adapted and modified from Johan et al. (2021). The red circles show ligand exchange between sulphate and orthophosphate ions on the edge of an Al oxide surface.

The creation of an inner sphere complex occurs when hydroxyl groups are replaced by orthophosphate ions on the surface of Al or Fe oxides and hydroxides, or the clay surface (**Figure 2.6**). This process is known as specific adsorption or the ligand exchange reaction (Johan *et al*., 2021). In the specific adsorption reaction, a strong covalent bond is formed between the phosphate and a valence unsatisfied surface with no water molecule occurring between the sorbent and sorbate (Penn and Camberato, 2019).

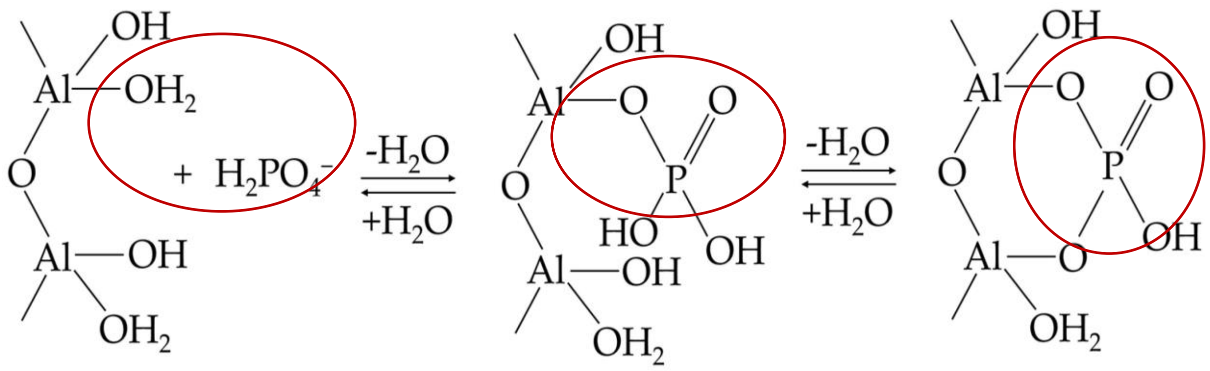

Figure 2.6: Phosphorus adsorption via ligand exchange on aluminium oxides. Adapted and modified from Johan et al. (2021). The red circles show covalent bonds between the Al oxide molecule and the orthophosphate ion as it specifically displaces the hydroxyl ion during the ligand exchange process.

For example, in the first step in **Figure 2.6**, P is bound to one Al ion through an Al-O-P bond, and at this stage P is still labile. In the second step, the second oxygen of the P replaces the second hydroxyl ion, forming a ring structure with two Al ions. After this reaction, the likelihood of P being desorbed into the soil solution is extremely low because it becomes an integral part of the oxide mineral (Brady and Weil, 2002; Johan *et al.*, 2021).

2.7.2 Potential aluminium phytotoxicity in Al-WTR amended soils.

The availability of Al in soils is dependent on soil pH (Kariuki *et al.*, 2007; Gérard, 2016). Aluminium toxicity in plants occur under low (< pH 5) soil pH conditions (Johan *et al.*, 2021). Under neutral and alkali conditions, plants are not normally exposed to Al as it is mainly found in the form of a mineral (aluminosilicates and aluminium oxides); however, at low pH, Al hydrolyses water molecules to form aluminum hydroxide as summed up in equation 2.2. The hydrolysis of Al increases the concentration of hydrogen (H^+) ions in soils, thus increasing soil acidity. Aluminium phytotoxicity results in rapid inhibition of root growth because of the impedance of cell division and elongation, thus reducing water and nutrient uptake, which induces poor plant growth (Johan *et al*,2021).

$$Al^{3+} + 3H_2O \rightleftharpoons Al\,(OH)_3 + 3H^+ \tag{2.2}$$

The addition of fresh Al oxide ions in Al-WTR can potentially increase the possibility of Al phytotoxicity under acidic conditions, particularly for soils in SSA which are highly acidic. However, the application of lime together with Al-WTR can reduce the dissolution of Al in Al-WTR amended soils (Mahmoud *et al*., 2021) whilst co-application with other organic nutrient resources such as compost reduces the availability Al and other heavy metals (Gwandu *et al*., 2022) by providing complexation sites for Al with organic matter functional groups (Johan *et al*., 2021).

2.8 The role of organic nutrient resources in reducing the P fixing capacity in Al-WTR amended soils.

While the use of P fertilisers can enhance availability of P in Al-WTR amended soils (Hyde and Morris, 2004), research has shown that the use of other organic nutrient resources such as compost or manure together with Al-WTR as co-amendments may reduce P sorption associated with Al-WTR (Lin *et al*., 2017; Yang *et al*., 2019; Gwandu *et al*., 2022). Apart from acting as a source of plant nutrients (Oldfield *et al*., 2018; Clarke *et al*., 2019); it has been shown that organic amendments do not only increase the soil P pool, but also influence P adsorption and desorption in soils (Wang and Liang, 2014; Gwandu *et al*., 2022). It is suggested that the decomposition products of OM (humic and fulvic acids) compete for positively charged sorption sites (e.g., Fe), on mineral surfaces with P and thus results in lower P sorption (Ohno and Erich, 1997; Lin *et al*., 2017; Yang *et al*., 2019). Another mechanism could be that the OM forms complexes with surface-bound Al or Fe to form soluble organic-metal compounds causing release of the previously adsorbed P (Yan *et al*., 2016). The contributions of organic matter in reducing P sorption in soils is summarised in **Figure 2.7** (Johan *et al*., 2021).

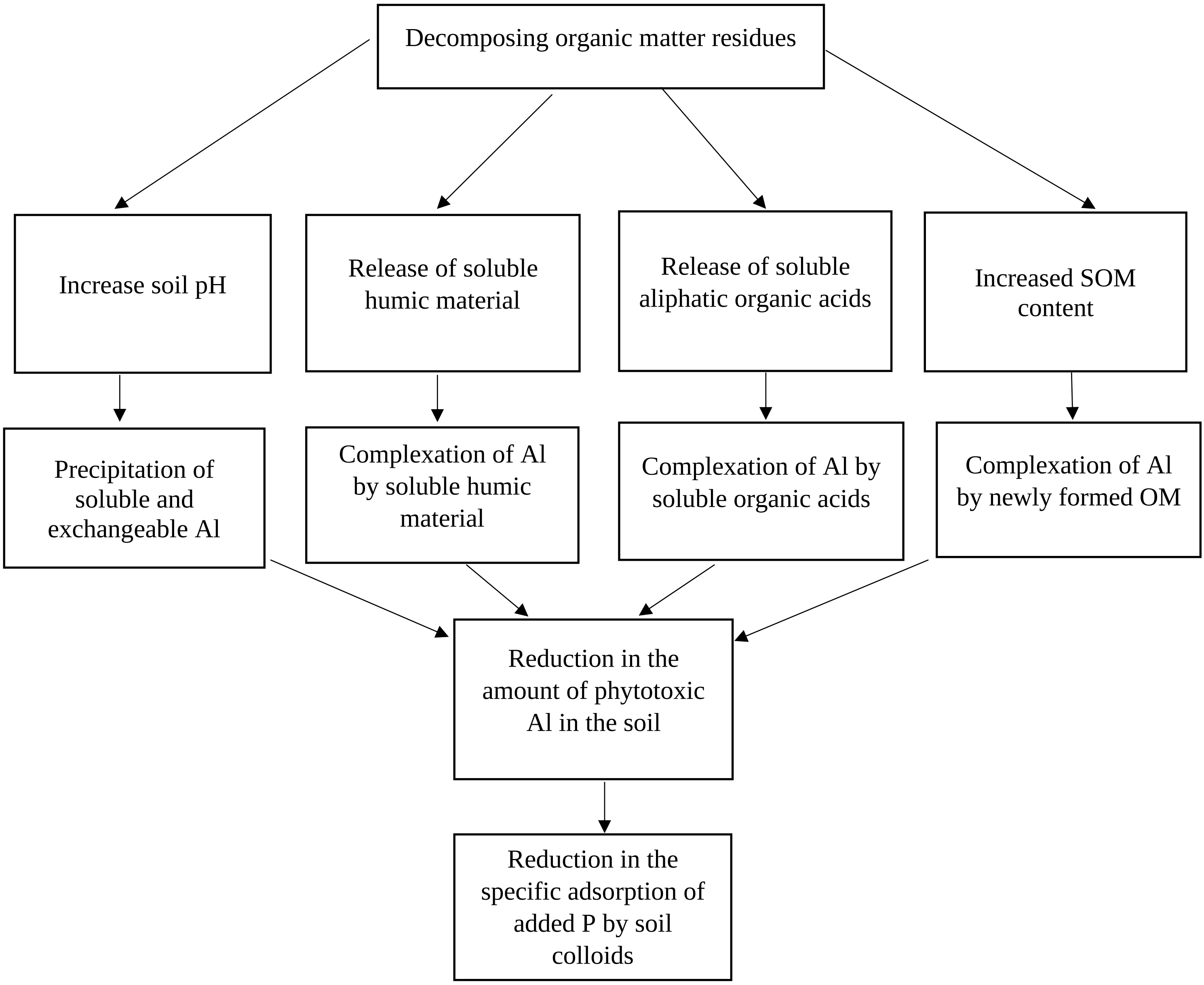

Figure 2.7: A conceptual model of major processes that lead to a reduction phytotoxic Al present in the soil and increased P availability when organic amendments are added to the soil (Adapted, modified, and redrawn from Johan *et al*., 2021).

While this synergy (Al-WTR plus organic matter) augments nutrient retention in particular P, the Fe and Al cations in the WTR are proven to stabilise soil aggregates (Rengasamy *et al*., 1980; Xue *et al*., 2019|), protecting the soil against wind and water erosion. No research has been done on the concept of co-application of Al-WTR with locally available organic soil amendments, such as manure or plant residues, in Zimbabwe.

Chapter 3

3.0 General materials and methods

3.1 Study sites

The field experiment was carried out at Domboshava Training Centre (17°36ʹ S; 31°08ʹ E; 1542 m above sea level), Mashonaland East province in Zimbabwe. Domboshava Training Centre is located just 30 km Northeast of the capital, Harare in Zimbabwe (**Figure 3.1**). Domboshava training centre is surrounded by peri-urban and communal settlements. The area is typified by a sub-humid climate (agro-ecological region II) receiving an annual rainfall of > 750 mm between November and April (Mtangadura *et al*., 2017). The soil at Domboshava is a granite-derived deeply weathered sandy clay loam composed of 730 g kg^{-1} sand, 50 g kg^{-1} silt, and 220 g kg^{-1} clay, classified as Haplic Lixisol (WRB, 2006) or Paraferallitic 6G (Zimbabwe soil classification) (Nyamapfene, 1991) and these are the dominant soils in smallholder farming systems of Zimbabwe (see Table 2.1). The soils exhibit low inherent fertility especially nitrogen (N), phosphorus (P), sulphur (S) and Zinc (Zn), low organic carbon and low water holding capacity (Nyamapfene, 1991). These soils are known to readily compact and crust under natural rainfall, are prone to runoff and thus are highly drought sensitive. The soils found at Domboshava are typical of soils in major smallholder farming systems of Zimbabwe and most parts of Southern Africa (Nyamapfene, 1991). As such, trial results are applicable to similar urban agroecologies across Southern Africa. Natural vegetation consists of disturbed remnants of miombo woodlands dominated by *Brachstegia spiciformis, B. boehmi, Uapaca kirkiana* and *Julbernadia globiflora* tree species. Domboshava Training Centre is Government-owned and set primarily for research and field-testing of agricultural technologies.

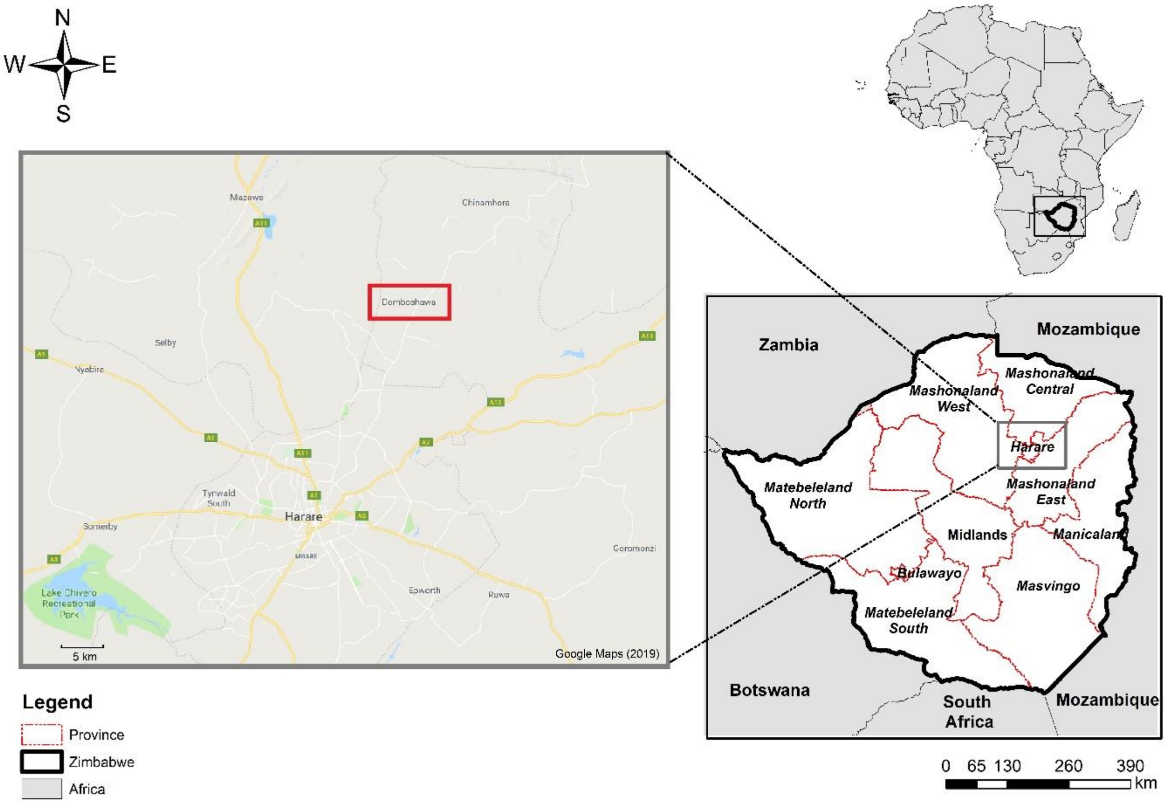

Figure 3.1: Map showing location of Domboshava Training Centre

Table 3. 1: Dominant soils of Zimbabwe

Soil type/group	Coverage and land use	Properties	Reference
Regosols (Arenosols[†])	• Found in the Western parts of Zimbabwe and South-Eastern parts of the country. • Covers 14.1% of total land area; 7.8% under cropland. • Mostly utilised for commercial forests but can sustain production of pumpkins and watermelons (*Citrullus lanatus*), sorghum (*Sorghum bicolor*), millets (*Panicum miliaceum*), and maize (*Zea mays L.*) with enhanced nutrient management.	•Characterised by very low nutrient reserves, relatively high permeability and low water holding capacity. •Very deep sands often >70% sand (0.05-2mm) and <15% clay (< 0.002 mm). •Characterised by very low pH often < 6. •< 10g kg-1 carbon.	Thompson & Purves (1978); Hartemink & Huting (2008).
Lithosols (Leptosols[†]; Entisols & Inceptisols[§])	• Occurrence mainly in the low rainfall areas of the northern and north-western parts of Zimbabwe. • Due to their shallowness, Lithosols are not arable and are mostly utilised as game reserves and national parks.	• Mostly refers to shallow soils with a depth of ≤ 25 cm overlying hard or partially weathered rock. • They vary widely in soil reactions, clay content and morphology depending on parent material. • For example, Mafic-derived Lithosols have more clay content than those derived from siliceous material.	Thompson & Purves (1978); Nyamapfene (1991)

Table 3.1 (continued)

Soil type/group	Coverage and land use	Properties	Reference
Vertisol	• Support production of cotton (aka black cotton soils) and irrigated wheat	• Are characterised by a loose surface horizon with a well-developed crumb structure which resembles a surface mulch. • Are characterised by a loose surface horizon with a well-developed crumb structure which resembles a surface mulch. • Very active clays with a high clay content (> 60%) consisting of expansive clays, which are characterised by seasonal soil cracking. • They have high levels of calcium and magnesium and carbonates but often require moderate applications of nitrogen fertilisers and micronutrients, particularly zinc. • Deep soils which can extend > 1m. They are mostly very dark grey, brownish-black, or black in colour.	Nyamapfene (1991)
Siallitic (Cambisols & Luvisols[‡]; Inceptisols[§])	• Mainly found in the low rainfall parts of Zimbabwe, south-eastern Lowveld, semi-arid south & south-west & the Zambezi valley. • These areas also experience very high temperatures and high rates of evaporation. • Support production of irrigated wheat & sugarcane and extensive Miombo (*Colophospermum mopane*) woodlands and therefore cattle ranching & wildlife	• Relatively unleached due to little moisture and thus high base status. • EC values not < 35. • They are active clays with a moderate to high clay content	Nyamapfene (1991)

Table 3.1 (continued)

Soil type/group	Coverage and land use	Properties	Reference
Fersiallitic (Luvisols, Lixisosl, Arenosols & Acrisols[ɫ])	• Most extensive in Zimbabwe & extensively used for agriculture purposes. • They occur in high rainfall areas and spans from natural region ii to iv.	• Moderately leached soils of moderate fertility. • Mixed clay • SC values between 6 to 30 and EC values 12 to 35. • Contains mineral reserves & appreciable amounts (up to 20%) of free sesquioxides. • Have relatively low P sorption capacity. • This group consists mainly of red clays but also the silty and the sandy soils derived from granite and sandstone.	Nyamapfene (1991); Thompson & Purves (1978); Sibanda & le Mare (1984)
Paraferrallitic (Acrisols and Lixisols[ɫ]; Ultisol and Oxisol[§])	• Paraferrallitic soils occur at relatively high-altitude areas which receive high rainfall. • Mostly used for tobacco (Nicotiana tabacum) and maize production	• Highly leached soils of the higher rainfall zone > 800 mm per year. • SC not > 6; EC value not > 12 with at least 5% weatherable minerals present. • Most Paraferrallitic soils in Zimbabwe are granite derived, contain up to 30% clay & 8% silt and thus relatively low fertility. • Derived from granite parent material and are therefore rich in potassium feldspars.	Nyamapfene (1991); Thompson & Purves (1978)

Table 3.1 (continued)

Soil type/ group	Coverage and land use	Properties	Reference
Orthoferrallitic (Ferralsols,Ferric Arenosols and Nitosols[ɫ]; Oxisols and Ultisols[§])	• Occur mostly in high rainfall areas (> 1000 mm per year) e.g., the eastern highlands, some parts of Mashonaland East • Mostly used for tea and coffee production, forestry, and dairy farming.	• Formed as a result of deep weathering of underlying rock. • Brightly coloured soils due to high oxide content and good internal drainage. • Relatively low fertile	Nyamapfene (1991)
Sodic	• Occurs mostly in the low rainfall areas of the Save and Zambezi valleys. • Generally used for cattle ranching or wildlife due to undesirable chemical characteristics for arable cropping.	• Exchangeable sodium percentage > 9. • Derived from parent material (particularly) rich in sodium-releasing feldspars. • Characterised by a high proportion of highly dispersible clay fraction with restricted drainage, making them highly susceptible to piping and erosion. High bulk densities in the subsoil making them impenetrable by plant roots and impermeable by water.	Thompson & Purves (1978)

[§] United States Taxonomy; [ɫ]FAO classification

3.2 Research approach and methodological framework

The study combined literature analysis, greenhouse, field, and laboratory experiments. A detailed literature review was done to identify drivers of urban agriculture in Zimbabwe and the legal and institutional frameworks impacting on urban agriculture therein. The study also identified constraints for optimal use of organic and inorganic nutrient resources currently being used by farmers practicing UA. The feasibility of using Al-WTR as a soil improvement technology (SIT) was explored leading to testing of different combinations of organic nutrient resources and Al-WTR on soil physical, biological, and chemical properties and maize growth and productivity in greenhouse, field, and laboratory experiments. In addition, a laboratory experiment was done to understand phosphorus (P) sorption characteristics of a sandy soil co-amended with different ratios of Al-WTR and compost. The best options for rebuilding soil health were then identified. **Figure 3.2** is a methodological framework showing the major activities and outputs of the study.

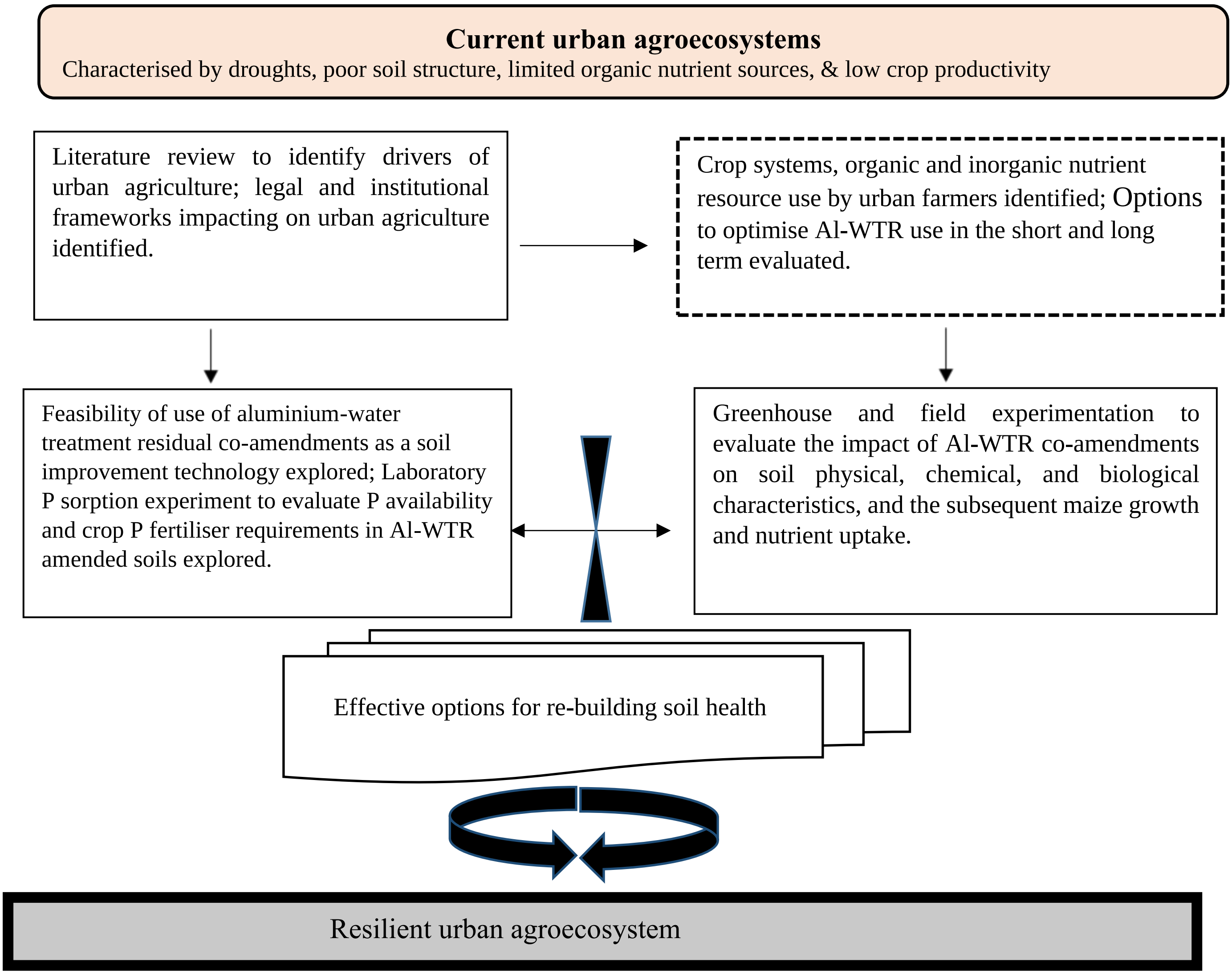

Figure 3.2: Schematic presentation of the research approach and major study outputs.

3.3. Greenhouse Experiment

3.3.1 Experimental set up.

An eight-week greenhouse pot experiment was set up at Durham University, United Kingdom (54°46'22.80"N -1°34'26.40W). The experiment consisted of 12 treatments as shown in chapter 5, **Table 5.1.** A sandy-loam soil which was sampled from Domboshava was shipped from Zimbabwe and used in the experiment. A commercial compost (peat-based Sure Grow) was sourced locally in the UK. The Al-WTR was sourced from Carmoney water treatment Works, Northern Ireland. Al-WTR is also commonly available in Zimbabwe, where most water treatment works use aluminium sulphate (alum) in their water treatment processes. All the three materials (soil, compost and Al-WTR) were sieved to 2 mm for characterisation of their physical and chemical properties and used in the pot trial.

The soil was limed to a target pH of 5.5, which is favourable for maize growth. The different soil mixtures were incubated for three weeks during which they were watered to field capacity. After three weeks, they were then transferred into one litre PVC-plastic pots with perforated bases to allow free drainage of excess water. The pots were arranged in a completely randomised design (CRD) with 6 replicates per treatment. One seed of maize variety SC513 (137 days to maturity), commonly grown in Zimbabwe, was planted in each pot. The greenhouse temperature was maintained at 24°C and daylight was supplemented with artificial light set on a 16-hour photoperiod for the duration of the experiment until harvest. Throughout the growth period, watering was done to maintain the soils' field capacity. For treatments with P, a compound fertiliser, Compound D (7% N, 14% P_2O_5, 7% K_2O), which is commonly used in Zimbabwe, was used as a source of available P. Compound D was applied by spreading on the soil and mixed-in to a depth of 5cm before planting. Fertiliser rates were differentially applied across treatments based on the targeted P rates of 26 kg P ha^{-1} (2.67g pot^{-1}) for treatment 7 (standard NPK) and a target of 14 kg P ha^{-1} (1.44g pot^{-1}) for compost and WTR treatments, following P fertilisation rates recommended by Mtambanengwe and Mapfumo (2009). Except for the unamended control (treatment 1), all treatments received additional N in the form of Ammonium nitrate (34.5% N), as topdressing at a rate of 90 kg N ha^{-1} and this was applied at 3 weeks after emergence.

3.3.2 Analysis of materials used in the experiment.

The pH of the material was measured with 0.01 M $CaCl_2$ (Anderson and Ingram, 1993), and readings taken using a standard pH meter (Hanna, H18424, Sigma-Aldrich, Germany). Electrical conductivity (EC) was determined using the water extraction method and readings taken using the conductivity meter (Jenway470J CO2, Triad Scientific, New Jersey, United States). Exchangeable bases (Ca, Mg, and K) were extracted using 1 M ammonium acetate (Anderson and Ingram, 1993) whilst available P was extracted using 0.5 M $NaHCO_3$ and all were measured using an inductively coupled plasma optical omission spectrometry (Agilent 5100 ICP-OES, Agilent Technologies, Australia). Exchangeable acidity was determined through titration using phenolphthalein indicator. Total C and N were determined by combustion using a Thermo Scientific Flash 2000 Organic Elemental Analyser. The metals, manganese (Mn), sodium (Na), zinc (Zn), copper (Cu), aluminium (Al), iron (Fe), magnesium (Mg), calcium (Ca) and potassium (K) were determined by X-Ray Fluoresence (XRF) via fused bead and wax pellet (Fitton, 1997).

3.3.3 Maize growth measurements, nutrient uptake, and residual soil chemical analysis

Weekly measurements of plant height and number of leaves were conducted for five (5) consecutive weeks beginning on the 7th day after emergence. Plant height was measured using a tape measure from the soil surface to the highest point of the arch of the uppermost leaf with its tip pointing down. The number of leaves was determined by physical counting based on the Leaf Tip method (Manitoba Crop Reports, 2020). The Leaf Tip method involves counting all leaves, including any leaf tips that have emerged from the whorl at the top of the plant. On the 35th day, maize plants were cut just above the soil surface to separate shoots and roots. Both the shoots and roots were washed in distilled water and left for 4 days under shade for air drying. After the 4 days, the biomass was oven dried at 65°C until a constant weight was reached. Total dry shoot and root biomass were then determined. The above-ground biomass (shoots) was ground to pass through a 2 mm sieve using a magic bullet nutri-blender (EAN: 5060191467360) for determination of total N, P, K, Ca, Mg, Cu, Mn, Zn, Al, Pb and Ni. P was extracted using the bicarbonate method (Olsen, 1954) and analysed using an ICP-OES (Agilent 5100). Ca, Mg, K, Cu, Mn, Zn, Al, Pb and Ni were extracted using the microwave assisted aqua-regia digestion method (Eskilsson and Björklund, 2000) and concentrations measured using the ICP-OES. Nutrient uptake was calculated with equation (3.1)

$$\text{Nutrient X (mg/kg)} = [(\text{X concentration (mg } L^{-1})/1000) \times \text{volume of the sample used (ml)}] / [\text{sample weight (g)} /1000] \quad (3.1)$$

Where X is N, P, K, Ca, Mg, Zn, Cu, Ni, Mn, Pb or Al

For N, P, Ca, Mg and K uptake was quantified in g kg^{-1}, while for Zn, Cu, Pb, Ni, Al and Mn uptake was measured in mg/kg

3.4 Field Experiment

3.4.1 Acquisition and pre-treatment of Al-WTR, cattle manure and maize stover

Cattle manure (CM) was obtained on site at Domboshava Experimental Research Station. Prior to application, the manure was dug out and aerobically composted for at least two months. A sub-sample was then drawn, air dried, sieved through a 2 mm sieve and characterised as reported **in Table 5.2.** Maize stover (MS) used in the first year was collected from an adjacent

Nuesom experimental field (see **Figure 3.2**), which was being run by the University of Zimbabwe (Mtangadura *et al*., 2017). In the second year, maize stover was obtained from within the experimental field itself. Maize stover in this study refers to above-ground maize biomass left on the field after harvest. In both instances, the maize stover was collected from the fields soon after harvest and stored under a shade throughout the dry period. For characterisation, a sub-sample of the maize stover was ground to pass through a 0.5 mm sieve and characterised as reported in **Table 5.2**. At the start of the season, the maize stover was finely chopped to maximum lengths of 0.2 m before incorporation into the soil.

Aluminium-Water Treatment Residual (Al-WTR) was sampled once to last the entire experimental period from a landfill stockpile at Prince Edward Water Treatment Plant (WTP) (17°58'45"S; 31°4'11"E), which is located 22 km to the Southwest of Harare, (**Figure 3.3**). The Al-WTR was heaped close to the experimental site where it was eventually sub-sampled for use in the experiments. The WTP uses the conventional water treatment system consisting of sludge blanket clarifiers and rapid sand filters. Aluminium sulphate ($Al_2(SO_4)_3.14H_2O$) is used as a flocculant. Sulphuric acid, chlorine gas, ammonia, flocculated carbon, and lime are used to optimise the water treatment process (Engineer C. Chinyanya, personal communication, March 23, 2020). After sampling, a sub-sample of the WTR was air dried for 30 days, sieved to 0.5 mm and characterised for physical and chemical properties as shown in **Table 5.2**.

Figure 3.3: Location of Prince Edward Water Treatment Plant.

3.4.2 Treatments and experimental layout

The experimental site had been under continuous fertilised maize for 5 years, preceding the experiment. The field experiment consisted of seven treatments comprising of Al-WTR, CM, MS applied as single amendments, Al-WTR + CM and Al-WTR + MS as co-amendments, standard NPK, which is the conventional method where NPK fertilisers are applied, and the unamended control. A summary of the treatment composition is given in Table 3.2. A field experiment in this study refers to an experiment that is carried out in a real field other than the laboratory or greenhouse, in this case at a research station, Domboshava Training Centre. The treatments were arranged in randomised complete block design (RCBD) with seven replicates per treatment that were imposed on plots measuring 4 × 5 m (**Figure 3.4**.). Maize (variety SC513 with 137 days to maturity) was planted at an inter-row spacing of 0.9 m and within-row of 0.3 m to give a total plant population of 37 000 plants ha^{-1}. All treatments except the control received inorganic fertiliser, Compound D. Compound D was applied at planting at a rate of 26 kg P ha^{-1} where it was solely applied and at 14 kg P ha^{-1} where it was used in combination with either cattle manure and / or maize stover, based on recommendations by Mtambanengwe and Mapfumo (2009). Maize stover and cattle manure were applied at 10 t ha^{-1} both where they were applied as single amendments or co-amendments. The Al-WTR was applied at a rate of 2 t ha^{-1} based on recommendations by Rengasamy et al. (1980). Maize stover, cattle manure and Al-WTR were incorporated four weeks before planting using hand hoes to a depth of about 15 cm. Additional N was provided by applying a top-dressing fertiliser, ammonium nitrate (AN; 34.5% N) at 90 kg N ha^{-1}. The AN fertiliser was split-applied in three phases of 30% at two weeks after emergence (WAE) of maize, 40% at six WAE and 30% at nine WAE to meet N demand of maize at various growth stages.

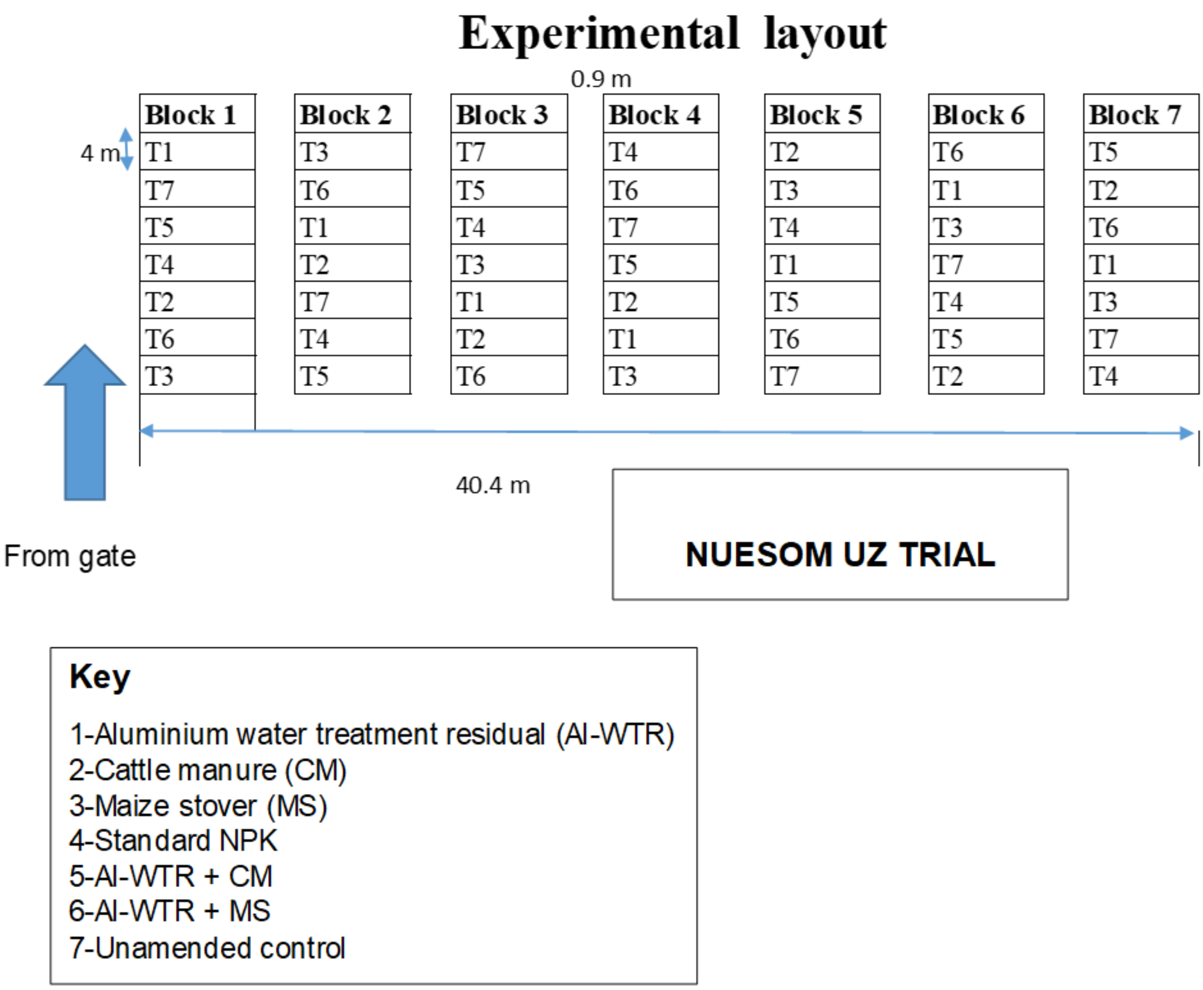

Figure 3.4: Experimental layout at Domboshava Training Centre, Zimbabwe.

In addition, all plots were limed to target a pH of 5.5, which is the optimal pH for maize production. All plots were initially tilled using the animal-drawn mouldboard plough in the first season and by hand hoes in the second season to incorporate the organic amendments. The fields were kept weed-free throughout all seasons by manual hand-hoe weeding. A broad-spectrum pesticide, Nemesis (Emamectin Benzoate 48 g and Acemiprid 64 g) was used for control of fall armyworm (*Spodoptera frugiperda*) where neccessary. A cumulative amount of 474 mm rainfall was received in the first year (2019/2020) whilst 932 mm was received in the second year (2020/21) (**Figure 3.5**).

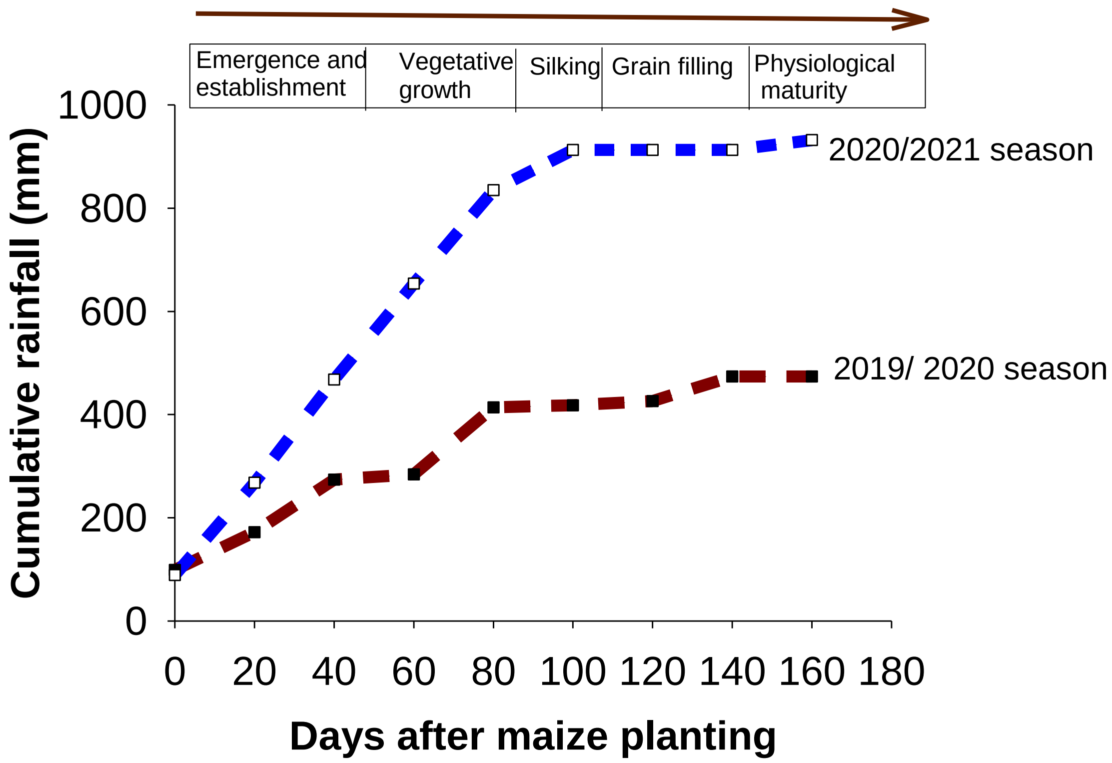

Figure 3.5: Cumulative rainfall received at Domboshava during the 2019/2020 and 2020/2021 season showing critical maize growth stages starting at crop emergence.

3.4.3 Measurement of selected soil physical properties

3.4.3.1 Bulk density

The bulk density of the soil was determined at the beginning (2019/2020) and end (2020/2021) of the experiment. One undisturbed soil core (5 cm diameter and height of 5 cm) was collected in each replicate from 3 depths, 0 - 5 cm, 5 - 10 cm, and 10 - 20 cm to calculate bulk density. Core samples were oven dried at 105°C for 24 h, and bulk density (ρb) calculated based on the oven dry weight (Okalebo *et al*., 2002) as in equation 1:

$$\rho b = \frac{Ms}{Vt} \tag{3.2}$$

where *Ms* is mass of oven dry soil (g), and *Vt* is total volume of soil (cm^3).

3.4.3.2 Soil organic carbon, water-stable aggregates and mean weighted diameter.

Soil samples for soil organic carbon (SOC) determination were collected from 0-5, 5-10 and 10-20 cm using an auger. The samples were air-dried and finely ground to pass through a 0.5 mm sieve. SOC was then determined using the wet oxidation method (Okalebo *et al*., 2002). The soil samples were oxidised using a combination of potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4). The mixture was titrated using ferrous ammonium sulphate. The difference between added and residual $K_2Cr_2O_7$ gives a measure of organic C content in the sample (Okalebo *et al*., 2002) The SOC concentration from the three soil depths were averaged to give Total Organic Carbon (TOC) concentration for the 0 - 20 cm profile.

For soil water-stable aggregates (WSA) and mean weight diameter (MWD) determination, five sub-samples were randomly collected in each treatment from all the seven blocks (replicates) to a depth of 20 cm using a spade and composited to obtain representative samples. A modified method was used for WSA and MWD determination. The samples were air-dried and wet-sieved into different fractions through a nested set of five sieves with opening diameters of 2, 1, 0.5, 0.2 and 0.1 mm stacked in a descending sequence on a bar. Aggregates had been initially passed through a 4.75 mm sieve to remove stones and grit. 20 g of aggregates retained on the 2 mm sieve were separated for wet sieving. The aggregates were kept on the top sieve (2 mm) and allowed to pre-wet under tension in deionised water for about 10 minutes. A motor-driven shaft and crank system oscillating through a vertical distance of 30 cm at 30 cycles per minute was used for sieving. Wet sieving was performed for 30 minutes, and material retained on each sieve was air-dried and stored separately. Water-stable aggregates from each sieve were then transferred into pre-weighed containers and oven dried at 105°C for 24 h and then weighed. The weight of oven-dry aggregates retained on the 0.1 - 2.0 mm diameter sieves was corrected for sand by soaking the aggregates in 0.5 M NaOH for 24 h and then washed to remove the clay. The sand was then oven dried, weighed and subtracted from WSA. Water-stable aggregates (WSA) and mean weight diameter (MWD) of aggregates were determined following Barthes and Roose (1996):

$$WSA\ (\%) = \sum_{i=1}^{n} wi * 100 \qquad (4.2)$$

$$\mathrm{MWD} = \sum_{j=1}^{n} wixi \qquad (4.3)$$

Where *n* is the number of aggregate size ranges, *wi* is the weight of aggregates retained in sieve as a fraction of total weight of sample used for aggregate stability analysis, and x_i is the mean diameter of adjacent sieves.

3.4.3.3 Water holding capacity.

Water holding capacity involved measurements of both gravimetric and volumetric water content. Undisturbed soil samples from field trials were collected after two consecutive cropping seasons using 5 cm by 5 cm long stainless-steel cylindrical cores to a depth of 20 cm in three incremental depths of 0 - 5 cm, 5 - 10 cm, and 10 - 20 cm. The samples were subjected to suctions of 5, 10, 20, 50, 100, 200 and 500 kPa using a Tension Table (Rose, 1966). Nylon cloths were securely tied to one end of the cores, allowed to soak overnight, and placed on tension tables set at 5kPa suction. The cores were weighed after every 2 days until constant mass, after which suction was increased till 20kPa and the same process repeated. Pressure plates were used for suctions > 20kPa (Klute, 1986). Sample retaining rings were placed on ceramic plates, and soil samples from 5, 10 and 20kPa determinations put in them. The samples were saturated with excess water in the ceramic plates for 24 hours after which the ceramic plates were placed into pressure chambers and the desired pressure applied. The samples were kept at the desired pressure until all moisture was extracted. This point was determined when no extra water was extracted within a 24-hour period. Soil samples were then transferred to pre-weighed metal trays, weighed, oven dried at 105°C for 24 hours and weighed again. Gravimetric moisture content (θ_g) of the soil was then calculated according to equation 4:

$$\theta_g\ (\%) = \left(\frac{Mw - Md}{Md}\right) * 100 \qquad (4.4)$$

where, M_w is wet mass of soil sample and M_d is dry mass of soil sample

Volumetric moisture content (θv) is calculated with an equation 5 (Hillel, 1982)

$$\theta_v\ (\%) = \left(\frac{\theta g \times \rho b}{\rho w}\right) * 100 \tag{4.5}$$

where ρ_b is soil bulk density and ρ_w is density of water (1 000 kg m^{-3}).

3.5. Laboratory analytical methods employed for the field experiment.

3.5.1 Soil pH and electrical conductivity determination

Soil pH determination was done using calcium chloride ($CaCl_2$). The $CaCl_2$ stabilises the cation composition of the soil exchange sites because it closely resembles the ion concentration of the soil solution. About 20 g of sieved soil (2 mm) was mixed with 5 mL of 0.01 M $CaCl_{2,}$ mixed with a magnetic stirrer for 10 minutes. The suspension was allowed to settle for a further 10 minutes and pH read on a pH meter, Hanna H198311 (Sigma-Aldrich, Germany).

3.5.2 Determination of organic carbon

Organic carbon was determined for soils, cattle manure, maize stover and compost using the wet oxidation method (Okalebo *et al*., 2002). The materials were finely ground to 0.5 mm About 0.5 g of material (plant or soil) was placed in a block digester tube and mixed with 5 mL of potassium dichromate solution ($K_2Cr_2O_7$) and 7.5 mL of concentrated sulphuric acid (H_2SO_4). The tube was placed in a pre-heated block at 125 °C for 30 minutes, removed and allowed to cool. The digest was titrated with ferrous ammonium sulphate in the presence of ferroin indicator.

3.5.3 Total nitrogen and phosphorus

This was determined in soils, cattle manure, maize stover residues, water treatment residual, maize plant biomass and grain using the micro-kjeldahl procedure (Anderson and Ingram, 1993; Okalebo *et al*., 2002). The material was ground to pass through a 0.25 mm sieve and 0.3 g was weighed into a digestion tube. A 2.5 mL aliquot of the digestion mixture consisting of concentrated H_2SO_4, and hydrogen peroxide (H_2O_2) was added, and the mixture heated 360 °C for two hours until the mixture attained a clear light-yellow colour. Selenium powder was used as a catalyst and lithium sulphate (Li_2SO_4) added to raise the temperature. The mixture was cooled and then transferred to a 50 mL volumetric flask and the filled to volume with distilled water.

Total N was then determined by distillation procedure. Aliquots (5 mL for plants and 10 mL for soil) of the digested sample (as outlined above) was transferred into the distillation chamber and 10 mL of 1% sodium hydroxide (NaOH) was added. The mixture was steam distilled directly into 5 mL of 1% boric acid in the presence of a mixed indicator. Distillation was continued until the mixture turned green. The distillate was removed and titrated with N/70 hydrochloric acid (HCl) for plants and N/140 HCl for soil. The concentration in mg kg^{-1} of N was calculated as in equation 3.1.

Total P was then determined using ascorbic acid. Following micro-kjeldahl procedure, ascorbic acid was added to the samples including a set of standards and left to stand for one hour for colour development. The supernatant P concentration was read colorimetrically on an Ultraviolet-visible Spectrophotometer (UV-Vis Cintra 303, GBC Scientific, Australia) at 880 nm. A graph of absorbance against concentration was plotted. The P in mg kg^{-1} in samples was also calculated as given in equation 3.1.

3.5.4 Total basic cations

The basic cations, potassium (K), calcium (Ca) and magnesium (Mg) were determined in cattle manure, maize stover residues, water treatment residual, maize plant biomass and grain. The total cationic contents were measured by complete oxidation using the Kjeldahl procedure as outlined in section 3.3.3, followed by spectrometric analysis using an atomic absorption spectrophotometer (AAS) (Varian AA-1275, Australia) set at a wavelength of 765.5 nm. The concentration of K, Ca and Mg were calculated following equation 3.1.

3.5.5 Micronutrients and heavy metal determination

The determination of zinc (Zn), copper (Cu), manganese (Mn), lead (Pb), aluminium (Al), iron (Fe) and nickel (Ni) were determined using the aqua-regia method (Okalebo *et al*., 2002). To 0.3 g of finely ground material (plants and soils), 2.5 ml of aqua-regia (2 mL 50% HCl: 5 mL 25% HNO_3) solution were added. The mixture was heated to 110 °C for 1 hour. It was allowed to cool, and 3 mL of hydrogen peroxide (H_2O_2) added in 3 successive portions of 1 mL each. The mixture was the re-heated to 330 °C until it turned light yellow. After cooling, the contents were transferred into a 50 mL volumetric flask and made to the mark with distilled water. The elemental concentrations were then read on an AAS (Varian AA-1275, Australia) using specific hollow cathode lamps. Total elemental concentration was calculated following equation 3.1.

3.5.6 Analytical determination of microbial biomass C and N and soil basal respiration

Soil microbial biomass C and N were determined by the chloroform fumigation extraction method (Jenkinson and Powlson, 1976; Vance *et al*., 1987; Anderson and Ingram, 1993). Three replicate soil samples from each of the seven treatments weighing 25 g were placed into 100-mL-capacity beakers and fumigated with ethanol-free chloroform ($CHCl_3$) for 24 hrs at 25°C. Residual $CHCl_3$ from the samples was removed through repeated evacuation in clean $CHCl_3$-free desiccators. After extraction, to both fumigated and unfumigated soils, 100 mL 0.5 M K_2SO_4 was added to the samples and left to settle for 30 min. A 10 mL aliquot from both the fumigated and unfumigated samples were taken for MBC and MBN. Extractable organic carbon (C) was analysed using the wet oxidation method (Anderson and Ingram, 1993) and is described in detail in Chapter 3, section 3.5.2. Microbial biomass C was then calculated by using equation 4.6.

$$MBC = E_C/K_{EC} \tag{4.6}$$

where E_C = (organic C extracted from fumigated soils) - (organic extracted from non-fumigated soils) and K_{EC} is the C- K_2SO_4 extract efficiency factor of 0.45 (Jenkinson and Powlson, 1976). Microbial biomass N was analysed using micro-kjeldahl procedure (Anderson and Ingram, 1993) as described in detail in Chapter 3, section 3.5.3. Microbial biomass N was then calculated as shown in equation 4.7.

$$MBN = E_N/K_{EN} \tag{4.7}$$

Where EN = (total N extracted from fumigated soils) – (total N extracted from non-fumigated soils) and K_{EN} is the N- K_2SO_4 extract efficiency factor of 0.54 (Brooks *et al*., 1985).

Soil basal respiration was determined only on soils sampled 6 weeks after maize planting. Three sets of 50 g samples from each treatment were weighed into plastic jars. Distilled water was added to bring the soils to field capacity (FC). The jars were sealed and incubated in the dark at a constant temperature of 25˚C to mimic soil conditions. The soils were pre-incubated for one week before introducing vials with NaOH, to allow the initial carbon flush to diminish. A small vial containing 10 ml of NaOH was then placed into each individual jar containing the soil sample to trap the released CO_2. The CO_2-C released (measured by the remaining OH ions) during soil basal respiration was precipitated with an excess of 0.5 M $BaCl_2$ and titrated against

0.5 M HCl in the presence of phenolphthalein indicator. The CO_2-C was quantified on days 1, 4, 8, 16 and 21. The amount of CO_2-C evolved on each prescribed day were then added to obtain the total CO_2-C evolved. Metabolic quotient (qCO_2), a measure of the efficiency of the microbial community, was calculated by dividing the amount of CO_2-C evolved on the first day of incubation by microbial biomass C (Anderson and Domsch, 1990).

Table 3.2: Summary of the study sites, treatments and experimental scale

Study site	Coordinates	Treatment number	Treatment composition	Experimental scale
Durham University, United Kingdom	54°46ˈ22.80"N -1°34ˈ26.40W	1	Control	Greenhouse experiment
		2	10% Al-WTR	
		3	10% Compost	
		4	20% Al-WTR	
		5	20% Compost	
		6	10% Al-WTR + 10% Compost	
		7	Std NPK	
		8	10% Al-WTR + P	
		9	10% Compost + P	
		10	20% Al-WTR + P	
		11	20% Compost + P	
		12	10% Al-WTR + 10% Compost + P	
Domboshava Training Centre, Zimbabwe	17°36ˈ S; 31°08ˈ E	1	Al-WTR	Field experiment
		2	CM	
		3	MS	
		4	Std NPK	
		5	Al-WTR + CM	
		6	Al-WTR + MS	
		7	Control	

Al-WTR- aluminium water treatment residual; CM- cattle manure; MS-maize stover, standard NPK-N.P. K fertilizer (7% N, 14% P_2O_5, 7% K_2O); P -P fertiliser (7% N, 14% P_2O_5, 7% K_2O)

Chapter 4

4.0 Field application of soil improvement technologies in Zimbabwe to address hidden hunger[§]

Abstract

Soil degradation is a major threat to sustainable food production and the extent of soil degradation, and its severity are predicted to exacerbate the occurrence of droughts, particularly in sub-Saharan African smallholder systems, which are already burdened by poor soil structure and low nutrient-holding capacity. A two-year field experiment was carried out to evaluate the impact of amending soil with single amendments of aluminium water treatment residual (Al-WTR), cattle manure (CM), maize stover (MS) or inorganic fertiliser (standard NPK) or the co-amendments, Al-WTR + CM and Al-WTR + MS in comparison to the unamended soil (control), on soil organic carbon (SOC), bulk density (BD), water-stable aggregates (WSA), mean weighted diameter (MWD), water holding capacity and maize grain yield. Soil samples were taken from 0 - 5, 5 - 10 and 10 - 30 cm depths at the end of the experiment. Although SOC significantly ($p < 0.001$) varied with soil fertility management, the effect of soil depth ($p > 0.05$) could not be confirmed. The highest amount of SOC (4.96 g kg^{-1}) was recorded for Al-WTR + CM, while the control had the least (4.55 g kg^{-1}). Similarly, significant variations ($p < 0.05$) in BD among the treatments was only observed in the top 5 cm soil layer, with the least (1.30 g cm^{-3}) and the highest (1.35 g cm^{-3}) recorded for Al-WTR + CM and the control, respectively. Both WSA and MWD were correlated to SOC ($p < 0.001$). The co-amendment, Al-WTR + CM exhibited greater stability, recording an average of 121.64 g kg^{-1} WSA and 0.17 mm in MWD, which equated to an increase of 393% (WSA) and 141% (MWD), relative to the control. The co-amendment, Al-WTR + CM resulted in increments of 0.02 cm^3 cm^{-3} and 0.06 cm^3 cm^{-3} in the readily available water (RAW) for the 0 - 5, 5 - 10 and 10 - 20 cm depths, respectively, whilst also retaining 31.8%, 17.3% and 12.9% more water at field capacity (FC) for the 0 – 5, 5 – 10 and 10 – 20 cm depths, respectively, compared to the control. Both Al-WTR + MS and Al-WTR + CM significantly ($p < 0.01$) yielded higher maize grain yields of 2.5 t ha^{-1} and 5.61 t ha^{-1} in the first and second seasons, respectively, whilst the control gave the least, 0.53 t ha^{-1} and 1.2 t ha^{-1}, respective for both seasons. The results showed that Al-WTR co-amendments have the potential to build and stabilise soil structure, improve soil water retention and increase maize grain yields. This offers prospects for use of the co-amendments to rebuild soil structure, enhance drought resilience and increase crop productivity and nutritional content, particularly in smallholder urban systems of Southern Africa which are currently under threat from a declining soil resource base and the increased frequencies of drought due to climate change effects.

[§]A modified version of this chapter will be submitted for publication as Gwandu et al (2023). Field application of soil improvement technologies in Zimbabwe to address hidden hunger. Nature Water.

4.1 Introduction

One of the 2030 Agenda for the United Nations Sustainable Development Goals (UN SDGs) is to restore degraded land and soil, including land affected by desertification, drought, and floods, and strive to achieve a land degradation-neutral world (UNGA, 2015). Soil degradation is a global challenge that threatens sustainable food production, and in cropping systems, is mainly driven by poor soil management practices that result in declines in soil health (Obalum *et al*., 2017; Stewart *et al*., 2020). Johnson et al. (2022) defines soil health as the ability of a soil to deliver essential ecosystem services, a subset of which includes food security, climate change adaptation and mitigation. The impact of soil degradation is more pronounced in sub-Saharan Africa (SSA) where > 65% of arable land is classified as degraded (Nezomba *et al*., 2015; Stewart *et al*., 2020), and the soils are characterised by poor soil structure and low water holding capacity (Twomlow *et al*., 2006; Johnson *et al*., 2022; Kerr *et al*., 2022). While soils in SSA are prone to rapid Organic Carbon (OC) turnover due mainly to low clay content (< 10%) (Mapfumo *et al*., 2005) coupled with relatively high temperatures that promotes rapid soil organic matter (SOM) mineralisation (Henao and Baanate, 2006); obtaining sufficient organic matter (OM) inputs is a challenge for most smallholder farmers (Obalum *et al*., 2017). Thus, poor SOM management is the major cause for diminishing soil productivity in SSA (Obalum *et al*., 2017; Zingore *et al*., 2021).

Soil organic matter directly impacts on crop yields through supplying plant nutrients in the short-term or by indirectly modifying soil properties in the medium to long-term (Oldfield *et al*., 2018). The presence of OM alone may also increase plant available water, regardless of improved soil physical properties (Somerville *et al*., 2018). While, African smallholder farmers have been relying mainly on locally available organic nutrient resources, e.g., manure and woodland litter, as sources of OM (Manzeke *et al*., 2012), they have become scarce (Herrero *et al*., 2014; Chagumaira *et al*., 2016). In addition, crop residues are rarely retained in the fields due to competing uses e.g., as animal fodder (Olson *et al*., 2021) and biofuel feedstocks (Blanco-Canqui and Lal, 2009). In urban areas, farmers prefer to burn crop residues prior to tilling their land due to the labour involved in their incorporation, a practice that reduces labile SOM (Blanco-Canqui and Lal, 2009; Sarkar *et al*., 2020). Burning crop residues also result in greenhouse gas (GHG) emissions (Sarkar *et al*., 2020), which contributes to global warming. Overwhelmed by the need to supplement dietary requirements through farming on the increasingly fragile soils, building SOM levels amidst challenges of limited organic nutrient sources requires interventions in exploring additional OM-based technologies to rehabilitate such degraded soils and improve crop yields.

Aluminium water treatment residual (Al-WTR), a by-product of drinking water treatment, is a potential organo-mineral resource containing both mineral and organic particles, that can be used to improve soil health (Gwandu *et al*., 2022). Water treatment residual can potentially build soil C due to their high C content (Dassayanake *et al*., 2015; Kerr *et al*., 2022), while the Al and Fe oxides within the WTR matrix, sorb organic molecules, shielding them from microbial attack (Kögel-Knabner *et al*., 2008). The Al and Fe oxides also form strong complexes with humic acids, which contributes to soil aggregation (von Fromm *et al*., 2021), hence improved soil structure (Kerr *et al*., 2022). Moreso, recent research has increasingly shown superior benefits by co-applying WTR and other organic amendments (e.g., Gwandu *et al*., 2022, 2023) and Kerr *et al*., 2022). Most research on benefits / disadvantages of co-amending soils with Al-WTR and other organic materials has largely focused on plant growth and soil phosphorus (P) dynamics (Agyin-Birikorang *et al*., 2008; O'Rourke *et al*., 2012), only a few studies have looked at effects on soil physical characteristics (e.g., Hsu and Hseu, 2011; Ibrahim *et al*., 2020; Kerr *et al*., 2022). Thus, there is paucity of information on effect of co-amending Al-WTR and other organic amendments, in particular cattle manure and maize stover on soil physical characteristics. This study presents an investigation of the effects of co-amending soil with Al-WTR and locally available organic nutrient sources, cattle manure and/ or maize stover on SOC, soil aggregate stability, water holding capacity and maize grain yields under field conditions.

The application of OM in form of cattle manure or maize stover improves SOC, soil water holding capacity and consequently crop yields (Bolinder *et al*., 2020; Gautam *et al*., 2022;). Soil aggregates stabilise SOC from rapid mineralisation by soil microorganisms through several mechanisms that include physical protection by the macro-and micro- aggregates, chemical protection through OM adsorption by the soil mineral component mainly constituted by Al and Fe oxides and through biological stabilisation mechanisms where stable organic compounds such as polysaccharides and organic mucilages strongly cement aggregates (Gautam *et al*., 2022). Soil organic matter also lowers soil bulk density by means of a dilution effect to the soil dense fraction (Haynes and Naidu, 1998; Guo *et al*., 2016). Bulk density in turn directly influences air-soil-water interactions, indirectly impacting on soil nutrient dynamics (Gautam *et al*., 2022) and thus crop yields. By improving soil water holding capacity, SOM enhances the resilience of soils to droughts (Lal, 2020a). Crop residues such as maize stover also mitigate against climate change by sequestering SOC and off-setting emissions of carbon dioxide and other GHGs (Lal, 2008).

This study is based on the hypothesis that use of aluminium-based water treatment residual (Al-WTR) in combination with organic nutrient resources as a soil amendment improves soil structure, water holding capacity and crop yields. The specific objectives were to: (i) determine the influence of co-application of Al-WTR and cattle manure and / or maize stover on SOC content, bulk density, aggregate stability, and water retention capacity of a sandy loam soil; (ii) to determine the impacts of co-application of Al-WTR and cattle manure and /or maize stover on maize yield.

4.2 Materials and methods

4.2.1 Experimental site and treatment layout

The study was carried out between 2019 and 2021 at Domboshava Experimental Research Station, Zimbabwe. A detailed description of the study site is given in Chapter 3 section 3.1. A maize crop (variety SC513) was planted to seven treatments consisting of single amendments of cattle manure (CM), maize stover (MS), Al-WTR, or their combinations, Al-WTR + CM, Al-WTR + MS, an unamended control and standard NPK and these are described in detail in Chapter 3, section 3.4.2.

4.2.2 Determination of bulk density, SOC, aggregate stability, and soil moisture retention characteristics

Bulky density was determined from the volume of soil cores and oven-dry mass of soil cores as detailed in Chapter 3, section 3.4.3.1. SOC was determined by the wet oxidation method (Okalebo *et al*., 2002) as described in detail in Chapter 3, section 3.5.2. The effect of different treatments on soil aggregate stability was evaluated by the proportion (g kg^{-1}) of water-stable aggregates (WSA) and mean weighted diameter (MWD) and is described in detail in Chapter 3, section 3.4.3.2. Soil moisture release curves were obtained by plotting the volumetric water content of the soil against the pF of the respective matric suctions. The pF values were calculated as pF = $\log_{10}$ suction (mH2O) (Nyamangara *et al*., 2001) or directly plotted based on gravimetric moisture content as described in detail in Chapter 3, section 3.4.3.3.

4.2.3 Maize grain and biomass yield determination

At physiological maturity, maize cobs were harvested from net plots measuring 3 m × 3 m to prevent edge effect. The cobs were separated from the stover by hands followed by shelling. After shelling, the grain was air dried to 12.5% moisture content and yield determined by weighing. Both stover biomass and grain yield was expressed in t ha^{-1}.

4.3 Statistical analyses

The effect of different treatments on soil bulk density, SOC, gravimetric and volumetric water content, WSA, MWD and maize yield data were subjected to analysis of variance (ANOVA) using GENSTAT 21st edition (VSN International, 2022). The Fisher's least significance difference (LSD) test was used to compare treatment means at probability $p < 0.05$. The data was further subjected to Tukey's Honest Significant Difference (HSD) test to differentiate significant treatment means at $p < 0.05$. A linear regression analysis was done to determine the relationship between soil organic carbon and the aggregate stability indices.

4.6 Results

4.6.1 Soil Organic Carbon

Soil organic carbon (SOC) differed significantly ($p < 0.001$) among treatments within the same soil depth (**Table 4.1**). There were, however, no significant differences ($p > 0.05$) in SOC with depth across all treatments. The SOC was highest in the upper 0 - 5 cm and then generally decreased with increase in depth (**Table 4.1**). The highest concentration of SOC was observed for Al-WTR + CM in the 0 – 5 cm soil layer with (4.96 ± 0.07 g. kg^{1}), whilst the control had the least with 4.52 ± 0.05 g. kg^{-1} for the 10-20 cm depth (**Table 4.1**). The co-amendment of Al-WTR + MS also resulted in significantly ($p < 0.05$) higher SOC by > 0.30 g. kg^{-1} across all depths, relative to both the control and standard NPK. The single amendment of Al-WTR ($p > 0.05$) had ~ 0.15 g. kg^{-1} higher SOC compared to the control and standard NPK, across all soil depths (**Table 4.1**).

Table 4.1: Mean soil organic carbon at 0 - 5, 5 – 10 and 10 – 20 cm depths as affected by different soil fertility amendments

Treatment	Soil depth (cm)		
	0 - 5	5 - 10	10 - 20
Al-WTR	4.74±0.04ab	4.73±0.04a	4.70±0.04a
CM	4.79±0.07ab	4.78±0.07ab	4.73±0.06ab
MS	4.77±0.04ab	4.77±0.03ab	4.73±0.04ab
Standard NPK	4.57±0.09a	4.56±0.08a	4.54±0.08a
Al-WTR + CM	4.97±0.07b	4.96±0.08b	4.93±0.07b
Al-WTR + MS	4.90±0.03b	4.89±0.03b	4.86±0.03b
Control	4.56±0.05a	4.55±0.05a	4.52±0.05a
	Statistical significance§		
Treatment	*		
Depth	ns		
Treatment × Depth	ns		

§ Significantly different at $^{*}p < 0.05$; ns = not significant ($p > 0.05$). Data are means ± standard error of means (SEM) ($N = 7$). Different lowercase letters indicate significant differences among different treatments based on Tukey's HSD test ($p < 0.05$). Al-WTR, CM, MS, Standard NPK, Al-WTR + CM, Al-WTR + MS represent aluminium-water treatment residual, cattle manure, maize stover, fertiliser NPK (7% N, 14% P_2O_5, 7% K_2O), aluminium-water treatment residual plus cattle manure, aluminium-water treatment residual plus maize stover and control (unamended soil), respectively.

4.6.2 Bulk density

Significant variations ($p < 0.05$) in bulk density among the treatments was observed in the top 5 cm soil layer (**Table 4.2**), but no significant differences ($p > 0.05$) could be attested with soil depth for all treatments. This is consistent with trends in SOC, indicating the link between SOC and soil bulk density. The control and standard NPK recorded the highest bulk densities (1.35 ± 0.07 g. cm^{-3}) whilst Al-WTR + CM had the least at 1.30 ± 0.01g. cm^{-3} (**Table 4.2**). The co-amendment of Al-WTR + MS also resulted in significantly lower bulk density (1.31 ± 0.02 g. cm^{-3}) compared to the control and standard NPK. Although not significantly different, the single amendment of Al-WTR resulted in lower soil bulk density compared to the control and Standard NPK (**Table 4.2**). Overall, soil bulk density was lower in the top 10 cm depth compared to the 10-20 cm soil layer for each treatment but with no differences between treatments (**Table 4.2**).

Table 4.2: Soil fertility management effects on soil bulk density at 0 – 5, 5 -10 and 10-20 cm at Domboshava, Zimbabwe

Treatment	Soil depth (cm)		
	0 – 5	5 - 10	10 - 20
Al-WTR	1.34 ± 0.06bc	1.34 ± 0.01a	1.36 ± 0.01a
CM	1.32 ± 0.03abc	1.32 ± 0.03a	1.34 ± 0.05a
MS	1.33 ± 0.06abc	1.33 ± 0.02a	1.35 ± 0.06a
Standard NPK	1.35 ± 0.04c	1.35 ± 0.05a	1.36 ± 0.03a
Al-WTR + CM	1.30 ± 0.01a	1.31 ± 0.04a	1.33 ± 0.01a
Al-WTR + MS	1.31 ± 0.02ab	1.32 ± 0.03a	1.34 ± 0.01a
Control	1.35 ± 0.06c	1.36 ± 0.01a	1.36 ± 0.01a
	Statistical significance§		
Treatment	*		
Depth	ns		
Treatment × Depth	ns		

§ Significantly different at $^{*}p < 0.05$ (at 0 – 5 cm depth only); ns = not significant ($p > 0.05$). Data are means ± standard error of means (SEM) ($N = 7$). Different lowercase letters indicate significant differences among different treatments based on Tukey's HSD test ($p < 0.05$). Al-WTR, CM, MS, Standard NPK, Al-WTR + CM, Al-WTR + MS represent aluminium-water treatment residual, cattle manure, maize stover, fertiliser NPK (7% N, 14% P_2O_5, 7% K_2O), aluminium-water treatment residual plus cattle manure, aluminium-water treatment residual plus maize stover and control (unamended soil), respectively.

4.6.3 Aggregate stability and mean weight diameter (MWD)

Both WSA and MWD significantly ($p < 0.05$) varied among treatments (**Figure 4.1**). At the termination of the experiment, the control and Standard NPK exhibited very poor aggregation with average WSA proportions of 24.46 ± 0.35- and 26.57 ± 0.38- g kg^{-1} and mean weight diameter of 0.07 ± 0.008- and 0.05 ± 0.007-mm, respectively. The single amendment of Al-WTR showed significantly ($p < 0.05$) higher proportion of WSA (51.21 ± 0.83 g kg^{-1}) and MWD (0.1 ± 0.001 mm) compared to the proportions of both the control and standard NPK (**Figure 4.1**). However, its proportion of WSA was significantly ($p < 0.05$) lower than that of CM (85.07 ± 0.84 g kg^{-1}) but statistically comparable to MS (54.21 ± 0.75 g kg^{-1}). The co-amendments, Al-WTR + CM and Al-WTR + MS proved more effective, resulting in significantly ($p < 0.05$) higher aggregate stability with WSA proportions of 121.64 ± 2.33 g kg^{-1} and 108.04 ± 1.30 g kg^{-1}, respectively, relative to all other treatments (**Figure 4.1**). The co-amendment of Al-WTR + CM increased in the proportion of WSA by 393% and MWD by 141%, relative to the control. While the single amendment of CM increased the proportion of WSA and MWD in respect to the single amendment of Al-WTR by 138% and 71%, respectively (**Figure 4.1**). Similarly, Al-WTR + MS resulted in increases of 338% and 105% for WSA and MWD, respectively, compared to the control and by 111% and 46% for WSA and MWD, respectively, relative to sole Al-WTR. Overall, the data revealed that co-application of Al-WTR with either cattle manure or maize stover resulted in higher aggregate stability relative to the control, standard NPK and single amendments of CM, MS and Al-WTR.

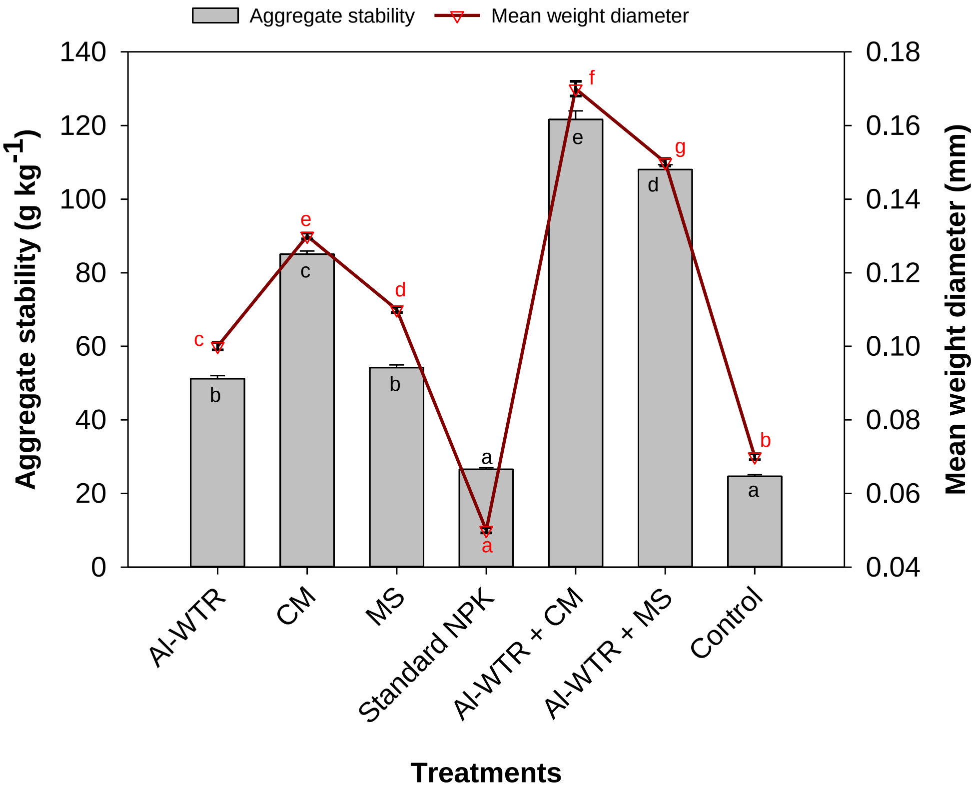

Figure 4.1: Aggregate stability (g kg^{-1}) and mean weight diameter (mm) due to different treatments. Data are means ± standard error of means (SEM) (N = 7). Different lowercase letters indicate significant differences among different treatments for each size of soil aggregates based on Tukey's HSD test ($p < 0.05$).

4.6.4 Size distribution of water-stable aggregates

After the two-year experiment, results showed a lower proportion of WSA macro-aggregates ($WSA_{> 0.25\ mm}$) compared to the WSA micro-aggregates ($WSA_{< 0.25\ mm}$) across all the treatments. Among the seven treatments, the highest proportion of $WSA_{> 2\ mm}$, $WSA_{1\text{-}2\ mm}$, $WSA_{0.5\text{-}1\ mm}$, $WSA_{0.18\text{-}0.5\ mm}$ and $WSA_{0.063\text{-}0.18\ mm}$ were obtained in the co-amendment of Al-WTR + CM with 3.13 ± 0.03%, 5.61 ± 0.07%, 5.39 ± 0.20%, 4.73 ± 0.19% and 3.64 ± 0.04%, correspondingly, whilst the highest share of $WSA_{< 0.063\ mm}$ was obtained in the control with 95.35 ± 0.06% (**Table 4.3**). The lowest proportion of $WSA_{> 2\ mm}$, $WSA_{1\text{-}2\ mm}$ and $WSA_{0.5\text{-}1\ mm}$ were found in the control with 1.01 ± 0.03%, 1.56 ± 0.04% and 0.91 ± 0.04%, respectively (**Table 4.3**). Standard NPK had the lowest proportion of $WSA_{0.18\text{-}0.5\ mm}$ (0.50 ± 0.03%) and $WSA_{0.063\text{-}0.18\ mm}$ (0.51 ± 0.01%), whilst Al-WTR + CM had the least (77.43 ± 0.40%) in the $WSA_{< 0.063\ mm}$ fraction. Compared with the control, Al-WTR significantly ($p < 0.05$) increased the proportion of $WSA_{> 2\ mm}$, $WSA_{1\text{-}2\ mm}$, $WSA_{0.5\text{-}1\ mm}$ by 118%, 123% and 111%, respectively. The Al-WTR also increased $WSA_{0.18\text{-}0.5\ mm}$ and $WSA_{0.063\text{-}0.18\ mm}$ by 134% and 94%, respectively, relative to Standard NPK (**Table 4.3**). The co-amendment, Al-WTR + CM on the other hand, increased significantly ($p < 0.05$) the proportion of $WSA_{> 2\ mm}$, $WSA_{1\text{-}2\ mm}$, $WSA_{0.5\text{-}1\ mm}$, $WSA_{0.18\text{-}0.5\ mm}$ and $WSA_{0.063\text{-}0.18\ mm}$ by 209.9%, 259. 61%, 492%, 662.90%, 561.82 relative to the control and by 41.6%, 61.2%, 180.7%, 304.3%, 267.7%, respectively compared to the single amendment of Al-WTR (**Table 4.3**). In general, aggregate stability (both WSA and MWD) followed the trend Al-WTR + CM > Al-WTR + MS > CM > MS > Al-WTR > Std NPK > control.

Table 4.3: Percentage distribution of soil water-stable aggregate size farctions due to different treatments

Treatments	Aggregate size (%)					
	$WSA_{> 2\ mm}$	$WSA_{1\text{-}2\ mm}$	$WSA_{0.5\text{-}1\ mm}$	$WSA_{0.18\text{-}0.5\ mm}$	$WSA_{0.063\text{-}0.18\ mm}$	$WSA_{< 0.063\ mm}$
Al-WTR	$2.21^{c} \pm 0.04$	$3.48^{c} \pm 0.05$	$1.92^{b} \pm 0.07$	$1.17^{b} \pm 0.05$	$0.99^{b} \pm 0.03$	$90.23^{d} \pm 0.17$
CM	$2.49^{d} \pm 0.03$	$4.21^{e} \pm 0.03$	$3.90^{c} \pm 0.04$	$3.33^{c} \pm 0.06$	$2.11^{c} \pm 0.05$	$83.95^{c} \pm 0.15$
MS	$2.53^{d} \pm 0.02$	$3.84^{d} \pm 0.04$	$1.96^{b} \pm 0.06$	$1.13^{b} \pm 0.05$	$0.93^{b} \pm 0.04$	$89.61^{d} \pm 0.14$
Standard NPK	$1.22^{b} \pm 0.02$	$1.89^{b} \pm 0.04$	$0.93^{a} \pm 0.04$	$0.50^{a} \pm 0.03$	$0.51^{a} \pm 0.01$	$94.96^{e} \pm 0.07$
Al-WTR + CM	$3.13^{e} \pm 0.03$	$5.61^{g} \pm 0.07$	$5.39^{d} \pm 0.20$	$4.73^{d} \pm 0.19$	$3.64^{e} \pm 0.04$	$77.43^{a} \pm 0.40$
Al-WTR + MS	$2.41^{d} \pm 0.03$	$4.91^{f} \pm 0.05$	$5.26^{d} \pm 0.11$	$4.45^{d} \pm 0.11$	$3.13^{d} \pm 0.03$	$79.83^{b} \pm 0.26$
Control	$1.01^{a} \pm 0.03$	$1.56^{a} \pm 0.04$	$0.91^{a} \pm 0.04$	$0.62^{a} \pm 0.04$	$0.55^{a} \pm 0.04$	$95.35^{e} \pm 0.06$

$WSA_{> 2\ mm}$, $WSA_{1\text{-}2\ mm}$, $WSA_{0.5\text{-}1\ mm}$, $WSA_{0.18\text{-}0.5\ mm}$, $WSA_{0.063\text{-}0.18\ mm}$ and $WSA_{< 0.063\ mm}$ represents water-stable aggregates greater than 2 mm, between 1 and 2 mm, 0.5 and 1 mm, 0.18 and 0.5 mm, 0.063 and 0.18 mm and those less than 0.063 mm. Data are means ± standard error of means (SEM) ($N = 7$). Mean value ± SEM in the same column followed by the different superscript letters indicate significant differences among different treatments for each size of soil aggregates based on Tukey's HSD test ($p < 0.05$).

4.6.5 Relationship between soil organic carbon and aggregate stability

A linear regression function to investigate the general relationship between SOC, WSA and MWD for all treatments showed that both WSA and MWD showed a significant ($p < 0.001$) positive relationship with SOC (**Figure 4.2**). The linear relationship showed that both WSA and MWD are dependent on SOM.

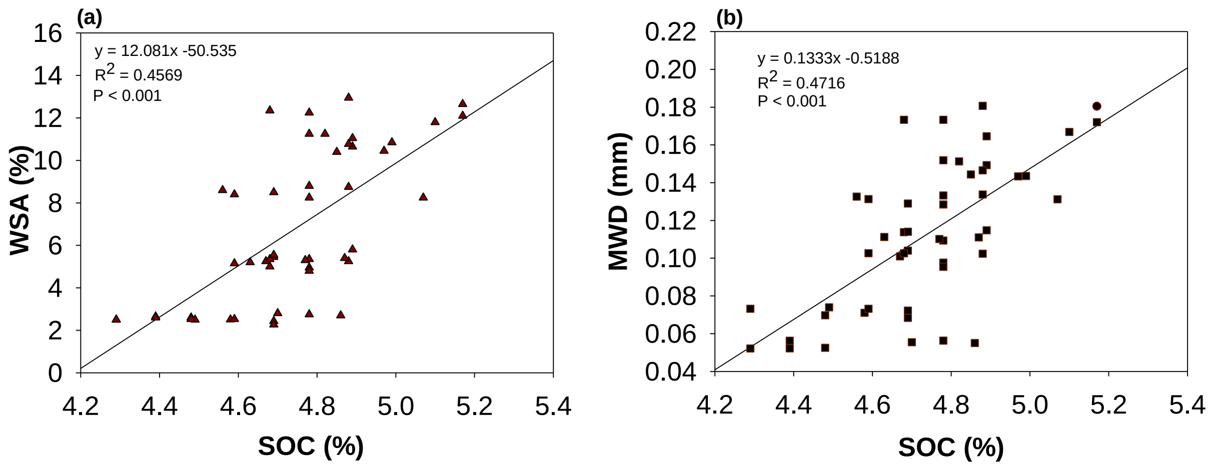

Figure 4.2: Regression relationship between SOC and (a) water-stable aggregates and (b) mean weight diameter due to different soil treatments (aggregate data).

4.6.6 Soil moisture retention characteristics

The most significant differences in volumetric soil moisture among treatments were observed for the top 0 - 5 cm, but the differences were on only significant at low suctions (5 to 10 kPa) (**Figure 4.3**). Volumetric soil moisture retention significantly ($p < 0.05$) increased with soil depth, with the highest volumes attained in the 10 - 20 cm soil layer, whilst the top 5 cm layer had the least (**Figure 4.3**). Correspondingly, more water was retained at lower suctions compared to higher suctions. Increments of 0.02 cm^3 cm^{-3} and 0.06 cm^3 cm^{-3} in the readily available water (RAW) were recorded for the 0 - 5, 5 - 10 and 10 - 20 cm depths, respectively, in Al-WTR + CM. The readily available water is the amount of water held between -5 kPa and -200 kPa. At field capacity (FC), which is estimated at -10 kPa (pF 1) for a sandy loam soil, Al-WTR + CM resulted in 31.8%, 17.3% and 12.9% more water for the 0 – 5, 5 – 10 and 10 – 20 cm depths, compared to the control. Measured at FC, Al-WTR + MS resulted in volumetric water increases of 26.7%, 15.7% and 12.0%, for the 0 - 5 cm, 5 - 10 cm, and 10 - 20 cm soil layers, respectively, relative to the control. While Al-WTR + CM consistently retained more water in respect to the control, no significant differences ($p > 0.05$) were observed between the control and standard NPK (**Figure 4.3**).

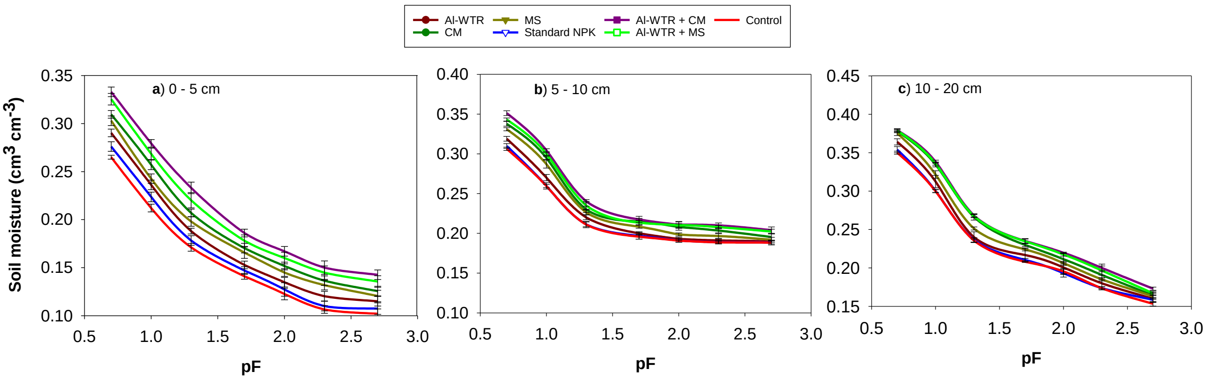

Figure 4.3: Volumetric soil moisture retention curves for a sandy loam soil amended with different treatments at a) 0 – 5 cm depth, b) 5-10 cm depth and c) 10 – 20 cm depth. Data are means ± SEM represented as error bars (*N* = 7).

Similarly, the gravimetric moisture content increased with soil depth, whilst it decreased with increase in suction (**Figure 4.4**). The co-amendments (Al-WTR + CM and Al-WTR + MS) significantly ($p < 0.05$) retained more water at lower suctions compared to higher suctions across all soil depths (**Figure 4.4**). For example, at 0 – 5 cm soil depth both Al-WTR + CM and Al-WTR + MS retained ~ 2% more water compared to the unamended control at -5 kPa suction, whilst retaining just about 1% more water at -500 kPa (**Figure 4.4**). The co-amendments (Al-WTR + CM and Al-WTR + MS) also retained more water at all suctions compared to the single amendments of either Al-WTR, CM or MS (**Figure 4.4**). For example, for the 0 – 5 cm depth at 200 kPa, Al-WTR + CM (9.1 ± 0.44%) retained > 0.5% more water relative to CM, MS and Al-WTR with 8.6 ± 0.18%; 8.1 ± 0.38% and 8.4% ± 0.33%, respectively (**Figure 4.4**). Similarly, Al-WTR + MS (8.8 ± 0.50%) retained > 0.2% more water relative to the single amendment of Al-WTR, CM and MS.

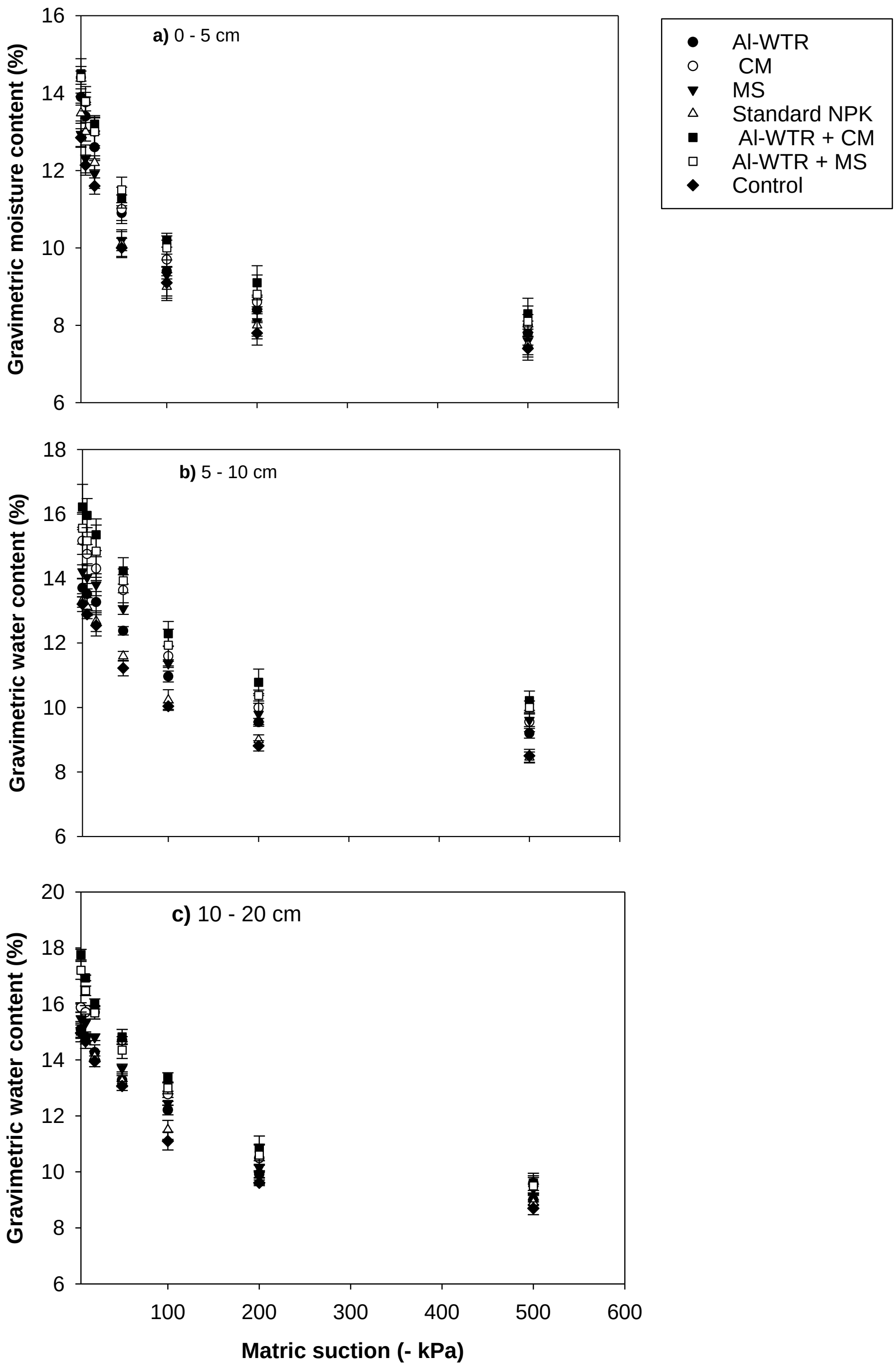

Figure 4.4: Soil water retention curves based on gravimetric water content for a sandy loam soil amended with different treatments at a) 0 – 5 cm depth, b) 5-10 cm depth and c) 10 – 20 cm depth. Data are means ± standard error of means (SEM) represented as error bars (N = 7).

4.6.7 Maize grain and biomass yield

In year 1 (2019/2020 cropping season), Al-WTR + MS resulted in the highest yields of maize grain (2.5 ± 0.03 t ha^{-1}) and biomass (4.14 t ha^{-1}) whilst the unamended control yielded the least with a maize grain yield of 0.53 ± 0.07 t ha^{-1} and a biomass yield of 2.14 ± 0.24 t ha^{-1} (**Figure 4.5 a, b**). First year, maize grain yield for the co-amendment, Al-WTR + CM and the single amendment of maize stover (MS) was similar, whilst biomass yield was statistically comparable to most treatments except for standard NPK and the control (**Figure 4.5 a, b**). During the second year (2020/ 2021), Al-WTR + CM significantly ($p < 0.05$) yielded superior maize yields relative to all other treatments, accumulating 5.61 ± 0.05 t ha^{-1} in grain yield and 7.02 ± 0.62 t ha^{-1} biomass (**Figure 4.5 c, d**). Al-WTR + MS followed with 4.84 ±0.03 t ha^{-1} in grain yield and 5.81 ± 0.89 t ha^{-1} of biomass. Whilst the unamended control consistently gave lower yields in both years, the single amendment of Al-WTR yielded two- and four- times more grain yield, in years 1 and 2, respectively. Similarly, the single amendment of Al-WTR accumulated almost double the maize biomass yield in both years, relative to the unamended control (**Figure 4.5**). Overall, both maize grain and biomass yields across treatments were lower in the first year (2019/2020) than in the second year (2020/2021) due to a prolonged midseason dry spell, which coincided with critical maize growth stages such as silking and grain filling (see **Figure 3.1**).

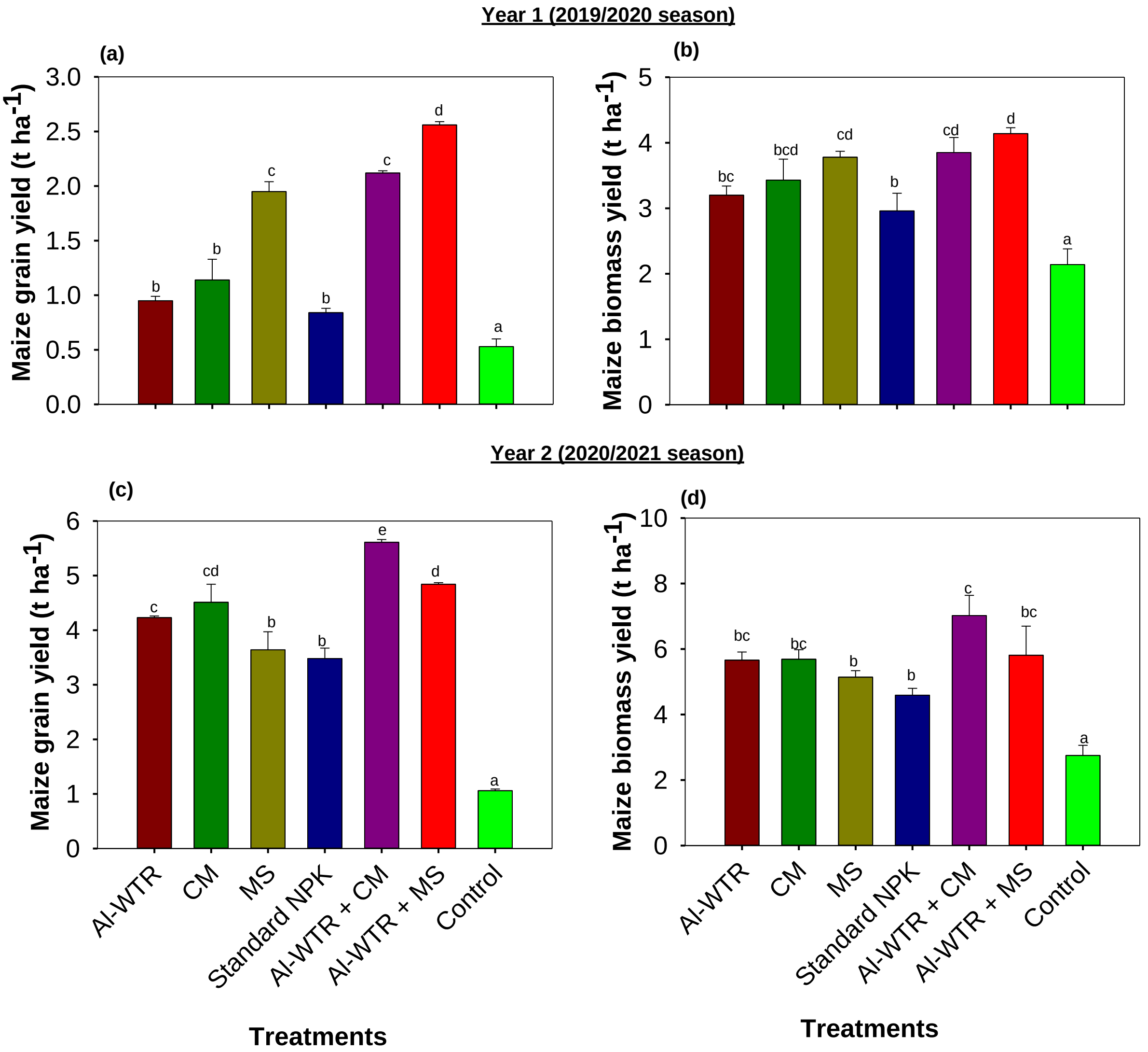

Figure 4.5: Maize grain and biomass yield due to different treatments. Data are means ± standard error of means (SEM) (N=7). Bars with different letters are significantly different according to Tukey's HSD test ($p < 0.05$).

4.7 Discussion

4.7.1 Soil fertility management effects on SOC and bulk density

The distribution of SOC was influenced by soil fertility management practices as evidenced by the increase in SOC concentration with addition of OM compared to the unamended control and standard NPK. It is well known that improvements in SOC occur after additions of OM (Mtambanengwe *et al.*, 2005; Luo *et al*., 2017; Bolinder *et al*., 2020; Gautam *et al*., 2022). For example, the addition of crop residues and cattle manure have both been associated with improvements in SOC (Guo *et al*., 2016; Fu *et al*., 2021). Although SOM is not a direct requirement of plant growth per se (Katyal *et al*., 2001), it is very important for water and nutrient holding capacity (Somerville *et al*., 2018) and is thus an important indicator of soil degradation (Lorenz *et al*., 2019; Lal, 2020b; Zingore *et al*., 2021). Although, single amendments of cattle manure, Al-WTR and MS did not result in significant increases in SOC relative to the unamended control and standard NPK, their application as co-amendments resulted in significantly more soil C build-up compared to the control and standard NPK. This was more likely due to the presence of Al and / or Fe oxides in the WTR. Al-WTR directly contributes to OM due to their high C content (Dassanayake *et al*., 2015; Kerr *et al*., 2022). In addition, the Al and Fe oxides on the surface of WTR can form strong inner sphere complexes with OM through various OM functional groups such as the carboxyl (-COOH), alcoholic hydroxyl groups (-OH) and phenolic hydroxyl groups (Yang *et al*., 2019). The Al and Fe oxides within the WTR matrix also adsorb OM molecules due to their high surface area and active adsorption sites (Wang *et al*., 2015; Yang *et al*., 2019), shielding the OM from microbial degradation (Kögel-Knabner *et al*., 2008) and can therefore contribute to long term C storage (Kramer and Chadwick, 2018). Research has increasingly shown the importance of extractable Al and Fe contributions to SOC stabilisation in highly weathered and acidic soils such as those in Domboshava (Kramer and Chadwick, 2018; von Fromm *et al*., 2021). The SOC content due to Standard NPK and the unamended control were not statistically different. This contrasts with other studies which reported significant increases in SOC due to use of inorganic fertilisers (e.g., Haynes and Naidu, 1998; Mi *et al*., 2016). In these studies, the increase in SOC was attributed to greater inputs of rhizo-deposited OM, root biomass and crop stubble relative to the control. Contrastingly, Guo et al. (2016) argues that root biomass as an individual C source input does not significantly affect the changes in SOC storage. In this study significant changes were only realised in the co-amendments, which we attribute to the synergy between freshly added OM and the Al and Fe oxides in WTR. The incorporation of organic amendments by conventional hand hoeing into the deeper soil layer (10 - 20 cm) could explain the similarities observed in SOC with soil depth across all treatments that received OM.

The differences ($p < 0.05$) in soil bulk density that were observed among treatments in the top 5 cm soil layer could be linked to SOC variations within soil depths. The co-amendments, which resulted in higher SOC were most effective at reducing soil bulk density. Organic materials are generally characterised by low bulk density and higher porosity, and their addition to the denser soil mineral fraction results in low bulk density (Haynes and Naidu, 1998; Guo *et al*., 2016). The decrease in soil bulk density due to soil additions of Al-WTR and other organic sources have also been reported elsewhere (e.g., Ibrahim *et al*., 2015). However, Hsu and Hseu (2011) reported inconsistences regarding the effect of co-amendments on soil bulk density and no conclusive evidence could be elucidated, henceforth. In addition, WTRs are highly porous (Babatunde *et al*., 2008) and have low bulk densities ranging from 0.56 to 1.30 g cm^{-3} (Dayton and Basta, 2001), which may lower soil bulk density when they are added to the soil. Although the co-amendments significantly differed in their SOC contents relative to the unamended control and standard NPK across all three depths, no significant effects could be attested relative to the single amendments of Al-WTR, CM and MS in the 5 - 10 and 10 - 20 cm depths. A much longer time frame with repeated applications could be needed to realise significant changes in bulk density after adding both organic and mineral soil amendments. Under this scenario, the co-amendments showed great potential to improve soil bulk density.

4.7.2 Importance of Al and Fe oxides and organic matter co-amendments in aggregate stability and soil water-retention capacity

Aggregate stability is a soil quality indicator which is directly linked to SOM (Chivenge *et al*., 2011; Zhao *et al*., 2017). The proportion of WSA and MWD increased linearly with increase in SOC (**Figure 4.6**), suggesting that SOM plays an important role in the stability of soil aggregates. The weak correlation, however, could be attributed to the shorter time frame of the study in re-building SOC. There is ample evidence to show that combined use of OM and inorganic fertilisers improve soil aggregate stability and water holding capacity (Haynes and Naidu, 1998; Zhao *et al*., 2017; Gautam *et al*., 2020). However, the declining trend, (Al-WTR + CM > Al-WTR + MS > CM > MS> Al-WTR > Standard NPK > Control) in WSA, MWD and water holding capacity showed the importance of both OM and soil mineral components in improving soil aggregate stability and water holding capacity (Kerr *et al*., 2021). Al-WTR contains about 40% OM and 60% mineral component in form of Al and / or Fe oxides (Kerr *et al.*, 2022). As previously highlighted, emerging evidence has revealed the important contribution of Al and Fe oxides mineral components in SOM stabilisation which enhance soil aggregate stability (Zhao *et al*., 2017; Xue *et al*., 2019; von Fromm *et al*., 2021). While the OM provided for by the co-amendments increase soil aggregate stability by directly contributing to humic acids and polysaccharides which bind soil aggregates together (Gautam *et al*., 2022), the Fe and Al oxides binds strongly to the SOM, resulting in the formation of stable organo-mineral complexes that can enhance the tensile strength and stability of the aggregates (Zhao *et al*., 2017; Xue *et al*., 2019). The improvements in WSA and MWD due to the co-amendments has been confirmed in other studies (Hsu and Hseu, 2011; Ibrahim *et al*., 2020). Overall, the soils generally showed poor soil aggregation, with very low values of WSA and MWD compared to what has previously been reported in related stability studies at Domboshava 15 – 20 years ago (Nyamangara *et al*., 2001; Nyamadzawo *et al*., 2008), and elsewhere in Zimbabwe (Gwenzi *et al*., 2009). This could be attributed to the declining fertility levels, in particular SOC over the years (Mutegi *et al*., 2018; Kihara *et al*., 2020a).

In this study, the highest proportion of aggregates were < 0.25 mm across all treatments, suggesting a weak structural stability of the soils and therefore poor resilience to water destruction (Six *et al*., 2000a). WSA are classified as either macro-aggregates (> 0.25mm) or micro-aggregates (< 0.25 mm) (Six *et al*., 2000b). It is envisaged that macro-aggregates proffer the best soil structural stability (Six *et al*., 2000b; Zhou *et al*., 2020), and their abundance is often associated with improved soil aeration, water infiltration and drainage (Papadopoulos, 2011). The sandy soils in Domboshava are known to readily compact and crust under natural rainfall due to their poor structure (Nyamapfene, 1991), and are therefore susceptible to soil loss through water erosion. Despite that, the proportion of $WSA_{> 0.25\ mm}$ was greater in the co-amendments suggesting that they have the potential to build and stabilise soil structure in the long-term.

The soils' water holding capacity followed a similar pattern to aggregate stability. Improved soil aggregation can enhance soil water holding capacity by not only increasing pore space which allows water to pass through down the soil profile but by also enhancing water storage through intra-aggregate pores (Romero *et al*., 2011). The co-amendments exhibited superior water-retention capacity ahead of all other treatments. Increased soil water retention by the co-amendments has also been confirmed by Kerr et al. (2022). Kerr et al. (2022) noted that co-amendments contained higher OC content and were therefore able to hold more water than those with less OC because they exhibited greater propensity to swell. While the increase in soil water-holding capacity due to OM addition has been widely confirmed (Haynes and Naidu, 1998; Somerville *et al*., 2018; Lal, 2020a), the soil water retention characteristics of unsaturated soil is also dependent on the soil mineralogical component (Romero *et al*., 2011; Lal, 2020a), to which Al and Fe oxides play an important role.

At low suctions, macropores control the amount of water held in the soil (Romero *et al*., 2011), as such increases in RAW by the co-amendments was expected as they had a positive influence on macroaggregates and hence macropores as shown in **Table 4.1**. For high suctions, volumetric water in the soil is more dependent on micropores, which are more influenced by soil texture (Hall, 1991; Romero *et al*., 2011;). In this study, co-amendments enhanced soil water-retention capacity of a sandy soil likely due to their influence on macro-aggregates and hence soil macroporosity; their use could enhance the resilience of these soils to drought. Such immediate benefits provide an incentive for re-use of Al-WTR as co-amendments by farmers especially in drought-prone areas.

4.7.3 Co-amendments improve maize grain and biomass yields

The higher maize grain and biomass yields observed in Al-WTR + MS and the single amendment of MS during the first year were attributed to enhanced soil moisture due to the mulching effect of maize stover residues rather that to improved soil conditions. The first year was characterised by low moisture content due to a prolonged dry spell which coincided with critical maize growth stages, silking, and grain filling, resulting in low yields (see **Figure 3.1**). Maize stover residues provided a surface covering during the prolonged dry periods, conserving soil moisture in the process. The crop yield benefits of using mulch have been established (Mbanyele *et al*.,2021; Mhlanga *et al*., 2021). During the second year, Al-WTR + CM yielded higher grain and biomass yield. Ibrahim et al. (2020) reported increased wheat grain yield due to co-application of rice straw compost and WTR, which they partly attributed to improved soil physical conditions and the enhanced soil fertility benefits from OM additions (Clarke *et al*., 2019). Similarly, Mahmoud et al. (2021) reported improved maize yields due to use of WTR and phosphogypsum ($CaSO_4 \cdot 2H_2O$) compared to unamended soil. Based on these observations, crop yield improvements are more pronounced where WTR is used in co-amendments. Although other biochemical factors could be at play, in this study, higher maize grain yields due to Al-WTR + CM was likely attributed to the conducive environment brought about by the improved soil properties and soil moisture.

4.8 Conclusions

In this study, a two-year field experiment was carried out to investigate the influence of different soil fertility amendments on SOC, bulk density, aggregate stability and soil water retention and the associated maize grain yields in Domboshava, Zimbabwe. The sandy soils in Domboshava are characterised by low SOC, poor aggregation, and low water retention capacity. The co-amendments of Al-WTR + CM and Al-WTR + MS were more effective at improving SOC by > 7% relative to the unamended control. Significant ($p < 0.05$) variations in bulk density were observed in the top 5 cm and the control was 0.05 g cm^{-3} denser, compared to Al-WTR + CM with 1.30 g cm^{-3}. This could be attributed to higher SOC in Al-WTR + CM compared to the control. Both WSA and MWD were correlated ($p < 0.001$) to SOC and Al-WTR + CM in turn exhibited greater stability ($p < 0.05$), achieving an increase of 393% (WSA) and 141% (MWD), relative to the unamended control. The co-amendment, Al-WTR + CM resulted in increments of 0.02 cm^3 cm^{-3} and 0.06 cm^3 cm^{-3} in the readily available water (RAW) for the 0 - 5, 5 - 10 and 10 - 20 cm depths, respectively, whilst also retaining 31.8%, 17.3% and 12.9% more water at field capacity (FC) for the 0 – 5, 5 – 10 and 10 – 20 cm depths, respectively, compared to the control. Both Al-WTR + MS and Al-WTR + CM significantly

($p < 0.01$) yielded higher maize grain yields of 2.5 t ha^{-1} and 5.61 t ha^{-1} in the first and second seasons, respectively, equating to > 350% yield increments to the control which yielded 0.53- and 1.2- t. ha^{-1}, respective for both seasons. This was attributed to the improved soil conditions such as increased SOC and soil moisture proffered by the co-amendments. The results offer prospects for use of Al-WTR co-amendments in rebuilding soil structure, partly contributing to the achievement of sustainable goal number 15 (restoring degraded soils). Increasing the capacity of soils to store water can potentially enhance drought resilience and increase maize grain yields in urban systems in Southern Africa, which are currently under threat from a declining soil resource base and the increased frequencies of drought.

Chapter 5

5.0. Soil chemical properties, maize dry matter yield, and nutritional quality as influenced by aluminium water treatment residual co-amendments[§]

Abstract

Soil degradation which is linked to poor soil organic matter management remains a major constraint to sustained crop production in smallholder urban agriculture (UA) in sub-Saharan Africa (SSA). While organic nutrient resources are often used in UA to complement inorganic fertilisers in soil fertility management, they are usually scarce and of poor quality to provide optimum nutrients for crop uptake. Alternative soil nutrient management options are required. In the first part of the study, an eight-week greenhouse experiment was established with 12 treatments to evaluate the short-term benefits of applying an aluminium-based water treatment residual (Al-WTR), in combination with compost and inorganic P fertiliser, on soil chemical properties, and maize (*Zea mays* L.) productivity and nutrient uptake. The co-amendment (10% Al-WTR+10% compost) produced maize shoot biomass of 3.92 ± 0.16 g at 5 weeks after emergence, significantly ($p < 0.05$) out-yielding the unamended control which yielded 1.33 ± 0.17 g. The addition of P fertiliser to the co-amendment further increased maize shoot yield by about two-fold (7.23 ± 0.07 g). The co-amendment (10% Al-WTR + 10% C) with P increased maize uptake of Zinc (Zn), Copper (Cu) and Manganese (Mn) by 13.63-, 1.08- and 0.79- mg kg^{-1}, respectively, compared with 10% C + P. In the second complementary study, a two-year field experiment was established to evaluate the influence of Al-WTR, cattle manure (CM) and maize stover (MS) and inorganic P fertiliser co-amendments on maize grain yield, harvest index (HI) and grain nutrient content. The co-amendment (Al-WTR + CM) significantly ($p < 0.05$) out-yielded the unamended control five-fold recording 5610 ± 0.05 kg ha^{-1} maize grain yield against 1060 ± 0.03 kg ha^{-1} for the control. The co-amendment of Al-WTR + MS recorded the highest maize HI of 0.47 ± 0.03 kg kg^{-1} whilst the control gave the least index of 0.29 ± 0.02 kg kg^{-1}. The co-amendment of Al-WTR + CM also enhanced Zn and Cu grain concentration by 92.8% and 37.3% respectively relative to the unamended control. Overall, the results demonstrate that co-amending soil with Al-WTR and either CM, MS, compost, and inorganic P fertiliser increase maize productivity and micronutrient uptake in comparison to their single amendments. The enhanced micronutrient uptake improves maize grain nutritional quality, and subsequently human nutrition for the urban population of SSA, partly addressing the UN's Sustainable Development Goal number 3 of improving diets.

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5.1 Introduction

There are increased concerns over food and nutrition insecurity in the urban communities of Southern Africa, due to rapid human population growth coupled with limited job opportunities against limited livelihood alternatives (Cockx *et al*., 2018; Awad, 2019). To cope with these changes, many urban dwellers in the region are increasingly resorting to urban agriculture (UA) for household food, nutrition, and income security (Kutiwa *et al*., 2010; D'Alessandro *et al*., 2018). However, as is the case in many rural communities in Southern Africa (Giller *et al*., 2021; Zingore *et al*., 2021), crop production has remained low in urban areas due to a combination of factors, including declining soil fertility (Nyamasoka *et al*., 2015; Mtangadura *et al*., 2017) and a changing climate (Rurinda *et al*., 2015), hampering efforts towards achievement of Sustainable Development Goals, most of which are underpinned by soil health (Keesstra *et al*., 2016; Lal, 2019). Without addressing poor soil fertility and the negative impacts of the changing climate, crop yields will remain poor, increasing the number of households vulnerable to food deficits.

Although inorganic fertiliser is a precursor to rebuilding soil nutrient stocks and increased crop productivity (Kihara *et al*., 2020b; Rurinda *et al*., 2020), many farmers in sub–Saharan Africa (SSA) have limited or no access to inorganic fertiliser due to high costs and inaccessibility (Bonilla Cedrez *et al*., 2020). Current fertiliser application rates in SSA average only about 16 kg ha^{-1}. $year^{-1}$, compared with over 100 kg ha^{-1}. $year^{-1}$ in Europe and North America, and over 150 kg ha^{-1}. $year^{-1}$ in China (FAOSTAT, 2019). To increase and maintain crop production in SSA, use of organic nutrient resources is important (Mapfumo and Giller, 2001). Organic nutrient resources increase crop yields by supplying plant nutrients in the short to medium term while improving soil organic matter and other soil physicochemical and biological properties in the long term (Oldfield *et al*., 2018). Farmers in rural areas of SSA rely on locally available nutrient resources such as partially composted woodland litter, and livestock manure for crop production (Manzeke *et al*., 2012; Gwandu *et al*., 2022). In urban communities, crop residues from previous harvests are the most available organic nutrient resource because of little competition for their use as livestock feed. However, some farmers prefer to burn the crop residues due to the drudgery involved during their incorporation. Water treatment residual (WTR) is a potential organo-mineral resource that could be used for soil fertility improvement, and soil health in UA, but its potential use remains largely untapped. WTRs can potentially contribute to soil C build-up in the long term because the organic matter becomes tightly bound in the Fe and Al oxide matrix (Elliott and Dempsey, 1991; Novak and Watts, 2004), and is thus protected from microbial attack (Kögel-Knabner *et al*., 2008). On a global scale, it is estimated that 10 000 t of WTR, on average, are produced daily from standard water treatment works (Gibbons and Gagnon, 2011; Ahmad *et al*., 2016). While information on WTR production trends from Africa are largely missing; given the rapid urbanization, more water will be purified to meet the increasing human demand, and inevitably more WTR will be generated. Since the WTR contains mineral nutrients and organic matter, it can therefore, be used as an alternative source of soil nutrients including micronutrients for plant nutrition and soil health in UA (Gwandu *et al*., 2022). Use of WTR as a soil amendment can minimize costs of its disposal and the undesirable impacts on the environment.

Research has been done to understand the potential of WTR as a soil ameliorant (Dassanayake *et al*., 2015; Turner *et al*., 2019). Of major concern, however, is phosphorus (P) dynamics following addition of WTR to soil. Phosphorus is an important macronutrient in plant growth (Malhotra *et al*., 2018); and is one of the most limiting nutrients in the predominantly sandy soils of Southern Africa (Rurinda *et al*., 2020). Jonasson (1996) and Cox et al. (1997) demonstrated that Al or Fe oxides present in WTR potentially bind P in soil, making it unavailable for plant uptake. On the contrary, studies by Grabarek and Krug (1987), and

Geertsema et al. (1994) have shown that the application of WTR to soil has no effect on P uptake and plant growth in tree species. Other reports (Rengasamy *et al*., 1980; Mahdy *et al*., 2007) have confirmed improved soil properties and dry matter yields of maize in fertilised and unfertilised pots amended with WTRs, albeit at certain threshold application levels. However, this also differed with soil type (Mahdy *et al*., 2007). Evaluating options that reduce the P-fixing ability of WTR would be key for sustainable use of WTR in crop production. Co-application of WTR with P fertiliser may eliminate the problem of P deficiencies for plant growth (Hyde and Morris, 2004). Alternatively, co-application of WTR with compost or other organic plant or animal-based waste may help to alleviate P sorption by the Fe and Al oxides in soils (Havlin *et al*., 2005; Gwandu *et al*., 2023). Hsu and Hseu (2011) reported an increase in shoot biomass production of Bahia grass (*Paspalum notatum*) without changes in soil P availability due to co-application of WTR and pine bark compost. Recent work in Southern Africa has also proven that when WTR is used in combination with organic compost with a 1:1 co-application ratio, wheat (*Triticum aestivum*) productivity increased by 33% (Clarke *et al*., 2019). The resultant wheat growth was attributed to balanced nutrition, with P and potassium (K) from the compost and nitrogen (N) from WTR. However, this has not yet been tested in maize (*Zea mays* L.), a strategic crop for food security in Southern Africa, including Zimbabwe. This study is based on the hypothesis that application of Al-WTR in combination with other organic nutrient resources and P fertiliser improve soil chemical properties, nutrient uptake and maize dry matter yield relative to unfertilised maize.

5.2 Study Approach

The study was done in two parts, (i) through a greenhouse plant trial to understand the effects applying Al-WTR, compost and inorganic P fertiliser, on soil chemical properties, and maize (*Zea mays* L.) productivity and nutrient uptake and (ii) through a complementary field experiment to determine the influence of co-application of Al-WTR, inorganic P fertiliser, and locally available organic nutrient resources that included cattle manure and / or maize stover on maize grain yield, harvest index and grain nutrient content.

5.3 Materials and methods

The greenhouse study was carried out in the UK as outlined in Chapter 3 section 3.1. The greenhouse study comprised of 12 treatments (see **Table 5.1**). The detailed description of the treatments, experimental layout and data collection protocols are given in Chapter 3 section 3.3.1. A sandy-loam soil was sampled from the experimental field in Domboshava a year prior to the establishment of the field experiment and shipped to the UK for use in the greenhouse study. The field study was carried at Domboshava Training Centre (described in detail in Chapter 3, section 3.1) and comprised of 7 treatments arranged in a randomized block design which are also described in detail in Chapter 3 section 3.4. The treatments for both the greenhouse and field study are shown in Table **5.1**.

Table 5.1: Experimental treatments

Greenhouse experiment		Field experiment	
Treatment number	Treatment composition	Treatment number	Treatment composition
1	Control (unamended soil)	1	Al-WTR
2	10% Al-WTR	2	CM
3	10% compost	3	MS
4	20% Al-WTR	4	Standard NPK
5	20% compost	5	Al-WTR + CM
6	10% Al-WTR + 10% compost	6	Al-WTR + MS
7	Standard NPK	7	Control (unamended soil)
8	10% Al-WTR + P		
9	10% compost + P		
10	20% Al-WTR + P		
11	20% compost + P		
12	10% Al-WTR +10% compost + P		

Al-WTR- aluminium water treatment residual; CM- cattle manure; MS-maize stover, standard NPK-N.P. K fertilizer (7% N, 14% P_2O_5, 7% K_2O); P -P fertiliser (7% N, 14% P_2O_5, 7% K_2O)

5.4 Chemical characteristics of soil, Al-WTR and the organic amendments (compost, cattle manure and maize stover)

The soil used in this study had high sand content (73%), very low pH (4.0) and a relatively high exchangeable acidity (6.0 meq $100g^{-1}$) (**Table 5.2**). The soil had low organic C (0.47%) and nutrient content, including total N (0.03%) and P (0.06%), compared with Al-WTR and all the organic amendments. The low level of cations (< 0.2 g kg^{-1}) in the soil were also consistent with a low CEC (6.5). The compost used in the study had a high nutrient content in general and a very high CEC (84.3 cmol $_{(+)}$ kg^{-1}), but low pH (4.8) and a high C: N ratio (36.7) (**Table 5.2**). Cattle manure and maize stover also had higher nutrient values compared to the soil. Both cattle manure and maize stover had higher pH values of 6.8 and 8.1, respectively (**Table 5.2**). The Al-WTR, on the other hand, had a moderate pH (pH 5.7), which is favourable for maize production. The optimum pH for maize production is pH 5.5. The Al-WTR also had total N, which was equivalent to compost averaging 1.28% and higher than maize stover and cattle manure (**Table 5.2**). Background levels of heavy metals in the soil and the co-amendments were also determined and reported in **Table 5.2**. Aluminium-WTR recorded the highest levels of Pb, Cu, Zn, Ni, Mn and Al with 4.1 mg kg^{-1}, 0.4 mg kg^{-1}, 0.5 mg kg^{-1}, 5.1 mg kg^{-1}, 29 mg kg^{-1} and 1.2 g kg^{-1}, respectively (**Table 5.2**). However, the levels were all well below the maximum permissible limits for heavy metals in agricultural soils according to the European Community guidelines (Tóth *et al*., 2016).

Table 5.2: Chemical characteristics of soil, Al-WTR, compost, maize stover and cattle manure used in the experiment

Parameter	*Soil	*Al-WTR	*Compost	*MS	*CM	European Community Maximum limit[2]
Sand (%)	73	Nd	Nd	Nd	Nd	
Silt (%)	5.0	Nd	Nd	Nd	Nd	
Clay (%)	22	Nd	Nd	Nd	Nd	
pH (0.01m $CaCl_2$)	4.0	5.7	4.8	6.8	8.1	
EC (µS cm^{-1})	80	872	2010	417	7120	
Exchangeable acidity (meq/100g)	6.00	2.50	10.50	Nd	Nd	
CEC (cmol $_{(+)}$ kg^{-1})	6.5	31.0	84.3	11.3	52.0	
Total P (%)	0.06	0.12	0.10	0.10	0.28	
Total N (%)	0.03	1.28	1.28	0.60	0.90	
Organic C (%)	0.47	18.37	46.9	31.0	45.0	
C/N ratio	15.70	14.00	36.70	69.00	50.00	
Ca (g kg^{-1})	0.10	0.58	11.18	3.00	15.00	
Mg (g kg^{-1})	0.04	0.02	1.50	3.00	7.00	
K (g kg^{-1})	0.04	0.04	2.11	8.00	36.00	
Pb (mg kg^{-1})	4.10	17.60	7.50	1.20	2.80	750
Cu (mg kg^{-1})	0.40	45.70	5.70	7.60	120	200
Zn (mg kg^{-1})	0.50	203.8	35.40	20.20	24.0	400
Ni (mg kg^{-1})	5.10	41.00	2.80	0.20	1.10	150
Fe (g kg^{-1})	0.35	4.76	11.43	0.28	0.47	
Mn (mg kg^{-1})	29.00	4534	156	34.20	42.00	
Al (g kg^{-1})	1.20	15.20	2.20	0.02	0.06	

Nd-Not determined; *Al-WTR-aluminium water treatment residual; *MS- Maize stover; *CM-cattle manure; [2]European Community maximum allowable concentrations for heavy metals in soil; *The values for these physical and chemical parameters were not replicated, composite samples were analysed; EC-electrical conductivity; CEC-cation exchange capacity.

5.5 Statistical analyses

For the greenhouse study, analysis of variance (ANOVA) for a completely randomised design was used to analyse the effects of amendments on maize plant growth, nutrient uptake and post-harvest soil chemical properties using GENSTAT 19th Edition. Duncan's multiple-range test was then used to compare treatment means for all the measured parameters at $p < 0.05$. For the field experiment, a one-way ANOVA was used to analyse the effects of different amendments on grain yield, HI, and grain nutrient content using GENSTAT 21st Edition (VSN International, 2022). Tukey's Honest Significant Difference (HSD) test was then used to differentiate significant treatment means at $p < 0.05$.

5.6 Results

5.6.1 Greenhouse study

5.6.1.1 Effects of different treatments on maize growth and biomass partitioning

A slow growth response of plant height to all treatments was observed until day 14; thereafter a sudden increase in plant height was observed for compost treatments, the co-amendment and standard NPK (**Figure 5.1a**). At 35 days after planting, the maize plant height was 60.17 ± 1.2 cm for the co-amendment, 10% Al-WTR + 10% C + P, which was significantly higher than 40.83 ± 3.5 cm and 54.58 ± 1.6 cm observed for the unamended control and standard NPK, respectively. Maize plant height for 10% Al-WTR + 10% C + P (64.17 ± 1.2 cm), 10% C+ P (69 ± 1.8 cm) and 20% C+ P (70 ± 1.8 cm) were comparable (**Figure 5.1a**). Number of leaves also followed a similar trend to plant height in both instances (**Figure 5.1b**). Both the plant height and leaf number decreased with increased concentration of Al-WTR from 10 to 20%, while the opposite effect was observed with the increase in the compost amendment from 10 to 20% (**Figure 5.1**). Except in Al-WTR treatments, addition of P fertiliser resulted in significant increase in plant height for all treatments. Addition of P fertiliser had no influence in number of leaves except that they were only smaller in size in treatments without P (**Figure 5.1b**).

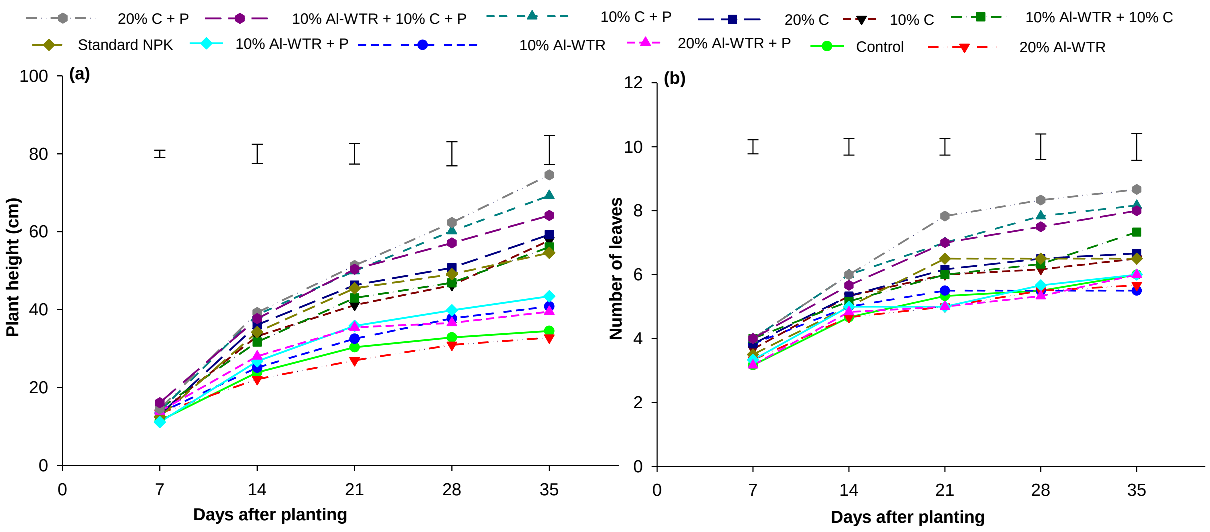

Figure 5.1: Effects of different soil amendments on (a) maize plant height and (b) mean number of leaves; C - compost; C + P - compost + inorganic basal P; Al-WTR - aluminium water treatment residual; Al-WTR + P - aluminium water treatment residual + inorganic basal P; Standard NPK – inorganic basal P fertiliser (7% N,14% P_2O_5, 7% K_2O). Error bars denote standard errors of the differences between means (SED) (*N* =6).

Maize above-ground (shoot) dry matter accumulation was highest (10.67 ± 0.55 g) in the 20% C + P treatment, whilst the least (0.76 ± 0.07 g) was observed for the 20% WTR (**Figure 5.2a**). The co-amendment, 10% Al-WTR + 10% C significantly ($p < 0.05$) yielded 3.92 ± 0.16 g higher shoot biomass than the unamended control which produced 1.33 ± 0.17 g. Addition of P fertiliser to the co-amendment (10% Al-WTR + 10% C) further increased maize dry matter yield about two-fold (7.23 ± 0.07 g) (**Figure 5.2a**). There was, however, no significant difference in maize shoot dry matter biomass between 10% Al-WTR + 10% C + P (7.23 ± 0.07 g) and 10% C + P which yielded 7.5 g ± 0.10 g (**Figure 5.2a**). The co-amendment of 10% Al-WTR + 10% C also yielded significantly ($p < 0.05$) higher shoot biomass compared with 10% C and standard NPK. Except for sole Al-WTR treatments, addition of P fertiliser significantly ($p < 0.05$) increased shoot biomass yield across all treatments (**Figure 5.2a**).

The highest root dry matter accumulation was attained in the treatment 20% C + P with 2.57 ± 0.22 g, but this did not differ significantly with 10% Al-WTR + 10% C + P with 2.4 ± 0.07 g and 10% C + P with 2.45 ± 0.17 g (**Figure 5.2b**). Likewise, root dry matter in the 10% C, 20% C and 10% Al-WTR + 10% C treatments did not differ statistically. Contrary to shoot biomass, the control yielded higher root biomass at 0.62 ± 0.09 g compared with 10% and 20% Al-WTR treatments both yielded < 0.35 g (**Figure 5.2b**). Consistent with shoot biomass, both 10% Al-WTR + 10% C + P and 10% Al-WTR + 10% C yielded significantly ($p<0.05$) higher root biomass relative to standard NPK (**Figure 5.2b**). Addition of P fertiliser significantly increased root biomass yield across all treatments.

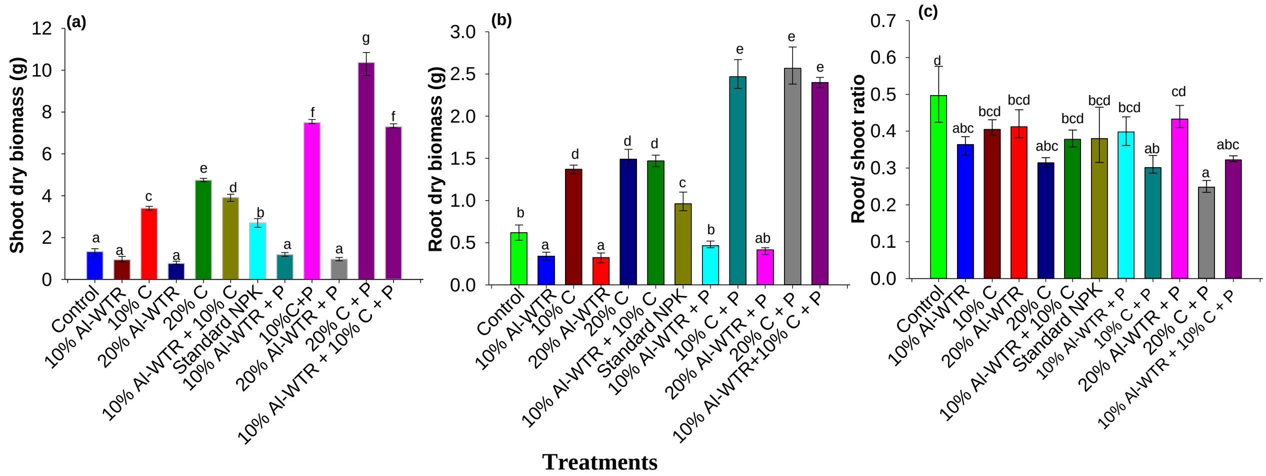

Figure 5.2: Shoot (**a**) and root (**b**) dry matter accumulation and root: shoot ratios (**c**) for different soil amendments at 5 weeks after emergence of maize. Bars represent mean ± SE (*N* = 6). Bars with different letters are significantly different at $p < 0.05$.

The control had the highest root to shoot ratio with 0.5 ± 0.02, whilst 20% C + P had the least at 0.25 ± 0.01 with the rest coming in between (**Figure 5.2c**). Root to shoot ratios were generally low in both 10% Al-WTR + 10% C + P and 10% Al-WTR + 10% C compared with sole Al-WTR and the control (**Figure 5.2c**). However, similar root: shoot ratios were observed in 10% Al-WTR + 10% C + P, and 10% C + P (**Figure 5.2c**). Overall, this data revealed that the co-amendment resulted in higher maize growth (plant height, number of leaves and dry matter accumulation) relative to the unamended control, standard NPK and sole Al-WTR treatments.

5.6.1.2 Uptake of nitrogen (N) and phosphorus (P) by maize

The highest uptake of N was recorded for 20% C + P with 39.38 ± 0.01 g N kg^{-1}, followed by the co-amendment (10% Al-WTR + 10% C + P) with 31.86 ± 0.01 g N kg^{-1} and both recorded significantly ($p < 0.05$) higher N uptake than for the rest of the treatments (**Figure 5.3a**). The least N uptake was observed in the unamended control with 1.43 ± 0.01 g N kg^{-1} (**Figure 5.3a**). Nitrogen uptake in the control, however, did not differ for both 10 and 20% Al-WTR treatments. Addition of P fertiliser had a significant influence on N uptake by maize across all treatments except for the sole Al-WTR treatments. Only the treatment 20% C + P exceeded the critical N limit in maize plant tissue (**Figure 5.3a**).

There was a contrasting trend in P uptake relative to N uptake. Uptake of P for both co-amendments of 10% Al-WTR + 10% C + P (1.08 ± 0.08 g P kg^{-1}) and 10% Al-WTR + 10% C (0.43 ± 0.06 g P kg^{-1}) was significantly ($p < 0.05$) higher than for the unamended control with 0.11 ± 0.04 g P kg^{-1} (**Figure 5.3b**). However, both 10 and 20% compost treatments (+/-P) resulted in significantly higher P uptake compared with 10% Al-WTR + 10% C and 10% Al-WTR + 10 % C + P (**Figure 5.3b**). Consistent with N uptake, 10% Al-WTR + 10% C + P had significantly higher P uptake compared with standard NPK which attained 0.67 ± 0.07 g P kg^{-1}. Although not significantly different, uptake of P declined with increase from 10 to 20% Al-WTR levels. Addition of P fertiliser did not result in significant changes in P uptake in Al-WTR treatments (**Figure 5.3b**). Phosphorus uptake across all treatments fell below the critical limit for P (3 g kg^{-1}) (**Figure 5.3b**).

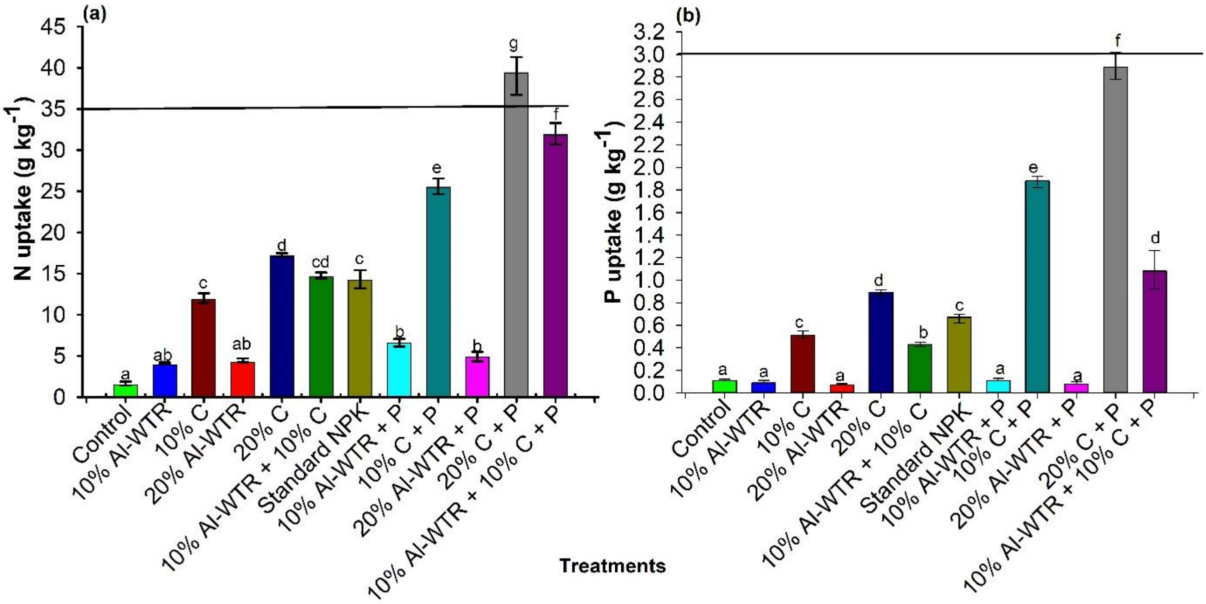

Figure 5.3: Total N (**a**) and P (**b**) uptake by maize for different soil amendments at 5 weeks after emergence of maize. The solid horizontal lines represent the critical N and P levels in maize tissue (Tandon, 1993). Bars are mean ± se (N = 3). Means with the same letter do not differ significantly at $p < 0.05$.

Generally, results revealed that addition of P fertiliser resulted in improved uptake of N and P by maize across all treatments except for sole Al-WTR treatments. P uptake was lower across all treatments in comparison to N (**Figure 5.3**).

5.6.1.3 Uptake of basic cations by maize

Following 20% C + P (4.35 ± 0.17 g Ca kg^{-1}), the co-amendment of 10% Al-WTR + 10% C + P (3.88 ± 0.23 g Ca kg^{-1}) resulted in higher Ca uptake by maize compared with the rest of the treatments (**Figure 5.4a**). The lowest uptake was in 20% Al-WTR with 0.79 ± 0.58 g Ca kg^{-1}. Addition of P fertiliser resulted in an increase in the uptake of Ca across all treatments except sole Al-WTR treatments (**Figure 5.4a**). The co-amendment, 10% Al-WTR + 10% C + P; 10% C+ P and 20% C + P attained more than 3 g Ca kg^{-1}; a value which is above the critical Ca level required in maize plant tissue.

Uptake of Mg followed a similar trend to Ca, with 20% C + P consistently attaining the highest uptake. The co-amendment, 10% Al-WTR + 10% C + P in turn attained higher Mg uptake than the control (0.17 ± 0.01 g Mg kg^{-1}) and standard NPK (**Figure 5.4b**). Similarities in the uptake of Mg were observed for 10% Al-WTR + 10% C + P and 10% C + P; 10% Al-WTR + 10% C and 10% C and for standard NPK, the control and Al-WTR treatments (**Figure 5.4b**). Except for the Al-WTR treatments, addition of P fertiliser increased uptake of Mg across all treatments. Overall, the co-amendment (10% Al-WTR + 10% C and 10% Al-WTR + 10% C + P), and the compost treatments (+/-P) exceeded 1.5 g Mg kg^{-1}, the critical Mg level in maize plant tissue.

Contrasting to Ca and Mg uptake, the highest K uptake was observed for the co-amendment, 10% Al-WTR +10% C + P which attained 31.25 ± 0.29 g K kg^{-1}, while the lowest was recorded for 20% Al-WTR with 1.72 ± 0.21 g K kg^{-1} (**Figure 5.4c**). Both co-amendments, 10% Al-WTR + 10% C and 10% Al-WTR + 10% C + P resulted in significantly ($p < 0.05$) higher K uptake relative to the control and standard NPK. Uptake of K was comparable for 10% C and 10% Al-WTR + 10% C. Addition of P fertiliser had a positive influence in K uptake across all the treatments. The co-amendment, 10% Al-WTR + 10% C + P was the only treatment that exceeded 25 g K kg^{-1}, the critical limit of K in maize plant tissue. Uptake of K by maize was generally higher than Ca and Mg uptake (**Figure 5.4**).

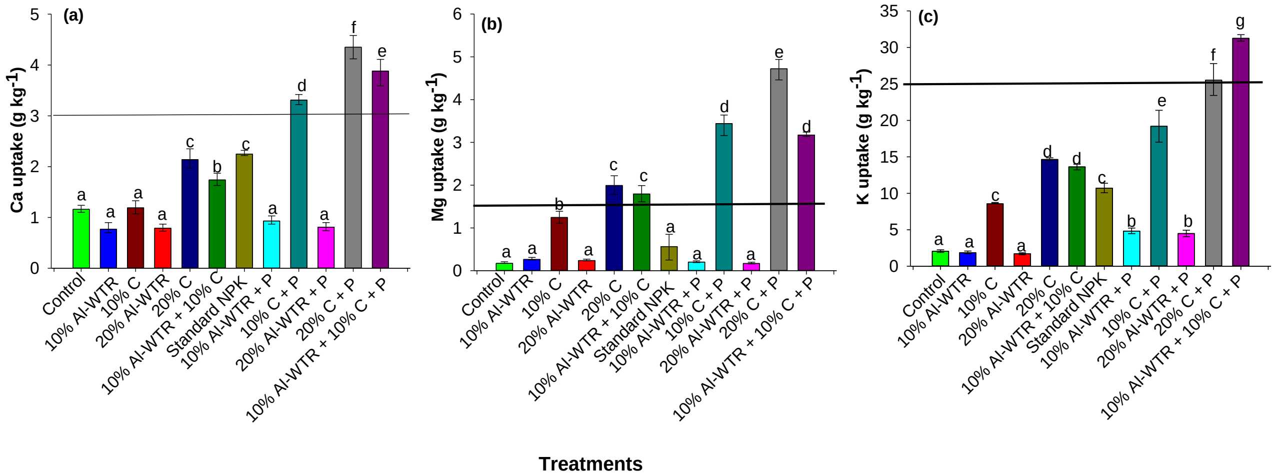

Figure 5.4: Mean values of Ca (**a**), Mg (**b**) and K (**c**) uptake by maize at 35 days after emergence. The solid horizontal lines represent critical limits for Ca, Mg and K in maize plant tissue (Tandon, 1993). Bars are mean ± SE (N = 3). Means that do not differ significantly at $p < 0.05$ contain the same letter.

5.6.1.4 Micronutrients uptake by maize

The highest Zn uptake by maize, 20.19 ± 0.02 mg Zn kg^{-1} was observed for the co-amendment, 10% Al-WTR + 10% C + P, whilst the lowest was observed for the unamended control with 0.86 ± 0.1 mg Zn kg^{-1} (**Figure 5.5a**). High Zn uptake by maize was also observed for the co-amendment (**Figure 5.5a**). Uptake of Cu followed a similar trend to Zn, with the highest amounts observed for 10% Al-WTR + 10% C + P (2.95 ± 0.15 mg Cu kg^{-1}). The control had the lowest uptake of 0.32 ± 0.03 mg Cu kg^{-1} (**Figure 5.5b**). Except for the sole Al-WTR treatments, addition of P fertiliser generally increased Zn and Cu uptake across the treatments.

Lead uptake was largest in compost treatments with the highest value of 0.26 ± 0.01 mg Pb kg^{-1} observed for 20% C + P. There were no observed differences in Pb uptake between 10% Al-WTR + 10% C and standard NPK (**Figure 5.5c**). Compared with compost treatments, 10% Al-WTR + 10% C + P resulted in reduced uptake of Pb (**Figure 5.5c**). Consistent with Pb uptake,

uptake of Ni followed a similar trend with 20% C + P yielding the highest uptake of 0.52 ± 0.02 mg Ni kg^{-1} whilst 20% Al-WTR had the least with 0.09 ± 0.01 mg Ni kg^{-1} (**Figure 5.5d**). The co-amendment, 10% Al-WTR + 10% C + P resulted in lower uptake of Ni by maize compared with 10% C + P. Except for Al-WTR treatments, the addition of P fertiliser resulted in an increase in Pb uptake in all treatments, whilst there were no significant effects on uptake of Ni across all treatments. All treatments were below the toxicity threshold levels for both Pb and Ni (**Figure 5.5c & d**).

The highest uptake of Al (79.95 ± 21.2 mg Al kg^{-}1) was observed for standard NPK, while the lowest (22.6 ± 3.7 mg Al kg^{-1}) was observed for 20% Al-WTR (**Figure 5.5e**). The Al uptake by maize observed for all treatments were below the toxicity threshold level of Al (200 mg kg^{-1}). Uptake of Mn was highest (47.5 ± 4.6 mg Mn kg^{-1}) in the 20% C + P and lowest (5.34 ± 0.32 mg Mn kg^{-1}) in the 20% Al-WTR. The co-amendment, 10% Al-WTR + 10% C + P resulted in higher Mn uptake compared with the unamended control (**Figure 5.5f**). Overall, the co-amendment 10% Al-WTR + 10% C + P resulted in lower uptake of Ni and Pb relative to sole compost treatments, whilst there were no significant differences in uptake of Al. Additionally, 10% Al-WTR + 10% C + P resulted in an increase in Zn and Cu uptake relative to all other treatments including the control (**Figure 5.5**).

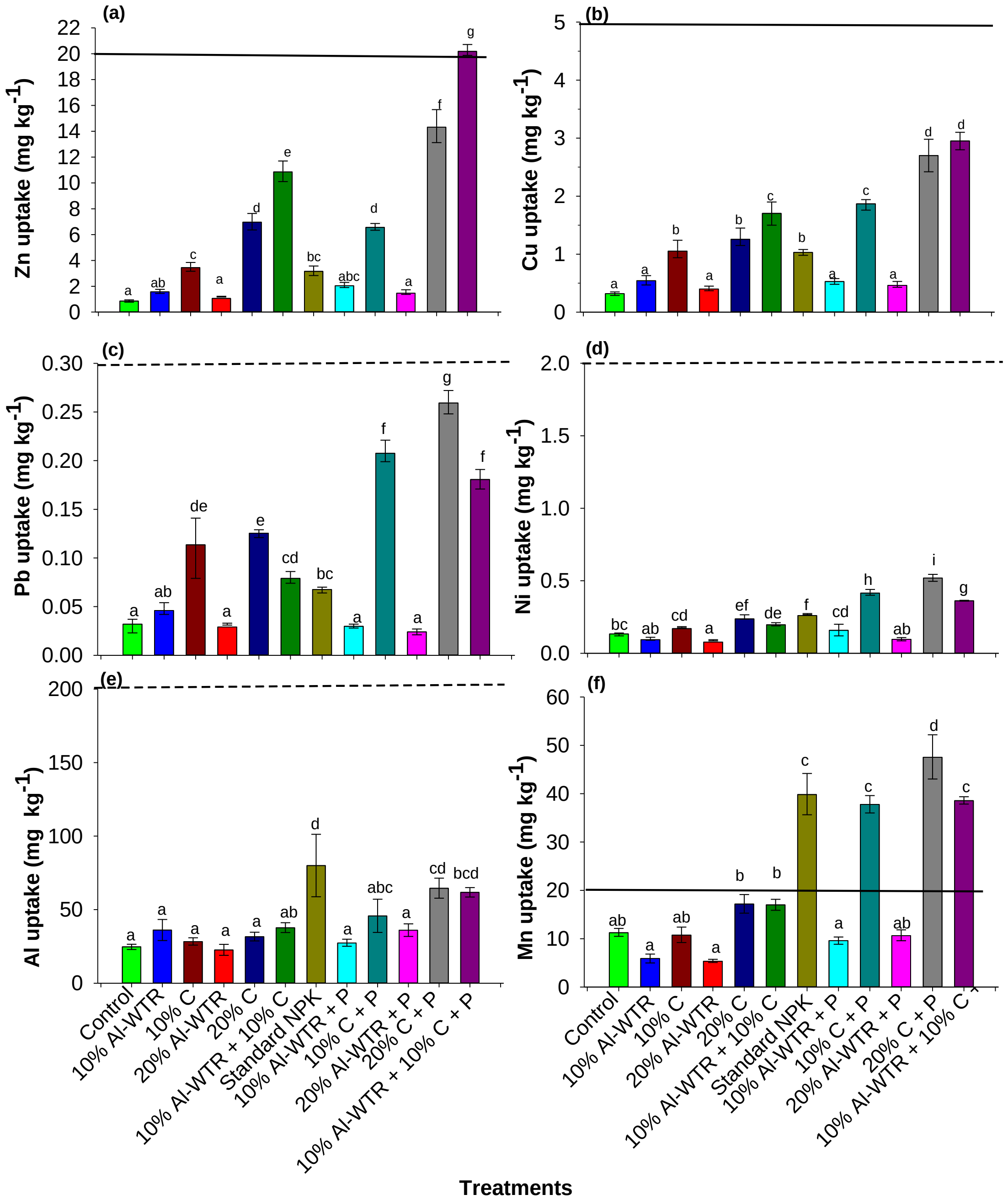

Figure 5.5: Average values of Zn (**a**) and Cu (**b**), Pb (**c**) and Ni (**d**), and Al (**e**) and Mn (**f**) uptake by maize at 5 weeks after emergence. The solid horizontal lines represent critical limits for Zn, Cu and Mn (Tandon, 1993) while the broken lines represent toxicity thresholds for Pb (FAO/WHO, 2001), Ni (WHO, 1996) and Al (Pais and Jones Jr, 1997). Bars are mean ± SE (*N* = 3). Means that do not differ significantly at $p < 0.05$ contain the same letter according to Duncan's multiple-range test at $p < 0.05$.

5.6.1.5 Effect of different soil amendments on soil chemical properties at harvest

Post-harvest soil pH due to sole Al-WTR treatments and both the 10% Al-WTR + 10% C and 10% Al-WTR + 10% C + P was comparable, whilst all compost treatments had a significantly lower pH (**Table 5.3**). This is potentially because the compost used in the experiment had a very low pH (see **Table 5.2**). Electrical conductivity (EC) in 10% Al-WTR + 10% C + P (1.79 ± 0.07) was comparable to 20% C (1.84 ± 0.07) and significantly ($p < 0.05$) higher relative to the unamended control, sole Al-WTR and standard NPK (**Table 5.3**). Although compost treatments had a significantly higher CEC compared to the rest of the treatments, both 10% Al-WTR + 10% C and 10% Al-WTR + 10% C + P, in turn had significantly higher CEC in comparison with the unamended control, standard NPK and sole Al-WTR treatments. The co-amendment, 10% C + 10% Al-WTR + P had the highest P content (0.083% ± 1.1) whilst the control (0.04% ± 0.03) had the least (**Table 5.3**).

Even though, residual soil basic cations (Ca and Mg) were generally higher in compost treatments, both 10% Al-WTR + 10% C and 10% Al-WTR + 10% C + P had significantly ($p < 0.05$) higher Ca and Mg than the control (**Table 5.3**). Contrastingly, soil residual K was significantly higher in soil only treatments- the control and standard NPK as compared to the rest of the other treatments. There were also significantly ($p < 0.05$) higher levels of post-harvest Zn, Cu and Mn in sole Al-WTR treatments compared to the rest of the other treatments (**Table 5.3**). Residual Pb and Ni were comparable among 10% Al-WTR + 10% C + P, Al-WTR treatments and standard NPK. On the other hand, 20% Al-WTR + P had significantly ($p < 0.05$)

higher Al levels as compared to the rest of the treatments. However, the post-harvest metal levels were lower than the maximum limits for the metals in agricultural soils (see **Table 5. 2**).

Table 5.3: Effects of different amendments on soil chemical properties at harvest

Parameter	Control	10% WTR	10% C	20% WTR	20%C	10% WTR + 10% C	Std NPK	10% WTR + P	10% C + P	20% WTR + P	20% C + P	10% WTR + 10% C + P
pH	6.4 ± 0.06cd	6.8 ±0.18d	5.6± 0.03b	6.4 ±0.06cd	5.0 ±0.03a	6.3 ±0.5cd	6.8 ±0.03d	6.8 ±0.003d	5.2 ±0.03ab	6.20 ±0.10c	4.90 ±0.08a	6.3 ±0.03cd
EC (dSm^{-1})	0.27 ±0.007a	0.59 ±0.07b	1.18± 0.17cde	0.77 ±0.07b	1.59 ±0.07fg	1.46 ±0.07ef	1.42 ±0.07def	1.07 ±0.07c	1.33 ±0.07cdef	1.15 ±0.07cd	1.84 ±0.07g	1.79 ±0.07g
CEC ($cmol_{(+)}kg^{-1}$)	4.33 ±0.33a	5.0 ±0.00a	14.33 ±0.88b	6.67 ±0.88a	23.67 ±0.88ef	16.33 ±0.33bc	4.0 ±0.00a	5.0 ±0.00a	21.67 ±0.33de	7.00 ±0.57a	26.0 ±0.33f	18.5 ±0.33cd
Total P (%)	0.042 ±0.30a	0.040 ±0.70d	0.045 ±0.60b	0.055 ±0.70e	0.048 ±0.30c	0.057 ±1.50g	0.068 ±0.70j	0.062 ±0.7h	0.057 ±0.6f	0.074 ±0.60k	0.066 ±0.90i	0.083 ±1.1i
Total N (%)	0.03 ±0.00a	0.17 ±0.05b	0.19 ±0.05b	0.25 ±0.05dcd	0.29 ±0.02cde	0.35 ±0.04e	0.07 ±0.003a	0.21 ±0.02bc	0.17 ±0.01b	0.30 ±0.03de	0.26 ±0.01bcde	0.32 ±0.02de
Total C (%)	0.41 ±0.01h	2.09 ±0.14g	3.83 ±0.28e	3.69 ±0.20ef	7.82 ±0.38a	7.64 ±0.05a	0.47 ±0.27h	2.23 ±0.38g	4.73 ±0.4d	3.42 ±0.39f	7.22 ±0.50b	6.47 ±0.30c
Ca ($g\ kg^{-1}$)	5.69 ±1.6ab	6.0 ±1.5abc	5.9 ±0.5abc	5.5 ±0.6ab	8.3 ±0.6bcd	7.8 ±0.7abcd	9.9 ±1.50d	6.2 ±0.5abc	7.4 ±0.4abcd	5.06 ±0.40a	8.70 ±0.70cd	6.9 ±0.23abc
Mg ($g\ kg^{-1}$)	0.40 ±0.01a	0.5 ±0.004a	1.6 ±0.18b	2.0 ±0.35bc	2.3 ±0.11c	1.6 ±0.24b	0.4 ±0.02a	0.5 ±0.005a	2.0 ±0.10bc	0.60 ±0.008a	2.50 ±0.10c	2.2 ±0.10c
K ($g\ kg^{-1}$)	10.7 ±0.32cd	10.6 ±0.23cd	9.9 ±0.01abc	9.2 ±0.21ab	8.9 ±0.13a	9.4 ±0.32ab	11.4 ±0.43d	10.7 ±0.33cd	9.4 ±0.31ab	9.50 ±0.14ab	8.80 ±0.11a	10 ±0.30bc
Zn ($mg\ kg^{-1}$)	15.3 ±0.29a	41.0 ±0.32f	18.1 ±0.15b	58.1 ±0.10h	21.3 ±0.30c	46.1 ±0.15g	21.1 ±0.00c	41.0 ±0.06f	23.4 ±0.32d	62.2 ±0.15i	25.5 ±0.23e	46.1 ±0.13g
Pb ($mg\ kg^{-1}$)	18.5 ±0.89abc	20.3 ±0.46cd	17.1 ±0.61ab	19.3 ±0.34 bcd	16.6 ±0.46a	17.2 ±1.00ab	20.3 ±0.65cd	18.9 ±0.6bcd	17.7 ±1.07ab	20.1 ±0.03cd	18.5 ±0.89abc	20.9 ±0.55d
Al ($g\ kg^{-1}$)	3.57 ±0.12d	4.64 ±0.35f	3.55 ±0.33d	3.080 ±0.03b	2.92 ±0.30a	5.24 ±0.03i	4.01 ±0.32e	4.82 ±0.03g	3.09 ±0.09b	5.45 ±0.33j	3.15 ±0.32c	4.91 ±0.35h
Cu ($mg\ kg^{-1}$)	4.90 ±0.28a	11.0 ±0.12e	6.1 ±0.03b	18.4 ±0.33g	9.5 ±0.20c	16.2 ±0.15f	6.5 ±0.11b	10.57 ±0.13e	10.6 ±0.12e	10.1 ±0.07d	9.60 ±0.15cd	15.7 ±0.09f
Ni ($mg\ kg^{-1}$)	9.13 ±0.78a	14.0 ±0.11b	13.8 ±0.70b	16.2 ±0.87bcd	15.3 ±3.6bc	17.9 ±2.2cd	10.7 ±0.12a	14.5 ±0.47b	14.03 ±0.84b	17.6 ±0.03cd	14.6 ±0.26b	18.9 ±0.54d
Mn ($mg\ kg^{-1}$)	338.3 ±0.33a	1042 ±0.58h	408 ±0.03c	1338.3 ±0.33k	410.4 ±0.32d	1233.7 ±0.33i	471 ±0.03f	1287.3 ±0.33j	404.3 ± 0.33b	1353.3 ±0.32i	423.1 ± 0.03e	1002 ±0.03g

Data are means ±standard error of the means for the three replicates. Mean data followed by a different letter within the same row are significantly different at 5% level according to Duncan’s multiple-range test.

5.6.2 Field study

5.6.2.1 Maize grain yield, nutrient uptake, and grain nutrient concentration

Maize grain yield significantly differed ($p < 0.05$) with soil fertility management. The co-amendment, Al-WTR + CM outyielded all the treatments resulting in a grain yield 5610 ± 0.05 kg. ha^{-1}, whilst the unamended control yielded the least with 1060 ± 0.03 kg ha^{-1} (**Table 5.4**). However, Al-WTR + MS gave a higher maize harvest index (HI) of 0.47 ± 0.03 kg kg^{-1} whilst the control had the least with 0.29 ± 0.02 kg kg^{-1}. Harvest index (HI) is the ratio of grain to total shoot dry matter and is an indicator of reproductive efficiency (Porker *et al*., 2020).

Maize grain nutrient uptake significantly ($p < 0.05$) varied with soil fertility management practice. The co-amendment of Al-WTR + CM significantly ($p < 0.001$) resulted in higher maize N and P uptake with79.21 ± 1.02 kg N ha^{-1} and 24.43 ± 0.37 kg P ha^{-1}, respectively, whilst the unamended control had the least with 3.59 ± 0.24 kg N ha^{-1} and 2.70 ± 0.09 kg P ha^{-1} (**Table 5.4**). Consequently, Al-WTR + CM resulted in the highest grain N and P concentrations of 13.94 ± 0.10 g N kg^{-1} and 4.30 ± 0.05 g P kg^{-1} whilst the control gave the least with 3.26 ± 0.18g N kg^{-1} and 2.46 ± 0.09 g P kg^{-1} (**Figure 5.6**). In contrast to the greenhouse study (**see figure 5.3**), Al-WTR + P resulted in significantly ($P < 0.05$) higher N and P uptake than the unamended control (**Figure 5.6**).

The co-amendment, Al-WTR + CM had significantly ($p > 0.05$) higher uptake of Ca, Zn and Cu with 0.12 ± 0.26 kg Ca ha^{-1}, 13.41 ± 0.41 g Zn ha^{-1} and 9.19 ± g Cu ha^{-1} in that respective order, whilst the control recorded the least with 0.04 ± 0.008 kg Ca ha^{-1}, 1.34 ± 0.05 g Zn ha^{-1} and 1.30 ± 0.01 g Cu ha^{-1} (**Table 5.4**). Accordingly high grain Ca, Zn and Cu concentration were recorded for Al-WTR + CM whilst the control had the least (**Figure 5.6**). The co-amendment of Al-WTR + CM enhanced Ca grain concentration by ranges of 5- to 16-% whilst grain Zn concentration increased between 14- to 28-% relative to the single amendments of Al-WTR, CM and MS. The co-amendment of Al-WTR + MS in turn resulted in increased maize grain Zn concentration by 5%, 13.6% and 21.4% relative to the single amendments of Al-WTR, CM and MS in that respective order (**Figure 5.6**).

Although not statistically significantly different from standard NPK ($p > 0.05$) the single amendment of Al-WTR resulted in a higher Al uptake of 0.72 ± 0.03g Al ha^{-1} corresponding to an Al grain concentration of 0.17 ± 0.07 g Al g^{-1}, whereas the control had the least with an overall uptake of 0.11 ± 0.01 g Al ha^{-1} grain equating to 0.01 ± 0.01 g Al g^{-1} in grain concentration. Both co-amendments, Al-WTR + CM and Al-WTR + MS, resulted in significantly lower uptake of Al by 13.9 % and 31.9%, respectively, relative to the single amendment of Al-WTR (**Table 5.4**).

Table 5.4: Effect of different soil fertility management on maize grain yield (GY), harvest index (HI), and grain nutrient uptake

Treatment	NPK (kg ha^{-1})	MS (kg ha^{-1})	CM (kg ha^{-1})	Al-WTR (kg ha^{-1})	GY (kg ha^{-1})	HI (kg kg^{-1})	N (kg ha^{-1})	P (kg ha^{-1})	Ca (kg ha^{-1})	Zn (g ha^{-1})	Cu (g ha^{-1})	Al (g ha^{-1})
Al-WTR	120	0	0	2000	4230c ±0.03	0.43b ±0.02	42.98bc ±1.16	12.93b ±0.54	0.16b ±0.003	8.64c ±0.29	5.70bc ±0.03	0.72d ±0.03
CM	120	0	10 000	0	4510cd ±0.33	0.44b ±0.02	6719de ±2.89	20.92de ±0.80	0.22c ±0.009	9.16cd ±0.31	7.23cd ±0.05	0.48bc ±0.05
MS	120	10 000	0	0	3640b ±0.33	0.41b ±0.01	49.50c ±5.47	13.80bc ±1.63	0.15b ±0.01	6.43b ±0.49	4.79b ±0.02	0.33b ±0.02
Standard NPK	150	0	0	0	3480b ±0.19	0.43b ±0.01	35.57b ± 2.98	11.19b ±0.52	0.14b ±0.007	5.47b ±0.54	4.66b ±0.04	0.55c ±0.04
Al-WTR + CM	120	0	10 000	2000	5610e ±0.05	0.45b ±0.03	79.21e ±1.02	24.43e ±0.37	0.26d ±0.003	13.41e ±0.41	9.19d ±0.04	0.62cd ±0.04
Al-WTR + MS	120	10 000	0	2000	4840d ±0.03	0.47b ±0.02	64.70d ± 1.04	17.51cd ±0.58	0.20c ±0.004	10.41d ±0.33	6.71bc ±0.03	0.49c ±0.03
Control	0	0	0	0	1060a ±0.03	0.29a ±0.03	3.59a ±0.24	2.70a ±0.09	0.04a ±0.008	1.34a ±0.05	1.30a± 0.01	0.11a ±0.01

Data are means ±standard error of the means for the five replicates. Mean data followed by a different letter within the same row are significantly different at 5% level according to Tukey's test.

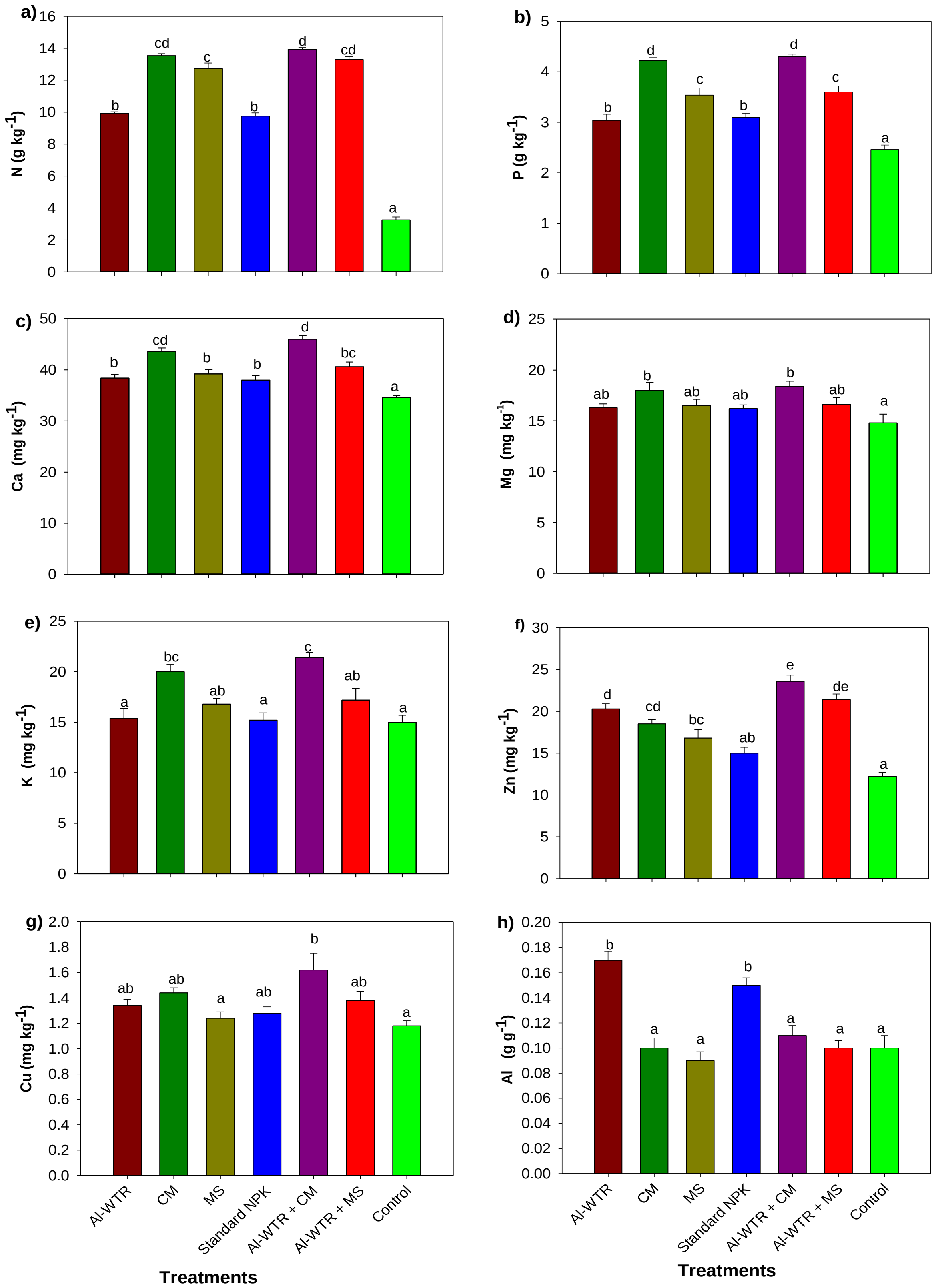

Figure 5.6: Average maize grain nutrient values of N **(a)** and P **(b)**, Ca **(c)** and Mg **(d)**, and K **(e)** and Zn **(f)**, and Cu **(g)** and Al **(h)** at physiological maturity (12.5% moisture content). Bars are mean ± SE (N = 5). Means that do not differ significantly at $p < 0.05$ contain the same letter according to Tukey's test.

5.7 Discussion

5.7.1 Characteristics of soil, Al-WTR and compost in relation to post-harvest soil chemical properties

The soil used in this study had high sand content (73%) and very low pH (4.0) which is considered very strongly acidic for Zimbabwean soils (Nyamangara and Mpofu, 1996). The high sand content means it has low nutrient retention capacity. The pH of 5.7 observed for Al-WTR is favourable for maize production whilst that of compost, pH 4.8 is considered acidic and too low for maize growth. Soil pH has an impact on nutrient availability as it can render some essential plant nutrients unavailable for plant uptake whilst making others toxic for plant growth. Thus, the Al-WTR can play a critical role as a liming material given that most of the soils in Zimbabwe as in many other countries in SSA are acidic. The Al-WTR's relatively higher CEC than the control means that it has a relatively higher capacity to retain and supply plant nutrients compared with the soil. Metal concentration of the Al-WTR was also higher than the control and compost but well below the European maximum permissible levels for heavy metals (Tóth *et al*., 2016). The Al-WTR is thus safe for land application as far as metal levels are concerned. The relatively high CEC in the compost proffers an advantage in nutrient retention capacity.

The similarity in post-harvest soil pH between the co-amendments (10% Al-WTR + 10% C + P and 10% Al-WTR + 10% C) and sole Al-WTR treatments is suggestive of the potential of WTR to modify soil pH (Hastings and Dawson, 2012). Al-WTR was able to mask the low pH due to compost in the co-amendment. The CEC of the residual soil due to the co-amendment was also higher than that for sole Al-WTR amended soils and this was consistent with findings by Hsu and Hseu 2011. This was attributed to the compost component in the co-amendment which had a high CEC. From these results, it is evident that there are synergistic benefits of combining Al-WTR and compost which are greater than the benefits of sole use of these nutrient resources. The resultant lower concentrations of Pb, Zn and Al in both 10% Al-WTR + 10% C + P and 10% Al-WTR + 10% C in comparison to sole Al-WTR could be attributed to the presence of organic matter from the compost. Heavy metals become sorbed on the active sites on OM surfaces and form stable complexes with humic substances (Clemente and Bernal, 2006), making them less bioavailable. Even though metal levels for 10% Al-WTR + 10% C + P were elevated relative to the control and standard NPK, they were not bioavailable (Hovsepyan and Bonzongo, 2009). We attributed this to the favourable pH conditions proffered due to Al-WTR. Most metals including Al are bioavailable in acidic soils with a pH < 5.5. Al toxicity inhibits root growth. The significantly higher amounts of Ni, Al and Mn following application of standard NPK mineral fertiliser could be linked to industrial processes during fertiliser manufacturing which may have resulted in heavy metal contamination of the fertiliser. In the absence of organic matter, the metals become bioavailable. However, total metal levels in all the treatments were low in comparison to the European Community maximum limits. The high K in the control soil could be attributed to the granitic nature of the soil, which is inherently high in K (Nyamapfene, 1991).

5.7.2 Impact of Al-WTR use in maize production

The observed decrease in plant growth and dry matter yield with increase in concentration of Al-WTR in the greenhouse study suggests that Al-WTR amendment levels greater than 10% could be detrimental to plant growth. This is consistent with findings by Rengasamy et al. (1980) and Mahdy et al. (2007) where growth of maize in WTR amended soils increased until threshold application levels of 10 g kg^{-1} and 30 g kg^{-1} respectively. However, compared to the control, the co-amendment of 10% Al-WTR, 10% C and P fertiliser resulted in higher maize growth and total biomass accumulation. This agrees with the work of Clarke et al. (2019) which also found higher wheat biomass yield due to combined use of compost and WTR as a soil amendment compared with unamended soil. Similarly, Hsu and Hseu (2011) reported that co-application of compost and Al-WTR resulted in higher dry matter accumulation of Bahia grass (*Paspalum notatum*), although in their case, the resultant yield was not significantly different to sole Al-WTR treatments. The enhanced growth and biomass noted could be attributed to the synergy in nutrient supply between compost and the Al-WTR. Although WTRs are typically low in P (Dassayanake *et al*., 2015), compost addition provided readily available P (due to its higher content of available P as shown in **Table 5.2** whilst WTR provided N and a favourable pH for nutrient uptake. Similarly, the increase in maize grain yield in the field experiment due to the co-amendments of Al-WTR with either cattle manure and / or maize stover also attest to the synergy in nutrient supply between cattle manure and / or maize stover and the Al-WTR. Land application of WTR for plant production is often constrained due to potential adsorption of P by the Al and Fe oxides normally present in WTR, making P unavailable for plant uptake (Babatunde *et al*., 2008; Norris and Titshall, 2012; Bai *et al*., 2014). However, higher maize grain yield and P uptake due to the single amendment of Al-WTR relative to the control in the field experiment might suggest that an Al-WTR application rate of 2000 kg ha^{-1} was not detrimental to plant growth and was sufficient to enhance maize growth and nutrient uptake. The similarity in maize dry matter yield between 10% Al-WTR + 10% C + P and 10% C + P in the greenhouse experiment suggest that Al- WTR can be used as a co-amendment with compost to increase maize yields and could thus reduce production costs by using half of expensive composts as the Al-WTR is freely available.

The increase in maize growth and biomass accumulation due to addition of P fertiliser in both studies accentuate the notion that addition of inorganic P may thus, help to alleviate problems of P fixation that leads to P deficiency in WTR amended soils (Basta, 2000). For example, Heil and Barbarick (1989) reported increased yield of *Sorghum bicolor* (Moench) in WTR amended soils through additions of inorganic P whilst Lucas et al. (1994) showed that P deficiency in Fescue (*Festuca arundinaceae*) caused by application of 40 g kg^{-1} alum sludge could be corrected by doubling the recommended P fertilisation rate. In the greenhouse study, a fixed P rate was used which could have been too low to offset the negative P-fixing capacity of WTR (see Chapter 6), whilst a field application rate of 2000 kg. ha^{-1} did not adversely affect maize grain yields. Further research may be needed to vary P rates and come up with optimal P application levels that can significantly offset the P-fixing capacity in the greenhouse study scenario whilst, Al-WTR application rates in the field could be increased to 5000 kg. ha^{-1}.

Poor plant growth and low biomass due to the unamended control attests that the soil used in the studies is inherently infertile (Nyamapfene, 1991; Nyamangara *et al*., 2000; Mapfumo and Giller, 2001), with additions of fertiliser and organic nutrient resources consequently improving maize plant growth and total biomass accumulation. The observed poor maize growth and biomass accumulation for standard NPK application in the greenhouse study, which is the common soil fertility management practice in Zimbabwe, could be an indicator of soil degradation. Degraded soils are known to show a general weak response to mineral fertiliser additions (Nezomba *et al*., 2015). Soil degradation due to poor soil fertility management is a major constraint to crop productivity in many smallholder farming areas in SSA (Mapfumo and Giller, 2001). Whilst combining organic and inorganic nutrient resources has generally been proven to increase crop yields and nutrient efficiency in nutrient-poor soils (Mtambanengwe and Mapfumo, 2006; Vanlauwe *et al*., 2010), Al-WTR co-amendments have also been proven to improve plant yield, with other potential benefits to the soil physical properties (Gwandu *et al*., 2022; Kerr *et al*., 2022). Research has also shown that farmers fail to access organic nutrients in sufficient quantity and quality to maintain the critical soil C levels for sustainable soil productivity (Mapfumo and Giller, 2001; Mtambanengwe and Mapfumo, 2006). WTRs can potentially contribute to soil C build-up in the long term because the organic carbon becomes tightly bound in the Fe and Al oxide matrix (Elliott and Dempsey, 1991; Novak and Watts, 2004;). Hence, co-application of WTR with other organic nutrient resources could be a complementary option to rebuild soils and increase SOM to sustain crop production and at the same time protect the environment.

The low root-to-shoot ratios observed in the co-amendment compared to the control signifies better nutrient availability in the co-amendment. It is generally understood that when nutrients are available, plants allocate relatively less to the roots and more to the shoots and grain (Tilman, 1985; Bonifas *et al*., 2005) with exceptions where Mg, K or Mn are limiting (Ericson, 1995). Likewise, higher HI values observed for the co-amendments (Al-WTR + MS and Al-WTR + CM) in the field experiment also reinforces the importance of balanced nutrient supply to achieve high yield stability (Jiang *et al*., 2019). However, in P-deficient soils, higher root-to-shoot ratios and low HI values are common. The highest root-to-shoot ratio and a low HI due to the control, is evident of the poor soil nutrient status in both circumstances. Root-to-shoot ratio and HI could thus be used as indicators of nutrient resource use efficiency in crop production.

5.7.3 Influence of Al-WTR amendment on plant nutrient uptake

The inverse relation between soil and plant P due to the co-amendment of 10% Al-WTR + 10% C + P in the greenhouse study could suggest that some P could have been adsorbed and was thus unavailable for plant uptake. This could be attributed to the Al-WTR component of the co-amendment. Phosphorus deficiency in crops normally occurs due to slow release of labile P into the soil solution. Several studies have demonstrated that in WTR amended soils, readily available P can be converted to forms inaccessible by plant roots (e.g., Babatunde *et al*., 2008; Bai *et al*., 2014). Higher P uptake due to additions of inorganic P fertiliser, was expected as the P in the fertiliser is readily available for plant uptake. Adding P fertilisers to soils amended with Al-WTR has a potential to reduce P sorption by the WTR, rendering the latter available for plant uptake. Babatunde and Zhao (2010) in their investigation on the kinetics of P-sorption of alum WTR (Al-WTR), reported that initial sorption occurs on surface functional sites until these are saturated. This implies that added P fertiliser must satisfy these functional sites before it becomes available for plant uptake. However, this also implies additional P fertiliser cost on farmers. Cost benefit analysis on long-term implications for WTR disposal into landfill *vis-a-vis* cost of P fertiliser will have to be done but taking into consideration that WTR is a free source of Zn in addition to benefits for improvements in soil structure. Alternatively, P fertiliser subsidies can be made available to farmers willing to incorporate Al-WTR in their farms. The higher N uptake due to the co-amendments both in the greenhouse and field experiments in comparison with the single amendment of Al-WTR reinforces the mutual benefits in nutrient supply when Al-WTR and other organic nutrient sources such as compost are used together (Clarke *et al*., 2019). The surge in N uptake observed in the co-amendment due to addition of fertiliser P was likely a result of an increase in P availability and thus improved root development which enabled the plants to take up more N from the soil.

The high uptake of cationic elements (Ca, Mg and K) accruing to 10% Al-WTR + 10% C + P and to Al-WTR + CM relative to the control, the single amendments of Al-WTR, CM, MS and compost was also ascribed to the mutual relation in nutrient supply for example, between the Al-WTR and the organic amendments which had high levels of bases in addition to those from the Al-WTR. The potential of WTR to supply cationic nutrients for plant growth and development has also been documented in the past (American Society of Civil Engineers *et al*., 1996; Dayton and Basta, 2001). More so, the high CEC of the WTR attests to its potential to hold and supply cations. The trend in uptake of the cationic bases also showed that maize has a higher demand for K compared with Ca and Mg. Potassium is required throughout the growth cycle as it plays a role in plant water relations and regulation of ionic balances within cells.

The superior response in uptake of Ca due to Al-WTR + CM in the field study and Ca, Mg and K due to 10% Al-WTR + 10% C + P over standard NPK in the greenhouse study showed that co-amendments of Al-WTR and cattle manure and/ or compost can be used as an alternative of the standard farming practice without any negative implications for uptake of Ca, Mg and K. Evidence has shown that a decline in the exchangeable basic cations leads to a decrease in maize yields (Mtangadura *et al*., 2017).

The relatively high uptake of Zn in the co-amendments was within optimal limits for maize production. Zn concentrations in maize plant tissue of between 20-60 mg kg^{-1} are considered sufficient (Tandon, 1993). Deficiencies of Zn have been reported in African soils (Manzeke *et al*., 2014; Kihara *et al*., 2020b). Some studies have shown that integrated nutrient management including application of organic nutrient resources can increase plant Zn concentration (Yang *et al*., 2007; Manzeke *et al*., 2014), thus WTR could potentially supply Zn in sandy soils (Dayton and Basta, 2001; Titshall and Hughes, 2005). The concentration of Cu in maize plant tissue due to the co-amendments in both the field and greenhouse experiments, was also well within the recommended limits of 300 mg. kg^{-1}. From these results, Al-WTR can therefore supply safe levels of Cu. Although copper is required in minute quantities, it is important in plants for many enzymatic processes. The greenhouse study also revealed that 10% Al-WTR + 10% C + P also enhanced Mn uptake by maize and that Pb, Ni and Al in both the greenhouse and field study were all well below the threshold toxicity levels in maize plant tissue (Tandon, 1993), signifying that Al-WTR co-amendments can be safely used as a soil amendment for maize growth without causing heavy metal toxicity. Manganese plays an important role in photosynthesis, thus has a bearing on plant growth and yield. Based on these results, Al-WTR could complement other organic nutrient resources to supply micronutrients to the soil for plant uptake. The supply of micronutrients for plant uptake is important given that micronutrient deficiencies are widespread in SSA arable soils (Kihara *et al*., 2020b). This has great implications for human health – the high nutritional quality of edible plant organs improves human nutrition (Yang *et al*., 2007; Kihara *et al*., 2020b). Improved human nutrition is important in Africa given that over 200 million people are undernourished (FAO *et al*., 2018).

5.8 Conclusions

The study demonstrated the superiority of combining Al-WTR and other organic nutrient sources like compost and cattle manure with P fertiliser in enhancing uptake of Zn, Cu and Mn by maize, which could provide an entry point for alleviating micronutrient deficiency in cereal-based diets in SSA. The study also showed that co-application of Al-WTR and compost; Al-WTR and cattle manure together with addition of inorganic P improved nutrient uptake, growth, and dry matter yield of maize. The results also indicated reduced heavy metal (Pb, Ni, Al) uptake by the cereal crop in comparison with the unamended control, sole Al-WTR, sole compost, CM, MS treatments and standard NPK. There was also a decrease in post-harvest heavy metal content in soils co-amended with a combination of compost and Al-WTR relative to sole Al-WTR treatments. The significant increase in soil pH due to the co-amendment proved essential in decreasing the bioavailability of heavy metals such as Pb and Ni and to reduce Al toxicity which can be problematic in sandy soils. Overall, the study revealed that WTR can be co-applied with other organic nutrient resources such as compost or cattle manure for improved soil health (measured in terms of decreased bioavailability of potentially toxic elements Pb, Ni and Al), and increased crop production and environmental protection. It is concluded that Al-WTR adds to the suite of available organic nutrient resources and can be co-applied with compost or cattle manure and / or maize stover and mineral fertilisers to enhance soil quality and associated crop growth presenting a plausible alternative for re-using the product for soil improvement. Further research should investigate potential for increasing Al-

WTR application rates for field trials from the current recommendation of 2000 kg. ha^{-1} to 5000 kg. ha^{-1}.

Chapter 6

6.0 Phosphorus sorption characteristics of a sandy soil as influenced by aluminium water treatment residual and compost co-amendments[§]

Abstract

Soil degradation coupled with poor access to organic nutrient resources remain major constraints to increased crop productivity in sub-Saharan Africa hindering the continent's efforts in achieving the United Nations' Sustainable Developmental Goals, particularly goals 1 (end poverty), 2 (zero hunger) and 3 (improve human health). Water treatment residual (WTR), a by-product of clean water treatment has been identified as an alternative organic nutrient resource for crop production. However, there are some inconsistencies on soil phosphorus (P) dynamics following Al-WTR application. We conducted experiments to evaluate P sorption of a sandy soil amended with 10% aluminium-WTR (Al-WTR), 10% compost (C) as a quasi-control, 10% C + 10% Al-WTR (10% co-amendment) and 5% C + 5% Al-WTR (5% co-amendment), under varying levels of pH, particle size and P concentration. We calculated crop P fertiliser requirements under the different amendments. The results demonstrated that all amendments exceeded the minimum of 0.2 mg P L^{-1} needed in soil solution at equilibrium to maintain plant growth. However, the maximum P sorption capacity was higher for 10% Al-WTR single amendment, ranging from 770 to 1000 mg P kg^{-1}, and from 714 to 1000 mg P kg^{-1} and 555 to 909 mg P kg^{-1} for 10%- and 5%- co-amendments, respectively, across a range of pH and soil particle size fractions. The co-amendments showed a reduction in crop P fertiliser requirements by ranges of 30 - 60% and 60 - 70% for the 10%- and 5%- co-amendment levels, respectively, across different pH and particle sizes, relative to 10% Al-WTR. Results show that the use of 5% co-amendment in sandy soils increases P availability sufficiently to improve crop yields. These results provide scope for using Al-WTR co-amendments to rebuild soil health in sandy soils in urban agriculture and increase macronutrient provision in crops to support human health.

[§]A modified version of this chapter has been published as Gwandu, T., Lukashe, N.S., Rurinda, J., Stone, W., Chivasa, S., Clarke, C.E., Nezomba, H., Mtambanengwe, F., Mapfumo, P., Steytler, J. G. and Johnson, K.L. (2023). Co-application of water treatment residual and compost for increased phosphorus availability in arable sandy soils. Journal of Sustainable Agriculture and Environment. https://doi.org/10.10002/sae2.12039

Introduction

Soil degradation and poor soil health remain major challenges for attaining food and nutrition security in sub–Saharan Africa (SSA), diminishing prospects for achieving the United Nations' Sustainable Development Goals (SDGs) numbers 1, 2 and 3 that aim to end poverty, hunger, and improve human health, respectively. This has largely been attributed to long-term mining of soil nutrients through harvested products with no or minimum use of fertilisers as well as limited retention of crop residues (Mtangadura *et al*., 2017; Obalum, 2017). African smallholder farmers rely mainly on locally available organic nutrient resources, e.g., manure and woodland litter, to replenish soil fertility for sustainable crop production (Mapfumo and Giller, 2001). However, the organic nutrient resources traditionally used by smallholder farmers have become scarce due to deterioration of livestock heads (Herrero *et al*., 2014) and woodlands (Chagumaira *et al*., 2016), prompting the need to explore alternative organic nutrient resources. Organic nutrient resources are a springboard for improved soil health and especially in rehabilitation of degraded soils (Zingore *et al*., 2005), which occupy about 30% of arable land in Africa (Nezomba *et al.*, 2015; Kihara *et al*., 2020). Aluminium water treatment residual (Al-WTR), a by-product of potable water treatment, has been identified as a potential organo-mineral soil nutrient resource for sustainable crop productivity in urban agriculture (Kerr *et al*., 2022). Urban agriculture has increasingly been embraced by African governments for increased food and nutrition security in cities (Dassanayake *et al*., 2015; Turner *et al*., 2019; Nkrumah, 2019).

Al-WTRs can potentially build soil organic carbon (SOC) in the long term due to their high carbon (C) content, which range from 12.7 to 26% as reported by Dassanayake *et al*. (2015) and Kerr *et al*. (2022). When Al-WTR is added to the soil, iron (Fe) and aluminium (Al) oxide mineral surfaces within the WTR potentially form strong bonds with soil organic matter (SOM)

(Yan *et al*., 2016), thus protecting SOM from microbial decomposition (Kögel-Knabner *et al*., 2008). The use of Al-WTR, as a co-amendment, has been associated with increased soil aeration, aggregation, and water retention (Hsu and Hseu, 2011; Kerr *et al*., 2022), and increased crop yield and plant micronutrients such as zinc and copper (Mahmoud *et al*., 2020; Gwandu *et al*., 2022). On the other hand, the use of Al-WTRs in agriculture serves as an important alternative disposal route to landfill (Turner *et al*., 2019). This saves urban authorities/councils millions of dollars that would have been used for disposal of Al-WTR, as its production is projected to drastically increase in African urban cities, with increase in demand for potable water (Saghir and Santoro, 2018). The projected increase in production of Al-WTR creates opportunities for its reuse as a resource. Water treatment works are also looking for sustainable ways of reusing their WTR, aligning with SDG12 that relates to responsible production and consumption.

Even though research has demonstrated the usefulness of Al-WTR as a soil amendment (e.g., Clarke *et al.*, 2019; Gwandu *et al*., 2022; Kerr *et al*., 2022), there are still concerns about the interaction of Al-WTR and soil phosphorus (P) (Lombi *et al*., 2010; Silveira *et al*., 2013), one of the most limiting nutrients for crop production in Africa (Rurinda *et al*., 2020). Increased soil P available for plant uptake enhances plant root development, which boosts their capacity to take up nutrients from the soil, thus improving overall crop productivity (Malhotra *et al*., 2018). Many studies have shown a decrease in plant-available P when Al-WTR is used as a single amendment (e.g., Penn and Camberato, 2019; Mahmoud *et al*., 2020). This has been attributed to P sorption by the amorphous Al and Fe present in the Al-WTR (Silveira *et al*., 2013; Brennan *et al*., 2019). It is suggested that P becomes fixed to Al-OH groups due to their high zero potential charge, rendering P unavailable for plant uptake (Babatunde *et al*., 2008; Bai *et al*., 2014). While this characteristic could be important in retaining excess P (O'Connor *et al*., 2002; Novak and Watts, 2004), it is a major drawback where soil P is in limited supply as in Africa. Most arable soils in Africa, many of which are sandy, require continual application of P to sustain crop production.

Use of Al-WTR in combination with other organic nutrient sources such as compost or manure may reduce P sorption associated with Al-WTR (Lin *et al*., 2017; Yang *et al*., 2019). Humidified substances produced during decomposition of organic materials enhance the bioavailability of P in acidic soils since they have greater affinity for Al oxides compared to phosphates (Quan-Xian *et al.*, 2008). Co-application of Al-WTR and P fertiliser has been suggested as a possible route for the alleviation of P limitations in Al-WTR amended soils (Hyde and Morris, 2004; Mahmoud *et al*., 2020) but the major challenge is that African smallholder farmers have limited access to P mineral fertilisers. Previous results from a greenhouse experiment with maize (*Zea mays* L.) as a test crop showed that addition of P fertiliser at a constant rate of 14 kg P ha^{-1} to 10% - or 20% - Al-WTR amendment levels was not enough to offset the P sorption associated with Al-WTR (Gwandu *et al*., 2022). Gwandu *et al*. (2022) showed the maize P content was < 3 g kg^{-1}, which is the critical limit for P accumulation in maize plant tissue (Tandon, 1993).

Phosphorus sorption refers to processes that result in the removal of P from soil solution mainly by surface adsorption and precipitation reactions (Arias *et al*., 2006). Sorption of applied P results in reduced plant available P, thus reduced plant productivity (Vitousek *et al*., 2010). Phosphorus sorption is dependent upon biogeochemical and environmental factors such as pH, soil texture, soil composition (clay type, organic matter, Al, and Fe oxides), soil management practices, and fertiliser sources (Fink *et al*., 2016a, b; Gérard, 2016). For example, the movement of P is limited in soils with high clay content due to sorption by soil colloids (He *et al*., 1999; Börling *et al*., 2001), whilst P leaching, and transportation is greater in sandy soils. Soil particle size also plays an important role in P retention in soils (Atalay, 2001). In high pH-soils, P retention and transportation is dependent upon surface adsorption and precipitation, whilst in acid soils, P is fixed into insoluble forms by sorption reactions with Fe and Al oxides (Börling *et al*., 2001; Gérard, 2016), which are abundant in Al-WTR.

Whilst emerging evidence proved that Al-WTR and compost can be co-applied and used as a source of crop nutrients (Clarke *et al*., 2019; Gwandu *et al*., 2022), their combined use remains largely unexploited and has not been optimised. As such, information on their P sorption characteristics when co-applied as soil amendment to sandy soils is scarce. This paper explores P availability and P sorption characteristics in a sandy soil amended with co-amendments of Al-WTR and compost and quantifies the crop P Fertiliser Requirements (PFRs) under different pH and soil particle size. The specific objectives were to (i) determine the effects of Al-WTR, and compost amendments on soil P sorption; (ii) determine the influence of particle size of amendments and soil solution pH on P sorption; and (iii) estimate crop P nutrient requirements under different soil amendments.

6.1 Materials and Methods

6.1.1 Soil sampling, Al-WTR and compost amendments

The sandy topsoil was sampled to a depth of 30 cm from a farm outside, Kuilsrivier, South Africa. The sandy parent material, in which the soils have formed results from aeolian processes and consist of well-sorted fine sand (Schloms *et al.,* 1983; Steytler, 2020). These soils are typified by very low pH (pH 4.2) and low nutrient content (N, P, Ca, Mg and K) (**Table 6.1**). The low nutrient content is consistent with most sandy soils used for crop production in SSA (Chikwuka, 2009; Mtambanengwe and Mapfumo, 2005). Soil macro- and micro-nutrient limitations have often been linked to low crop yields and malnutrition in smallholder farming systems in SSA (Mtangadura *et al*., 2017; Kihara *et al*., 2020b). The sandy soil was sampled to a depth of 30 cm, air-dried, and sieved to 2 mm. It was stored at room temperature before characterising for physical and chemical properties (**Table 6.1**). The compost used was a commercial grade, Prime Pure organic compost, sourced from a local hardware store in Stellenbosch, South Africa and three sub-samples were characterised for chemical properties as shown in **Table 6.1**.

Water treatment residual (WTR) was sampled from a landfill stockpile at Prince Edward Water Treatment Plant (WTP) (17°58'45"S; 31°4'11"E), which is located 22 km to the Southwest of Harare, the capital of Zimbabwe. The WTP uses the conventional water treatment system consisting of sludge blanket clarifiers and rapid sand filters. Aluminium sulphate ($Al_2(SO4)_3.14H_2O$) is used as a flocculant. Sulphuric acid, chlorine gas, ammonia, flocculated carbon, and lime are used to optimise the water treatment process (Engineer C. Chinyanya, personal communication, March 23, 2020). After sampling, the WTR was air-dried for 30 days. Three sub-samples were characterised for physical and chemical properties as shown in **Table 6.1**. The Zimbabwean Al-WTR was used because it represents the WTR generated from most WTPs in SSA, which use aluminium sulphate as the flocculant.

Table 6.1: The physical and chemical characteristics of sand, compost and Al-WTR used in the experiment

Parameter	Soil	Al-WTR	Compost
Sand (%)	99.76*	nd	nd
Silt & Clay (%)	0.24*	nd	nd
pH (0.01 M $CaCl_2$)	4.23 §	6.93 ± 0.01	7.73 ± 0.00
EC (µS cm^{-1})	10.00	870 ± 0.03	5630 ± 0.05
Total P (%)	0.005*	0.12 ± 0.05	0.18 ± 0.03
Available P (mg kg^{-1})	2.43*	7.6 ±0.06	139.3 ± 0.05
Total N (%)	0.03 *	0.74 ± 0.01	1.08 ± 0.01
Total C (%)	0.60 *	18.90 ± 0.05	19.59 ± 0.01
C/N ratio	15.00 *	25.50 ± 0.10	18.13 ± 0.01
Ca ($cmol_c$ kg^{-1})	0.55*	3.40 ± 0.003	46.28 ± 0.003
Mg ($cmol_c$ kg^{-1})	0.264*	0.58 ± 0.001	7.25 ± 0.005
K ($cmol_c$ kg^{-1})	< 0.001*	0.24 ± 0.002	21.00 ± 0.01
Al ($cmol_c$ kg^{-1})	nd	5.61 ± 0.05	0.37 ± 0.07
Dry matter (g) @ 105°C	98.60 (±0.02)	96.80 ± 0.03	41.50 ± 0.09

Data are means ± standard error of the means (*N*=3) except for soil where displayed data are means only; Al-WTR-aluminium water treatment residual, nd-not determined; §-determined using 1M KCl; *data obtained from Steytler (2020).

6.2.2 Pre-sorption incubation procedure

Compost and Al-WTR were ground to pass through three different sets of sieves to obtain particle sizes of 2 mm, 0.5 mm, and 0.25 mm before mixing with the sandy soil. The sandy soil was then mixed with compost or Al-WTR or their combination, culminating in 4 treatments consisting of (i) 10% Al-WTR, (ii) 10% compost, (iii) 10% compost + 10% Al-WTR (10% co-amendment) and (iv) 5% compost + 5% Al-WTR (5% co-amendment). A sample of 100 g from each amendment (dry matter basis), were placed into plastic containers and incubated at 25°C for 30 days. Deionised water was then added to each sample to field capacity, and this was maintained for the entire incubation period through weekly weight adjustments (Mafongoya *et al*., 2000). The container surfaces were covered using porous plastic films to maintain aerobic conditions.

6.2.3 Experimental design

The laboratory P adsorption experiment comprised of 4 soil amendments × 5 P concentrations × 3 soil pH levels × 3 amendments particle sizes arranged in a split-split plot design with three replications of each combination. Factorial combinations of treatments (4 levels) were considered as whole plot, P concentration (5 levels) as blocks, while particle size (3 levels) and pH (3 levels) were considered as sub-plot and sub-sub plot, respectively. Particle size, pH and P concentration were purposely defined in the experimental design and were thus considered as fixed factors.

6.2.4 Phosphorus extraction and analysis (adsorption test)

From each incubated sample, (5% co-amendment, 10% co-amendment, 10% C and 10% Al-WTR), 1 g was weighed into 50 mL centrifuge tubes. A range of different P concentrations (0, 10, 50, 100 and 200 ppm P) was set up, containing 0.01 M $CaCl_2$ to serve as a supporting electrolyte. The 0 ppm P was included in the experiment to take into account the release of P from the lyses of microbes. A 20 ml aliquot of each P concentration was added to a sample of each treatment. The pH was adjusted for each sample by adding predetermined amounts of either 0.01 M H_2SO_4 or 0.1 M NaOH. Chloroform (3 drops per sample) was added to the mixture to inhibit microbial activity. The samples were shaken for 24 hours at 200 rpm at 25°C, to facilitate absorption. After centrifugation (4500 rpm for 10 minutes) samples were filtered using 0.45-µm Millipore filter paper. The supernatant P concentration was determined colorimetrically with the ammonium molybdate-ascorbic acid method (Murphy and Riley, 1962) using a UV-VIS Jenway 6300 spectrophotometer at 880 nm. The pH and electrical conductivity of the different materials were measured with 0.01 M $CaCl_2$ (Anderson and Ingram, 1993) and readings taken using standard meters for pH (Metrohm 827, USA) and electrical conductivity (Jenway 4510, Triad Scientific, New Jersey, United States). Total organic carbon was determined using the wet oxidation method (Anderson and Ingram, 1993). The samples were oxidised using a combination of potassium dichromate ($K_2Cr_2O_7$) and sulphuric acid (H_2SO_4). The mixture was titrated using ferrous ammonium sulphate. The difference between added and residual $K_2Cr_2O_7$ gives a measure of organic C content in the sample (Okalebo *et al*., 2002).

6.2.5 Determination of sorption parameters

The Langmuir and Freundlich isotherms were used to understand the relationship between the quantity of P adsorbed per unit soil weight and the concentration of P in solution. The Langmuir and Freundlich isotherms have often been used to describe P sorption characteristics (e.g., Olsen and Watanabe, 1957; Jeppu and Clement, 2012; Saeed *et al*., 2021). Phosphorus adsorption parameters were calculated with the Langmuir isotherm equation:

$$Ce/Q = 1/bQo + Ce/Qo \quad (1) \qquad (6.1)$$

where Q = the mass of P adsorbed per unit mass of co-amendment, mg kg^{-1}; C_e = the equilibrium concentration of P (mg P L^{-1}) in suspension after 24-hour equilibrium; Q_o = the maximum adsorption capacity (mg P kg^{-1}) and b = a constant related to the binding strength of P at the adsorption sites (L mg^{-1} P). A linear regression analysis was performed between C_e and C_e/Q, and the values for b and Q_o obtained from the slope and intercept of the regression line, respectively. $Q_o \times b$ is the maximum adsorption buffering capacity (MBC, L kg^{-1}). The Freundlich equation is

$$Q = kCe^{b} \qquad (6.2)$$

where Q = the mass of P adsorbed per unit mass of coamendment, mg kg^{-1}; Ce = the equilibrium concentration of P (mg P L^{-1}) in suspension after 24-hour equilibrium; k = the proportionality constant for Freundlich equation, mg kg^{-1} and b ($b < 1$) = the slope of the curve log Q vs log

Ce/Q. Crop phosphorus fertiliser requirement (PFR) was calculated based on the assumption that a soil should contain 0.2 mg P L^{-1} in solution for optimum plant growth (Fox and Kamprath, 1970; Roy and De Datta, 1985; Mahmood-ul-Hassan *et al*., 1993). The P_2O_5 fertiliser requirement was calculated based on the method by Saeed et al. (2021). Briefly the method takes into account the targeted P concentration in equilibrium solution, the maximum buffering capacity, P bonding energy constant (Saeed *et al*., 2021).

6.3 Data analysis

The Analysis of variance (ANOVA) for a split -split-plot design was used to analyse the effect of Al-WTR and compost amendments (treatments), pH, particle size and P concentration as well as their interaction on P adsorption using GENSTAT 21st Edition (VSN International, 2022). Fischer's least significant difference (LSD) was used to separate significant treatments means at $p < 0.05$.

6.4 Results

6.4.1 Effect of different soil amendments on equilibrium P

The P sorption isotherms presented in **Figure 6.1**, generally show that equilibrium P in solution among the different soil amendments increased with increase in P concentration. The equilibrium P in solution increased exponentially with increase in initial P concentration from 50 mg L^{-1} to 200 mg L^{-1} P (**Figure 6.1**). The concentration of P in solution at any given point followed the trend 10% C > 5% co-amendment > 10% co-amendment > 10% Al-WTR (**Figure 6.1**). However, the equilibrium P in solution varied mainly with particle size and was higher for particle size of 0.5 mm than for particle sizes 0.25- and 2- mm across pH levels. The P in solution was generally similar for 0.25 mm particle size. At 2 mm particle size, the effects of treatment on equilibrium P in solution was more apparent until 100 mg P L^{-1}, and beyond this concentration, the treatments were similar. It is apparent from the results that the co-amendment of Al-WTR and compost resulted in an increase in equilibrium P concentration, relative to sole Al-WTR, but a decrease relative to sole compost. These results attest to the likelihood that organic matter reduced the P binding effects associated with Al-WTR, resulting in more P in equilibrium solution.

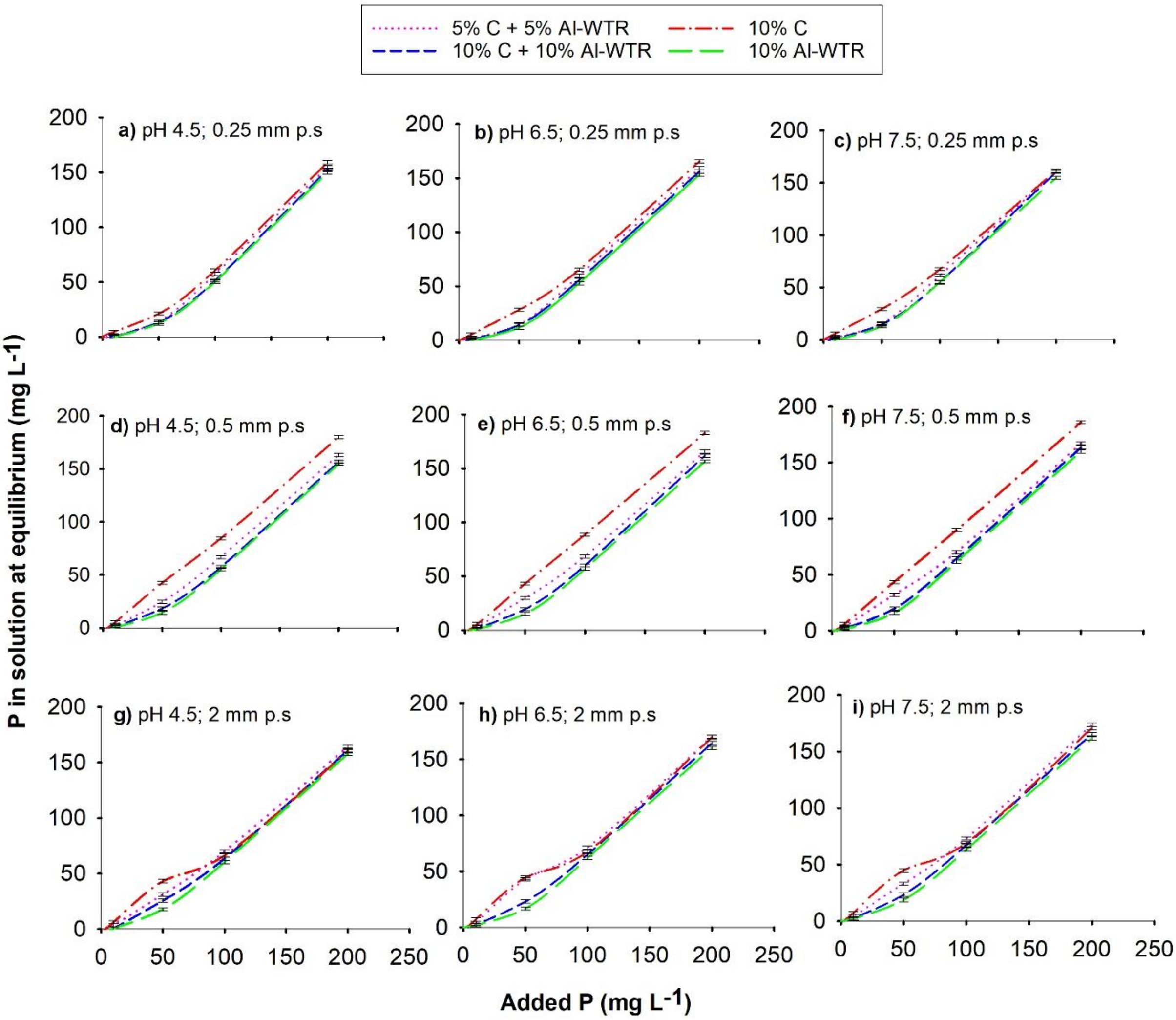

Figure 6.1: Equilibrium P concentration of a sandy soil amended with aluminium-water treatment residual and compost or their combination at different pH and particle size. Error bars are least significance differences of the treatment means (LSD) ($p < 0.05$); p.s-particle size; C-compost; Al-WTR- aluminium water treatment residual.

6.4.2 Effect of different soil amendments on P sorption

Apart from 10% C which increased steadily throughout, P sorption across amendments (including the 0.25 mm particle size of 10% C) increased exponentially with increase in P concentration until 50 mg L^{-1} P, thereafter a slow increase was observed between 100 and 200 mg L^{-1} P (**Figure 6.2**). The general trend shows that the amount of P sorbed at any given P concentration decreased in the order 10% Al-WTR > 10% co-amendment > 5% co-amendment

> 10% C (**Figure 6.2**). For example, the highest P sorption (995.15 ± 2.40 mg P kg^{-1}) was recorded for 10% Al-WTR at a pH of 4.5 and a particle size of 0.25 mm when 200 ppm P was added into the soil solution. This translates to 21.7%, 10.5% and 4.9% higher than 10% C, 5%- and 10%- co-amendments, which attained 817.61 ± 5.96 mg P kg^{-1}, 900.85 ± 8.94 mg P kg^{-1} and 948.25 ± 2.98 mg P kg^{-1}, respectively, under similar conditions (**Figure 6.2**). The lowest P sorption (158.87 ± 0.62mg P kg^{-1}) by 10% Al-WTR was recorded at pH 7.5 for the 2 mm fraction after an addition of 10 ppm P, equating to 187.8%, 37.3% and 6.7% more adsorbed P relative to 10% C, 5%- and 10%- co-amendment, in that respective order (**Figure 6.2**).

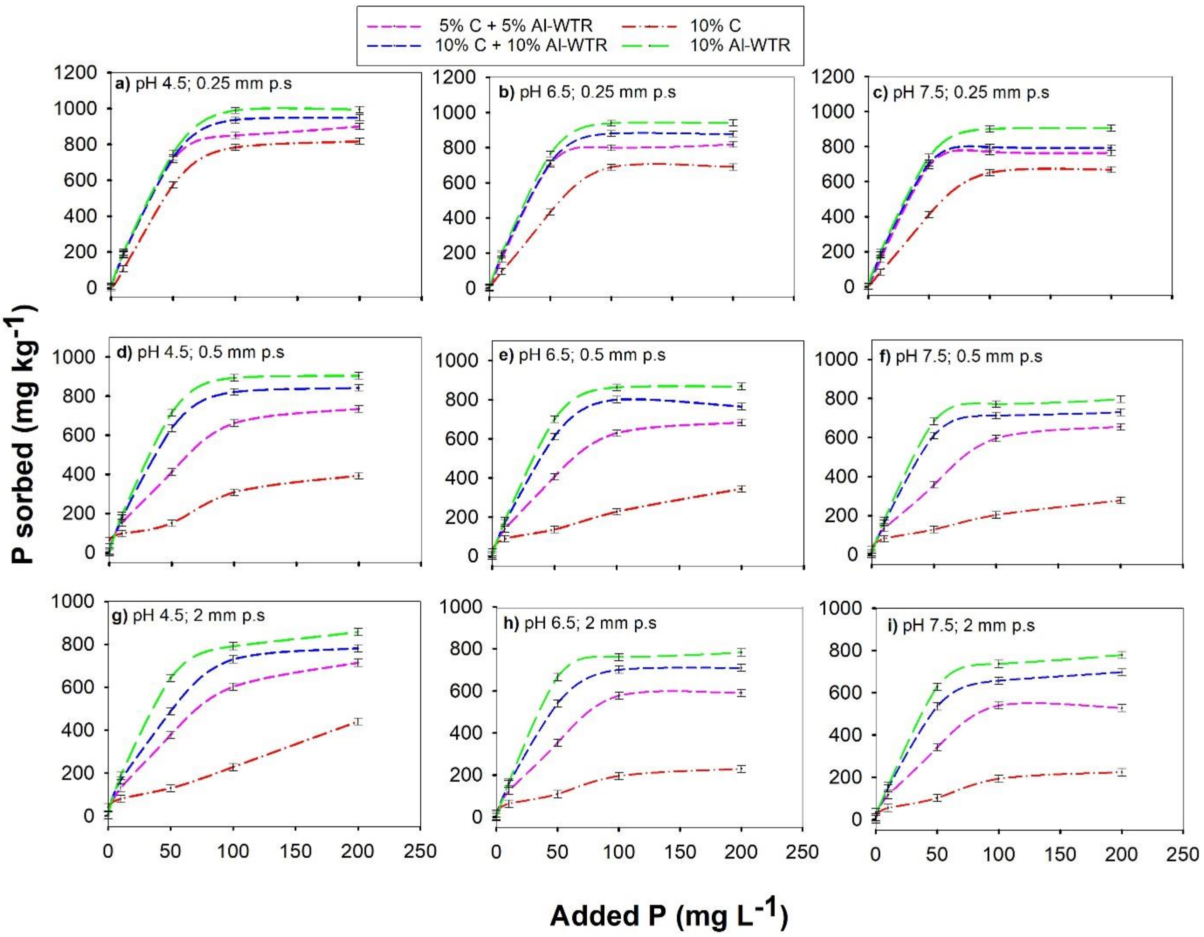

Figure 6.2: Phosphorus adsorption curves of a sandy soil amended with aluminium-water treatment residual and compost or their combination at different pH and particle size. Error bars denote least significance differences (LSDs) of the treatment means at $p < 0.05$ (N=3); p.s-particle size; C-compost; Al-WTR-aluminium water treatment residual.

The 10% C amendment consistently exhibited very low P sorption compared to the rest of the amendments., whilst the co-amendment of Al-WTR and compost, resulted in a marked decrease in P sorption compared to sole Al-WTR (**Figure 6.2**). However, this was dependent on the Al-WTR-compost ratio, with 5% level resulting in less P adsorption compared to 10% co-amendment. From these results, it is apparent that the addition of compost to Al-WTR greatly contributed to an increase in P availability in the soil solution.

6.4.3 Effect of pH and particle size of amendments on soil P sorption

Phosphorus sorption under the different amendments was strongly dependent on solution pH ($p < 0.001$) (refer to Appendix 1). P sorption across all the amendments was very high at pH 4.5 ranging from 79.25 mg P kg^{-1} to 940.89 mg P kg^{-1} across treatments and particle sizes and markedly decreased as pH increased, reaching the lowest (55.21 mg P kg^{-1} to 905.21 mg P kg^{-1}) at pH 7.5 (neutral) also across the different treatments and particle sizes (**Figure 6.2**). This was, however, more apparent at particle sizes of 2- and 0.5- mm, between added P concentrations of 50- and 100- ppm (**Figure 6.2 d-i**). There was an interaction between pH and particle size on P sorption (refer to Appendix 1).

Phosphorus sorption by the different amendments generally decreased in the order 0.25 mm > 0.5 mm > 2 mm, regarding particle size of the amendments (**Figure 6.2**). Coarser fractions quickly reached P saturation as the adsorption curves flattened prematurely compared to 0.25- and 0.5- mm particle sizes (**Figure 6.2**). At 0.25 mm particle size, all four amendments exhibited a higher affinity for P as shown by a steeper curve compared to the 2- and 0.5-mm particle sizes.

The percentage of adsorbed P (adsorbed P to added P) decreased with increasing P concentration across all treatments (**Figure 6.3**). The percentage of adsorbed P also decreased with increasing pH, whilst it increased with decrease in particle size (**Figure 6.3**). There was an increase in the relative P sorption between 10 and 50 mg P L^{-1}. After 50 mg L^{-1}, the relative P sorption decreased (**Figure 6.3**).

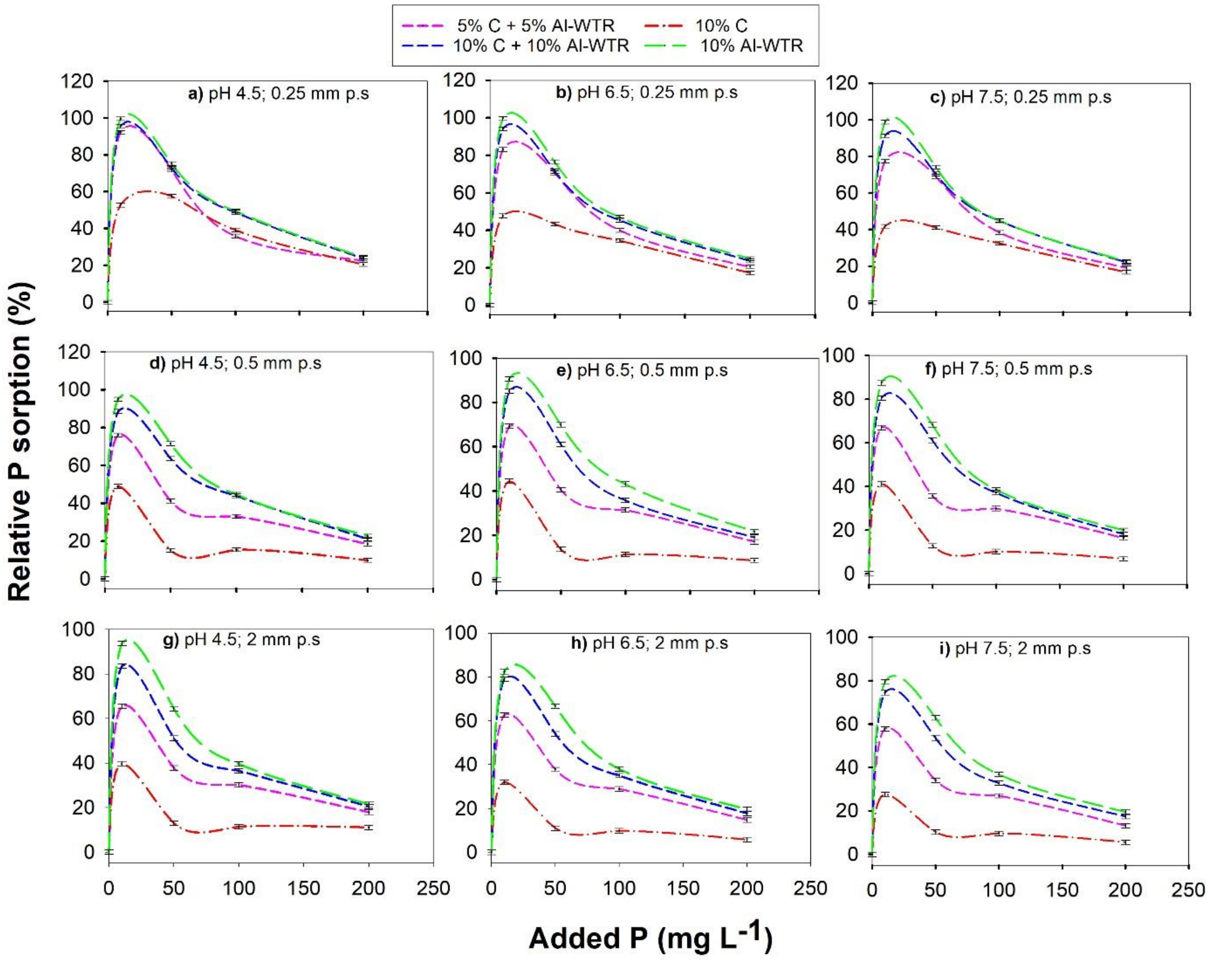

Figure 6.3: Relative P sorption (sorbed P/added P) for the different soil amendments (%) Error bars denote least significance differences (LSD) of the treatment means at $p < 0.05$ (N=3); C-compost; Al-WTR- aluminium water treatment residual.

6.4.4 Phosphorus adsorption equations

Several models have been put forward to describe P adsorption isotherms. The Langmuir and Freundlich adsorption isotherms are the most popular ones (Yang *et al*., 2019). Phosphorus sorption was well described by the Langmuir isotherm, with coefficients of determination (R^2) values ranging between 0.66 - 0.99 across all the treatments (**Table 6.2**). This indicated a better fit compared to the Freundlich isotherm, where R^2 varied from 0.22 to 0.88 (**Table 6.2**). Results from other related studies (Caporale *et al*., 2013; Bai *et al*., 2014; Yang *et al*., 2019) are consistent with these findings. Therefore, the P adsorption parameters that include the P maximum adsorption capacity (Qo), the bonding energy constant (b) and the Maximum buffering capacity (MBC) were calculated from the Langmuir isotherm. These parameters are generally used to determine the availability of P in soil and the related P adsorption capacity (Yang *et al*., 2019).

The P sorption parameters estimated from the Langmuir equation varied among the treatments. The maximum P adsorption capacity, (Qo), which has been widely used to estimate the P adsorption capacity of a soil (Yan *et al*., 2013), decreased with an increase in pH across treatments and generally also decreased as particle sizes increased (**Table 6.2**). Across treatments, the P adsorption maxima, decreased in the order 10% Al-WTR > 10% co-amendment > 5% co-amendment > 10% C ($p < 0.01$) (**Table 6.2**). The P bonding energy constant, b, is another important parameter, which is used to describe the affinity of soil for P. A higher constant value, b, indicates higher strength in P adsorption. The value of b also followed the same trend as the maximum adsorption capacity, Q, decreasing in the order 10% Al-WTR > 10% co-amendment > 5% co-amendment > 10% C (**Table 6.2**).

Table 6.2: Parameters of phosphorus adsorption characteristics

pH	Particle size (mm)	R^2 Freundlich	R^2 Langmuir	Qo (mg kg^{-1})	b (L mg^{-1})	MBC (L kg^{-1})
			5% C + 5% Al-WTR			
4.5	2	0.7686	0.9712	769.23	0.06	48.54
	0.5	0.6990	0.9813	769.23	0.09	70.42
	0.25	0.4991	0.9990	909.09	0.39	357.14
6.5	2	0.7764	0.9587	625.00	0.08	49.01
	0.5	0.7397	0.9839	714.29	0.09	65.36
	0.25	0.6014	0.9986	833.33	0.32	270.67
7.5	2	0.7848	0.9844	555.56	0.10	54.05
	0.5	0.7539	0.9752	714.29	0.07	52.08
	0.25	0.6423	0.9930	769.23	0.32	243.90
			10% C + 10% Al-WTR			
4.5	2	0.6334	0.9917	833.33	0.32	113.63
	0.5	0.5688	0.9960	833.33	0.32	263.16
	0.25	0.4393	0.9940	1000	0.45	588.23
6.5	2	0.6560	0.9975	714.29	0.32	156.65
	0.5	0.5981	0.9937	769.23	0.41	312.50
	0.25	0.4641	0.9995	909.09	0.61	500.00
7.5	2	0.6883	0.9967	714.29	0.22	121.95
	0.5	0.6340	0.9930	769.23	0.28	212.77
	0.25	0.5041	0.9952	909.09	0.76	454.55
			10% C			
4.5	2	0.8525	0.9977	476.19	0.02	9.28
	0.5	0.7461	0.9995	434.78	0.03	14.75
	0.25	0.8130	0.9993	909.09	0.07	62.11
6.5	2	0.8475	0.9980	243.90	0.04	10.95
	0.5	0.8100	0.9988	357.15	0.03	11.93
	0.25	0.8476	0.997	769.23	0.06	44.44
7.5	2	0.8685	0.9967	243.90	0.04	9.69
	0.5	0.7833	0.9987	294.12	0.04	12.47
	0.25	0.8699	0.9992	769.23	0.05	35.21
			10% Al-WTR			
4.5	2	0.4797	0.9977	833.33	0.32	263.16
	0.5	0.4460	0.9995	909.09	0.55	500.00
	0.25	0.2382	0.9993	1000	0.91	1000
6.5	2	0.6125	0.9980	769.23	0.32	243.90
	0.5	0.5258	0.9988	909.09	0.44	400
	0.25	0.2229	0.9997	909.09	1.00	909.09
7.5	2	0.6467	0.9967	769.23	0.23	175.43
	0.5	0.5590	0.9987	833.33	0.39	322.58
	0.25	0.3062	0.9992	909.09	1.00	909.09

Q_o-maximum P adsorption capacity (mg P kg^{-1}); b- a constant related to the binding strength of P at the adsorption sites (L mg^{-1} P); MBC-maximum buffering capacity (L kg^{-1}).

The bonding energy constant, generally increased as particle size became smaller as well with a decrease in solution pH except for a few exceptions where this was inconsistent e.g., for 5% co-amendment (5% C + 5% Al-WTR), particle size 2 mm, the P bonding energy increased with an increase in solution pH, recording 0.06, 0.08 and 0.10 L mg^{-1} P at pH 4.5, 6.5 and 7.5, respectively (**Table 6.2**). The highest maximum buffering capacity (MBC) values were observed for 10% Al-WTR, whereas the least were recorded for 10% C (**Table 6.2**). Maximum buffering capacity refers to the measure of the capacity of soil to resist a change in its P concentration as P is removed by plant uptake or added in fertiliser or organic materials (Holford, 1997). The MBC numerical value is a product of Qo and b in the Langmuir equation. Soil factors that influence Qo and b, directly influence the MBC. Consequently, MBC also increased with a decrease in particle size and was generally higher at low pH across the different treatments (**Table 6.2**).

6.4.5 Comparative P fertiliser requirements of the sandy soil under different soil amendments

The phosphorus fertiliser requirements (PFRs) due to the different amendments calculated based on the Langmuir isotherm showed that the P fertiliser required to maintain 0.2 mg P L^{-1} in soil solution increased in the order 10% Al-WTR > 10% co-amendment > 5% co-amendment > 10% C (**Table 6.3**). The PFRs increased also generally increased with decrease in both particle size and pH, although there were inconsistences in some instances (**Table 6.3**). For example, the highest PFR for a soil amended with 10% Al-WTR was 785.42 kg P_2O_5 ha^{-1} (pH 4.5; 0.25 mm particle size) compared to 503.52 kg P_2O_5 ha^{-1} (10% co-amendment), 312.08 kg P_2O_5 ha^{-1} (5% co-amendment) and 65.50 kg P_2O_5 ha^{-1} (10% C) at similar pH and particle size (**Table 6.3**). The least PFRs requirements were 17.63 kg P_2O_5 ha^{-1} for 10% C recorded at a pH of 4.5 and particle size of 2 mm, 53.12kg P_2O_5 ha^{-1} and 110 kg P_2O_5 ha^{-1} recorded for 5% and 10% co-amendments for similar pH and particle size whilst 10% Al-WTR recorded the least of 162.77 kg P_2O_5 ha^{-1} at pH 7.5 at the 2 mm fraction (**Table 6.3**). The results show a reduction in the PFRs by ranges of 30 - 60% and 60 - 70% for the 10%- and 5%- co-amendment levels, respectively, across different pH and particle sizes, relative to 10% Al-WTR.

Table 6.3: Stepwise calculation of the phosphorus fertiliser requirement (PFR) of soils based on the Langmuir adsorption isotherm

pH	Particle size	**A**	MBC	**B**	b	**C**	**B/C**	**A** × 10	P required (***Q*** + EPS)		
		($EPS_{0.2}$)		($MBC \times EPS_{0.2}$)		1 + b($EPS_{0.2}$)	***Q***	EPS	P	P_2O_5	P_2O_5
	mm	Mg L^{-1}	-	-		-	(mg L^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(kg ha^{-1})
						5% C + 5% Al-WTR					
4.5	2	0.2	48.54	9.71	0.06	1.01	9.59	2	11.59	26.55	53.10
	0.5	0.2	70.42	14.08	0.09	1.02	13.83	2	15.84	36.26	72.52
	0.25	0.2	357.14	71.43	0.39	1.08	66.26	2	68.26	156.32	312.63
6.5	2	0.2	49.01	9.80	0.08	1.02	9.65	2	11.65	26.67	53.35
	0.5	0.2	65.36	13.07	0.09	1.02	12.84	2	14.84	33.99	67.97
	0.25	0.2	270.27	54.05	0.32	1.06	50.80	2	52.80	120.92	241.84
7.5	2	0.2	54.05	10.81	0.10	1.02	10.60	2	12.60	28.85	57.70
	0.5	0.2	52.08	10.42	0.07	1.01	10.27	2	12.27	28.10	56.21
	0.25	0.2	243.90	48.78	0.32	1.06	45.85	2	47.85	109.57	219.13
						10% C + 10% Al-WTR					
4.5	2	0.2	113.63	22.73	0.32	1.06	21.36	2	23.36	53.49	110.41
	0.5	0.2	263.16	52.63	0.32	1.06	49.47	2	51.47	117.86	235.72
	0.25	0.2	588.23	117.65	0.45	1.09	107.93	2	109.93	251.75	503.49
6.5	2	0.2	156.25	31.25	0.32	1.06	29.37	2	31.37	71.84	273.72
	0.5	0.2	312.50	62.50	0.41	1.08	57.76	2	59.76	136.86	273.72
	0.25	0.2	500.00	100.00	0.61	1.12	89.13	2	91.13	208.68	417.36
7.5	2	0.2	121.95	24.39	0.22	1.04	23.36	2	25.36	58.08	117.19
	0.5	0.2	212.77	42.55	0.28	1.06	40.30	2	42.30	96.86	193.72
	0.25	0.2	454.55	90.91	0.76	1.15	78.91	2	80.91	185.30	370.59

Table 6.3 (continued)

pH	Particle size	**A**	MBC	**B**	b	**C**	**B/C**	A × 10	P required (**Q** + EPS)		
		$EPS_{0.2}$		MBC × $EPS_{0.2}$		1 + b($EPS_{0.2}$)	**Q**	EPS	P	P_2O_5	P_2O_5
	mm	mg L^{-1}	-	-	-	-	mg L^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	kg ha^{-1}
						10% C					
4.5	2	0.2	9.28	1.86	0.02	1.00	1.85	2	3.85	8.81	17.63
	0.5	0.2	14.75	2.95	0.03	1.01	2.93	2	4.93	11.30	22.59
	0.25	0.2	62.11	12.42	0.07	1.01	12.25	2	14.25	32.63	65.27
6.5	2	0.2	10.95	2.19	0.04	1.01	2.17	2	4.17	9.56	19.11
	0.5	0.2	11.93	2.39	0.03	1.01	2.37	2	4.37	10.01	20.02
7.5	2	0.2	9.69	1.94	0.04	1.01	1.92	2	3.92	8.98	17.97
	0.5	0.2	12.47	2.49	0.04	1.01	2.47	2	4.47	10.25	20.49
	0.25	0.2	35.21	7.04	0.05	1.01	6.97	2	8.97	20.25	41.09
						10% C + 10% Al-WTR					
4.5	2	0.2	270.27	54.05	0.32	1.06	50.80	2	52.80	117.86	235.72
	0.5	0.2	500.00	100.00	0.55	1.11	90.09	2	92.09	210.89	421.77
	0.25	0.2	909.09	181.82	0.91	1.18	153.82	2	155.82	392.06	784.12
6.5	2	0.2	243.90	48.78	0.32	1.06	45.85	2	47.85	109.57	219.13
	0.5	0.2	400.00	80.00	0.44	1.09	73.53	2	75.53	172.96	345.92
	0.25	0.2	909.09	181.82	1.00	1.20	151.52	2	153.52	351.55	703.10
7.5	2	0.2	175.43	35.09	0.23	1.05	33.54	2	35.54	81.39	162.79
	0.5	0.2	322.58	64.52	0.39	1.08	59.85	2	61.85	141.63	283.26
	0.25	0.2	909.09	181.82	1.00	1.20	151.52	2	153.52	351.55	703.10

$EPS_{0.2}$=Equilibrium P in solution based on 0.2 mg P L^{-1}; MBC= maximum buffering capacity (L kg^{-1}); b = bonding energy constant (L mg^{-1} P)

6.5 Discussion

6.5.1 Amendments differentially impact on P sorption

The high P sorption capacity by 10% Al-WTR could be likely attributed to a higher amount of Al oxides present in the 10% Al-WTR amendment compared to the other amendments. Some studies have suggested that Al bound by organic complexes make a large contribution to P sorption in soils (Bai *et al*., 2014; Gérard, 2016). Others suggest that P becomes fixed to Al-OH groups on the surface of the WTR and gets adsorbed via a precipitation reaction (Babatunde *et al*., 2008; Wang *et al*., 2012; Bai *et al*., 2014). Anions such as phosphate are not normally sorbed on OM due to repulsion by the negatively charged hydroxyl (-OH) and carboxyl (-COOH) ions in OM, hence a low P sorption observed for 10% C amendment (Wang *et al*., 2007; Caporale *et al*., 2013). One mechanism suggested could be that the OM forms complexes with surface-bound Al or Fe to form soluble organic-metal compounds causing release of the previously adsorbed P (Yan *et al*., 2016). Alternatively, OM may be adsorbed to soil particles at non-specific sorption sites, increasing negative charges on the soil surface, thus repealing phosphate ions (Erich *et al*., 2002). Other reports suggest that decomposition products of organic matter (humified substances) compete for sorption sites with P and thus result in lower P sorption (Ohno and Erich, 1997; Lin *et al*., 2017; Yang *et al*., 2019). However, this was not the case for the 0.25 mm particle size under the 10% C amendment – in fact the P sorption was higher than the 0.5- and 2- mm fractions. Although this behaviour could not be ascertained, some studies have demonstrated that particle size influences soil chemical composition and proffers different stability to microbial decomposition and thus different influence on P sorption stability (Sharpley *et al*., 1994). There is evidence to suggest that particle size of plant residues has an influence on the amount of C stabilised in the soil during residue decomposition (Angers and Recous, 1997), particularly for organic residues with high amounts of N such as compost. In smaller particles (< 1 mm), their C rapidly get stabilised in the very early stages of decomposition, resultant of the intimate contact between decomposing residues and soil mineral particles (Jensen, 1994, Angers and Recous, 1997). In the short-term, the decomposition products of OM will become less available to compete for sorption sites with P, hence a temporary increase in P sorption. This phenomenon is only temporary as the decomposition process proceeds in the long-term resulting in OM decomposition products occupying sorption sites previously occupied by P, hence an increase in P in the soil solution.

6.5.2 P sorption as a function of solution pH and particle size

The observed high dependence of P sorption on solution pH confirms that P sorption in soils is dependent on soil pH (Gérard, 2016), with P sorption more pronounced in acidic soils. Caporale *et al*. (2013) reported similar findings on the adsorption of Arsenate by Al-WTR. Arsenate (AsO_4^{3-}) and phosphate (PO_4^{3-}) exhibit similar chemical properties (Bodek *et al.*, 1988). P sorption is generally known to decrease with increasing pH (Haynes, 1982; Goldberg and Sposito, 1984). This is because high pH promotes variable negative charges which prevents clay particles in soils from absorbing phosphate ions (Zeng *et al*., 2004; Jin *et al*., 2005; Barrow, 2017). Some studies have also demonstrated mechanisms in which pH impacts P sorption. These include change of P forms in soil, exchange of ions and competition with other anions for adsorption sites (Zhou *et al*., 2005; Bai *et al*., 2017). At pH > 7, phosphate ions compete for adsorption sites with hydroxyl (OH^-) ions resulting in low P sorption (Liu *et al*., 2011). Positive charges become abundant at low pH, which enhance P adsorption. For example, when pH is low, Al and Fe oxides become highly soluble, resulting in greater propensity of soils containing these oxides for P sorption (Gustafsson *et al*., 2012; Gérard, 2016). These results support the need for liming soils to enhance availability of P for plant uptake.

The high P sorption by the finer 0.25 mm particle sizes as opposed to the coarse 2 mm fraction could be a result of the grinding process, which probably exposed new mineral surfaces that would not be normally available for P adsorption. The decrease in particle size also creates a greater surface area for P adsorption by finer particles (Atalay, 2001; Xu *et al*., 2006; Leader *et al*., 2008). Loyer and Aminot (2001) also reported significant correlations between higher Al- and Fe-bound P and the finer soil fractions. Consideration of Al-WTR particle size is therefore important for applications where the intention is to reduce P sorption. Finer particles would suit soil remediation purposes, for example, in instances where there is excess P or heavy metal contamination in the environment. Although it should be noted that there is no published information on the changes in particle size of WTR when added to soil in field applications. Although the 0.25 mm particle size for compost showed higher P sorption, we assume this would not be a serious challenge as this immobilisation should be only temporary as explained before and given that most compost used by farmers consists of particle sizes > 0.25 mm.

6.5.3 The Langmuir adsorption parameters and their implications for P adsorption and P fertiliser requirements

The maximum P adsorption capacity, (Qo), showed a decrease with increase in particle size and this underscores the important role of particle size in the retention of added P, which can have a bearing on Al-WTR disposal or its use in agriculture in the long-term. Xu et al. (2006) also reported a positive correlation between P sorption maximum and the finer soil fractions (< 0.5 mm particle sizes). Across treatments, the P adsorption maxima, decreased in the order 10% Al-WTR > 10% co-amendment > 5% co-amendment > 10% C, showing that 10% Al-WTR had a higher P sorption whilst 10% C exhibited the least. As a soil reaches its maximum sorption capacity, it is less able to sorb P, leading to increased soil solution P, but also increasing the risk of P loss by runoff or leaching (Kleinman, 2017). An amendment rate of 10% Al-WTR, would likely result in less P available to plants due to its high maximum P sorption, whilst soils amended with 10% C would possibly require best management practices to prevent P loss by leaching due to a low Qo. Based on our results, it would be best to amend soils at 5% co-amendment, which has a more moderate P sorption maxima than both 10% co-amendment and 10% Al-WTR, leaving more P available for plant requirements. As Qo reflects the relative number of P adsorption sites per unit soil weight, a higher Qo, automatically means a higher number of sites available for P adsorption. Results from this study point to a higher number of adsorption sites in 10% Al-WTR which is correlated to the higher amount of Al relative to the other treatments, whilst 10% C has fewer adsorption sites for P sorption due to high OM content which competes for adsorption sites. Some studies have demonstrated correlations between Qo and SOM contents or Fe and Al (Villapondo and Graetz, 2001; Zhang *et al*., 2005).

Higher P bonding energy constant values, b, as in 10% Al-WTR (see **Table 6.2**) indicates higher strength in P adsorption. Spontaneous P adsorption will occur readily as soil solution P declines (Wang and Liang, 2014). On the other hand, 10% C with the lowest b values, has the least affinity for P. However, 5% co-amendment had lower b values compared to 10% co-amendment, indicating its lower strength in sorbing P, despite equal ratios of Al-WTR and compost. The results show that the bonding energy constant increased with increase in Al-WTR loadings, implying an increase in adsorption sites. The bonding energy constant, like the P adsorption maximum capacity, generally increased as particle size became finer as well with a decrease in solution pH, although there were a few exceptions which were inconsistent, for example, in 5% co-amendment where the P adsorption maximum capacity increased with an increase in solution pH (see **Table 6.2**). That could only be likely related to a possible precipitation of P by calcium ions, as the pH increased.

The observed high maximum buffering capacity (MBC) recorded for 10% Al-WTR indicates a higher P sorption capacity, whilst 10% C recorded the least and therefore a low P sorption capacity. A higher MBC value indicates a higher P adsorption capacity, and vice versa. A higher MBC would also point to higher P fertiliser requirement (**Table 6.3**). Using this concept, results showed that a soil amended with 10% Al-WTR would adsorb more P as compared to the other amendments (see **Figures. 6.2 & 6.4**). Consequently, soils amended with Al-WTR would require high inorganic fertiliser P rates to maintain a desired P concentration in the soil solution for good plant growth. This was apparent by the higher P fertiliser requirements (PFRs) (**Table 6.3**). As discussed earlier on, the higher amount of exchangeable Al in the Al-WTR would have resulted in the high P sorption and consequently a higher amount of P fertiliser required to satisfy the P adsorption sites and maintain optimal P concentration in the soil solution for good plant growth. However, the 10%- and 5%- co-amendments showed an apparent reduction in PFRs by ranges of 30 - 60% and 60 - 70%, respectively, across the different pH and particle sizes relative to 10% Al-WTR (**Table 6.3**). In our previous work (Gwandu *et al*., 2022), application of 14 kg P ha^{-1}, which translate to 32 kg P_2O_5 ha^{-1} was far below the minimum of 57 and 117 kg P_2O_5 ha^{-1} estimated at a pH of 7.5- and 2-mm particle size for the 5%- and -10% co-amendment, respectively (**Table 6.3**). The ability of an organic material to reduce or increase P sorption is depended upon its type, its P concentration and the amount added (Singh and Jones, 1976). Organic materials containing 0.3% P or more result in a decrease in P sorption whilst those with less than 0.22% increase P sorption (Singh and Jones, 1976). The compost used in this study had 0.18% P (see **Table 6.1**). While results from this study showed about five-times as much PFR for the 5% co-amendment compared to 10% C, a good quality compost (> 0.3% P) can result in increased P availability and thus less P fertiliser requirements. Therefore, determining P levels of organic amendments is recommended before a decision can be made to co-apply with Al-WTR.

6.6 Environmental and agricultural implications for use of Al-WTR in soil health improvement

The experimental results confirmed that the maximum P adsorption increased with a corresponding decrease in particle size and in pH. This has potential implications for disposal of Al-WTR in the environment or its use as a soil applicant. Although research has provided evidence of the soil health benefits of co-amending Al-WTR and compost (Hsu and Hseu, 2011; Mahmoud *et al*., 2021; Gwandu *et al*., 2022; Kerr *et al*., 2022); consideration of Al-WTR particle size is important to reduce P sorption and increase P availability in co-amended soils. Considering these observations, a decision support framework for Al-WTR application in sandy soils based on Al-WTR particle size is proposed (**Figure 6.4**). Although it should be noted that the clay mineralogical component in soils (Gérard, 2016) play an equally important role in P sorption as much as the Al and Fe oxides, the framework is proposed to provide a guidance for applying Al-WTR to sand soils, where the. Al and Fe oxides in the Al-WTR could likely have a potentially deleterious effect on P sorption to the already naturally occurring oxides of Al and Fe in the sand soils. It would thus be necessary to consider other factors that can minimise the surface area available for P sorption in arable sandy soils. Finer particles would suit soil remediation purposes such as in instances where there is excess P or heavy metal contamination in the environment (**Figure 6.4**). Although in real circumstances, field applications of Al-WTR will not involve grinding into finer particles, we presume the Al-WTR will breakdown into smaller particles due to natural weathering and decomposition processes, resulting in a larger surface area, potentially exposing new P adsorption sites. Further studies to determine: (i) the rate of breakdown of Al-WTR in sandy soils, (ii) how often it might be required to add fresh compost to provide more P, and (iii) how many of the newly exposed sorption sites will be used up with stronger carboxyl bonds in existing or freshly added organic matter over time, might be required to come up with recommendations on P fertilisation strategies for use of Al-WTR in these soils. Meanwhile, to maintain yield stability, integrated use of Al-WTR, OM and P fertiliser is recommended. Apart from stabilising plant yields, combined use of organic materials and P fertilisers is an important component of integrated soil fertility management. This has also been proven to reduce greenhouse gas emissions from soils and fertilisers (Bayu, 2020), which is beneficial for human health.

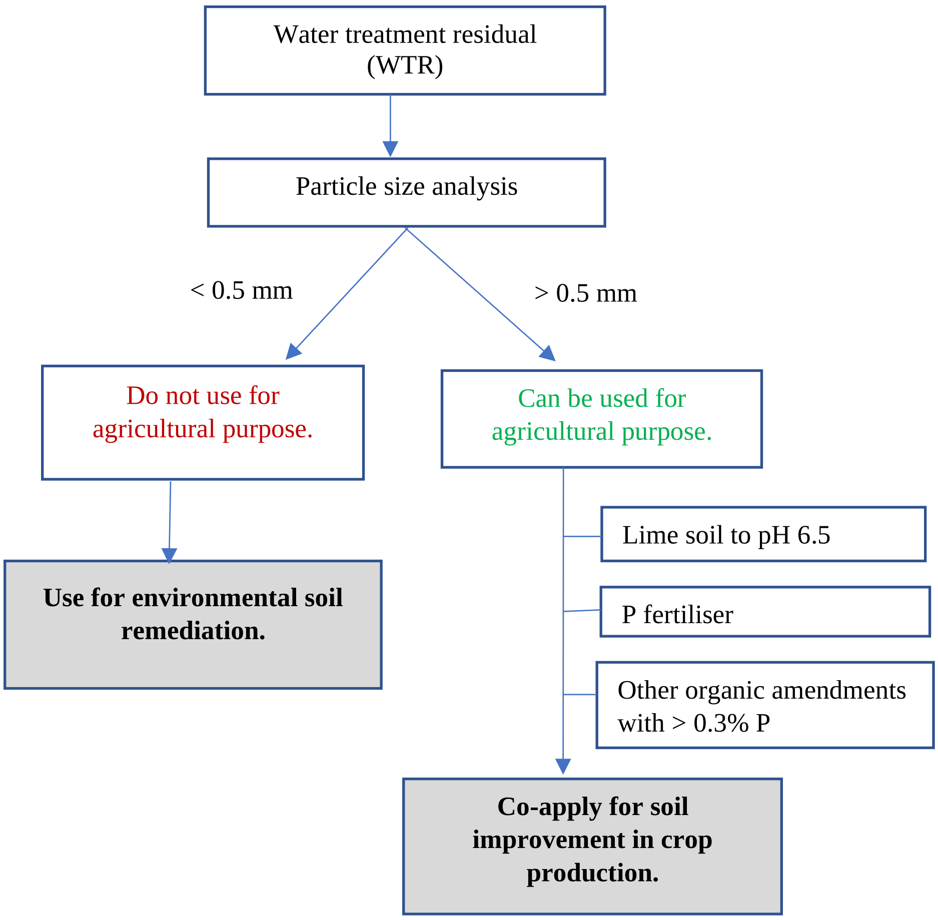

Figure 6.4: A decision supportframework for application of Al-WTR in arable sandy soils based on particle size and pH. Adapted and modified from Ribeiro *et al*. (2022).

6.7 Conclusions

Phosphorus sorption onto Al-WTR is best represented by the Langmuir adsorption isotherm. The maximum P sorption capacity were in the ranges of 770 to 1000 mg P kg^{-1} for 10% Al-

WTR single amendment, and from 714 to 1000 mg P kg^{-1} for 10%- and from 555 to 909 mg P kg^{-1} for 5%- co-amendments, respectively, across a range of pH and soil particle size fractions. The crop phosphorus fertilizer requirements, based on a minimum of 0.2 mg P L^{-1} in solution ranged from the lowest of 53 kg P_2O_5 ha^{-1} in 10% C (pH 7.5; 2 mm particle size) to the highest of 784 kg P_2O_5 ha^{-1} in 10% Al-WTR (pH 4.5; 0.25 mm particle size). Results also revealed that 10% co-amendment and 5% co-amendment reduced the P fertiliser required to maintain a minimum of 0.2 mg P L^{-1} by ranges of 30- to 60-% and 60- to 70-%, respectively, relative to 10% Al-WTR. The results indicate that co-amending Al-WTR and compost can increase P availability in Al-WTR amended soils, providing scope for use of Al-WTR in rebuilding soil health. Detailed analysis of factors such as particle size, soil pH and P concentration levels of the organic amendments, that can maintain and enhance P availability in co-amended sandy soils can be further exploited to inform long-term use of Al-WTR in rebuilding soil health and boost food production to support human health.

Chapter 7

7.0 Influence of soil fertility amendments on soil organic carbon, total nitrogen concentration, and soil biological properties[§]

Abstract

The use of organic and inorganic amendments to improve soil organic carbon (SOC) is key to maintain or enhance the soil's capacity to provide ecosystem services. Maintaining or increasing SOC can help to achieve the United Nations Sustainable Development Goals (UN SDGs) set up in 2015, such as increasing soil biodiversity (SDG 15) and ecosystem resilience in a changing climate (SDG 13). This study was carried out to investigate the influence of soil fertility management, soil depth and time of sampling on the temporal dynamics of SOC and total nitrogen (TN) content, microbial biomass carbon (MBC) and nitrogen (MBN), basal respiration, and the metabolic quotient. Soils were sampled at 3 and 6 weeks after planting (WAP) maize at 0- to 10- and 10- to 20- cm depths in Domboshava, Zimbabwe, during the 2020/2021 rainfall season. The experiment consisted of seven treatments that included single amendments of cattle manure (CM), aluminium water treatment residual (Al-WTR), maize stover (MS) or their co-amendments, Al-WTR + CM and Al-WTR + MS; an unamended control, and the conventional fertiliser treatment, standard NPK. Soil organic C and TN was significantly ($p < 0.05$) higher in the co-amendments which attained > 4.90 g kg^{-1} SOC and > 0.50 g kg^{-1} TN across soil depths. However, variations in both SOC and TN were not associated ($p > 0.05$) with soil depth and time of sampling. Findings have also shown that both microbial biomass C and N were higher at 6 WAP maize and decreased with soil depth. The co-amendment of Al-WTR + CM attained the highest MBC (190 ± 1.14 mg C kg^{-1}) and MBN (35.80 ± 0.51 mg N kg^{-1}) at 6 WAP (0-10 cm depth), whereas the least (120 ± 1.58 mg C kg^{-1} and 18.72 ± 0.35 mg N kg^{-1}) were recorded for the control. Consistent with SOC, TN and microbial biomass concentrations, basal respiration (CO_2-C emission) was higher in the 0 to 10 cm depth. While the co-amendment Al-WTR + MS gave the highest CO_2-C emission (167 ± 3.44 CO_2-C kg^{-1} soil), the unamended control recorded the highest metabolic quotient of 15 mg CO_2-C microbial C day^{-1}, suggesting more available C in the co-amendments and therefore less microbial strain compared to the unamended soil. Overall, findings show a higher biological activity in the co-amendments, suggestive of a high turnover potential of the co-amendments in restoring soil health. It is concluded that Al-WTR co-amendments can be used to sustain soil fertility and enhance microbial growth, which is a key component in rebuilding soil health in line with sustainable development goal number 15 of restoring degraded land and soils.

[§] A modified version of this chapter will be submitted for publication as Gwandu et al (2023). Field application of soil improvement technologies in Zimbabwe to address hidden hunger. Nature Water.

7.1 Introduction

Soil degradation, characterised by decline in quality and decrease in ecosystem goods and services, is a major constraint to achieving the required increases in agricultural production (Lal, 2015; Johnson *et al*., 2022). Greater than 65% of arable soils in sub-Saharan Africa (SSA) is degraded (Stewart *et al*., 2020), which is a major hurdle towards realising food security goals in a region that is characterised by extreme poverty and hunger (Bicaba *et al*., 2017). The population for SSA is predicted to increase 2.5-fold by 2050 (van Ittersum *et al*., 2016; AGRA 2022), yet the production of major food crops including maize is anticipated to decline by more than 30% by 2050 due to rising temperatures and changing rainfall patterns (Lobell *et al*., 2011; Rurinda *et al*., 2015). This calls for urgent need to reverse soil degradation and enhance food production, without expanding on the existing arable land, which can enhance further loss of biodiversity and increase greenhouse gas emissions (van Ittersum *et al*., 2016).

The application of inorganic chemical fertilisers is useful for increasing crop yield and soil nutrient stocks (Kihara *et al*., 2020a; Rurinda *et al*., 2020), which are necessary to build up soil carbon (C) stocks. Most smallholder farmers in SSA have continually farmed without inorganic fertilisers due to their high costs (Bonilla Cedrez *et al*., 2020), partially causing declines in soil organic matter (SOM) and soil microbial biomass (SMB), which are often regarded as important indicators for monitoring soil quality/health (Lal, 2015; Obalum *et al*., 2017; Singh and Gupta, 2018). Poor SOM management (Zingore *et al*., 2021) and the continued isolated application of inorganic fertilisers can result in a functional imbalance in the ecosystem, causing alterations in soil pH and microbial community composition and other chemical interactions that negatively affect SMB (Ren *et al*., 2019). In contrast to inorganic chemical fertilisers, organic amendments such as maize stover and cattle manure can boost C availability for soil microbes, which can be advantageous for enhancing microbial growth in comparison to the single amendment of inorganic fertilisers (Ren *et al*., 2019). It is widely known that the application of manure and maize stover result in improvements in both soil microbial biomass C and N (Heinze *et al*., 2011; Yang *et al*., 2017). However, most farming households in SSA have limited access to the scarce organic nutrient sources (Mapfumo and Giller, 2001), hence the need to invest in alternative SOM sources.

Water treatment residual (WTR) is the by-product of the coagulation-flocculation-sedimentation process of drinking water treatment (Turner *et al*., 2019). Apart from aluminium (Al) and iron (Fe) oxide coagulant residues, WTRs typically contain clay minerals, nutrients, and organic matter sediments from the raw water (Dayton and Basta, 2001; Matilainen *et al*., 2010). Due to their nutrient-supplying potential, WTRs are used for soil improvement (Stone *et al*., 2021; Gwandu *et al*., 2022). It is suggested that WTRs, can potentially improve soil organic carbon (C) in the long-term due to their high C content (Dassayanake *et al*., 2015; Kerr *et al*., 2022). Moreover, it is proposed that when fresh Fe and Al oxides in WTR are added to the soil, they form strong bonds with SOM (Novak and Watts, 2014), shielding it from further microbial decomposition (Kögel-Knabner *et al*., 2008), stabilising soil C. Stabilised SOC can improve the soil/ecosystem C balance, which can boost production and sequester more atmospheric CO_2 into the SOC pool (Lal, 2015). Soil organic C is a substrate for SMB (Nsabimana *et al*., 2004; Jenkinson and Ladd, 2021).

The added benefits of utilising WTR in combination with other organic and /or inorganic nutrient sources as ‘co-amendments’ in sandy soils include increased phosphorus availability, improved soil water holding capacity, crop yield and nutrient content (Gwandu *et al*., 2022; 2023; Kerr *et al*., 2022). The biological characteristics of the soil are positively impacted by the availability of soil nutrients and moisture (Chen *et al*., 2005; Gąsiorek and Halecki, 2022).

As such, there is also evidence to show that Al-WTR co-amendments can improve soil microbial biomass C (Hsu and Hseu, 2011; Mahmoud *et al*., 2021).

Soil microbial biomass is the living component of SOM that is very sensitive to soil ecosystem changes and can be used as an early indicator of soil degradation or improvements in arable practises (Hao *et al*., 2008; Jenkinson and Ladd, 2021). Although SMB constitutes a minor fraction (about 1 – 5%) of total organic C (Sparling, 1997; Jenkinson and Ladd, 2021), it is crucial for SOM and nutrient turnover and serves as a reservoir for labile nutrients in soils (Singh and Gupta, 2018). Soil basal respiration (SBR) is another important soil biological component useful for analysing changes in soil microbial activities (Fang and Moncrieff, 2005). Soil basal respiration is described as the constant rate of soil respiration that results from the mineralisation of OM (Pell *et al*., 2006), and it is calculated using either carbon dioxide (CO_2) evolution or O_2 uptake (Dilly and Zyakun, 2008). Soil basal respiration is used as an index for a healthy soil that is capable of decomposing organic residues and nutrient cycling for plant growth (Fang and Moncrieff, 2005). A high soil respiration is often associated with high biological activities (Fang and Moncrieff, 2005; Blaise *et al*., 2021). The metabolic quotient (respiration rate vs microbial biomass, qCO_2) is another metric for assessing the state and evolution of ecosystems and is used as an indicator of the microbial response to soil degradation (Sawada *et al*., 2009; Nunes *et al*., 2012). Disturbed/degraded soils are expected to have a higher qCO_2 compared to natural or well managed soils (Nunes *et al*., 2012).

While strides have now been made to study the role of Al-WTR co-amendments to improve soil biological properties, in particular microbial biomass C (e.g., Hsu and Hseu, 2011; Mahmoud., 2021), there is still paucity of information on the influence Al-WTR on other soil microbial properties such as microbial biomass nitrogen (N), basal respiration and metabolic quotient, which are equally important soil health indicators (Franchini *et al*., 2007). The objectives of this study were to investigate the influence of different soil amendments, soil depth and time of sampling on the temporal dynamics of (i) SOC and total N of the soils, (ii) soil microbial biomass C and N, MBC/SOC and MBN/TN ratios, and (iii) soil basal respiration, and metabolic quotient.

7.2 Materials and methods

7.2.1 Experimental layout

The experimental layout consisted of seven treatments: i) Aluminium water treatment residual (Al-WTR), (ii) cattle manure (CM), iii) maize stover (MS), (iv) standard NPK, (v) Al-WTR + CM, (vi) Al-WTR + MS and (vii) the unamended control, laid out in a randomised complete block design at Domboshava (17°36ˈ S; 31°08ˈ E) in Mashonaland East province, Zimbabwe. The experiment is fully described in detail in Chapter 3, section 3.1. All treatments except the unamended control received basal P fertiliser (7%N, 14% P_2O_5, 7% K_2O) and additional N (34.5% N as NH_4NO_3) during the different maize growth stages (see Chapter 3, section 3.4.2).

7.2.2 Sampling and pre-treatment of soils

Soils were sampled at 0 – 10 and 10 – 20 cm depths at 3 and 6 weeks after planting (WAP) of maize in the second year of the experiment (2020/2021 rainfall season) using an auger from 5 sampling points in each plot. The soils were bulked and samples for analysis of soil organic C and total N were separated, air -dried and ground to pass through a 0.5 mm sieve and analysed for SOC as described in Chapter 3, section 3.5.2 and total N as described in Chapter 3, section 3.5.3. Soils for soil microbial biomass C and N and basal respiration were archived in a freezer at -25°C until analysis.

7.2.3. Analytical determination of microbial biomass C and N and soil basal respiration

Soil microbial biomass C and N were determined by the chloroform fumigation extraction method (Jenkinson and Powlson, 1976; Vance *et al*., 1987; Anderson and Ingram, 1993) and this is described in detail in Chapter 3, Section 3.4.3.4.

7.3 Data analysis

The effects of different treatments, time of sampling and soil depth and their interactive effects on SOC, TN, MBC/SOC, MBN/TN, soil microbial biomass, basal respiration and metabolic quotient were assessed through an analysis of variance (ANOVA) using GenStat 21st version (VSN International, 2022). The separation of means was done using Tukey's Honest Significant Difference (HSD) test at $p < 0.05$.

7.4 Results

7.4.1 Soil organic C and total N

There were no significant differences ($p > 0.05$) in SOC at 3 WAP, while treatment effects ($p < 0.05$) were observed at 6 WAP. The trends in TN were inconsistent. While significant differences ($p < 0.05$) were observed within treatments for both soil depths at 3 WAP and at 6 WAP in the 10-20 cm depth, no significant treatment differences in TN concentration could be attested for the 0-10 cm depth at 6 WAP (**Table 7.1**). The influence of soil depth and time of sampling on both SOC and TN were also not significant ($p > 0.05$). However, the results showed that the co-amendment of Al-WTR + CM attained the highest SOC with 4.94 g kg^{-1} at 0-10 cm for both the 3- and 6- WAP (**Table 7.1**) whereas the control attained the least with 4.56g kg^{-1}, similar for both sampling time frames. At the 10 – 20 cm depth, Al-WTR + CM recorded 4.92 ± 0.09 g kg^{-1} whilst the control had the least with 4.54 ± 0.09 g kg^{-1} and both remained unchanged at 3- and 6- WAP (**Table 7.1**).

The highest concentration of total N was recorded for Al-WTR + CM (0.64 ± 0.06%) at 6 WAP for the 0 -10 cm depth, whilst the control recorded the least (0.27 ± 0.02%) (**Table 7.1**). At 3 WAP for the same soil depth, Al-WTR attained 0.56 ± 0.02% and control had the least with 0.30 ± 0.03%. At the 10- 20 cm depth, Al-WTR + CM attained 0.58% total N concentration at both 3- and 6- WAP, whilst the control consistently attained the least with 0.26% and 0.27%, respectively for 3 and 6 WAP.

The C/N ratio followed a similar trend to SOC and significantly differed ($p < 0.05$) with treatments for all soil depths, whilst no significant ($p > 0.05$) differences could be ascertained with soil depth and time of sampling (**Table 7.1**). For the 0 – 10 cm depth, the least C/N ratio (9.34 ± 0.007) was recorded for Al-WTR + CM whilst the highest (15.20 ± 0.03) was recorded for the unamended soil at 3 WAP (**Table 7.1**). For the same soil depth at 6 WAP, the lowest (8.82 ± 0.02) C/N ratio was attained by the single amendment of Al-WTR and the highest (16.62 ± 0.07) recorded for the control. At the 10-20 cm depth, Al-WTR + CM recorded the least C/N ratios of 8.92 ± 0.08 and 9.16 ± 0.10 at 3- and 6- WAP, respectively, whilst the control had the highest at 18.86 ± 0.03 and 12.82 ± 0.03 at 3- and 6-WAP in the respective order (**Table 7.1**). Results generally demonstrate that co-amendments obtained higher levels of SOC and total N and low C/N ratios compared to the control and single amendments of CM, MS and Al-WTR.

Table 7.1: Soil organic C, Total N, C/N ratios under different soil fertility management options at 3 and 6 weeks after planting maize at Domboshava Training Centre

	3 WAP			6 WAP		
Sampling depth/ Treatment	SOC (g kg-1)	TN (g kg-1)	C/N	SOC (g kg-1)	TN (g kg-1)	C/N
0 – 10 cm						
Al-WTR	4.74 ± 0.09a	0.50 ± 0.09ab	10.12 ± 0.06ab	4.73 ± 0.03ab	0.54 ± 0.06a	8.82 ± 0.02a
CM	4.74 ± 0.11a	0.44 ± 0.08ab	12.84 ± 0.06ab	4.74 ± 0.10ab	0.46 ± 0.09a	12.98 ±0.09a
MS	4.72 ± 0.09a	0.42 ± 0.06ab	12.20 ± 0.05ab	4.72 ± 0.07ab	0.43 ± 0.05a	11.70 ± 0.06a
Standard NPK	4.58 ± 0.12a	0.38 ± 0.04ab	12.50 ± 0.08ab	4.58 ± 0.08ab	0.40 ± 0.03a	11.72 ± 0.04a
Al-WTR + CM	4.94 ± 0.11a	0.54 ± 0.04b	9.34 ± 0.07ab	4.94 ± 0.10b	0.64 ± 0.06a	8.86 ± 0.03a
Al-WTR + MS	4.88 ± 0.07a	0.56 ± 0.02b	8.76 ± 0.06a	4.88 ± 0.05ab	0.56 ± 0.02a	8.78 ± 0.06a
Control	4.56 ± 0.05a	0.30 ± 0.03a	15.20 ± 0.03b	4.56 ± 0.09a	0.32 ± 0.06a	16.26 ± 0.07a
10 - 20 cm						
Al-WTR	4.72 ± 0.04a	0.50 ± 0.07bc	10.28 ± 1.52a	4.70 ± 0.03ab	0.51 ± 0.05b	9.28 ± 0.04a
CM	4.74 ± 0.14a	0.42 ± 0.04abc	11.72 ±1.22a	4.72 ± 0.06ab	0.45 ± 0.04ab	10.78 ± 0.05a
MS	4.72 ± 0.06a	0.38 ± 0.04abc	12.80 ± 1.23ab	4.70 ± 0.03ab	0.40 ± 0.04ab	12.40 ± 0.04a
Standard NPK	4.56 ± 0.07a	0.36 ± 0.05ab	14.12 ± 2.61ab	4.56 ± 0.09a	0.36 ± 0.05ab	14.08 ± 0.06a
Al-WTR + CM	4.92 ± 0.09a	0.58 ± 0.07c	8.92 ± 0.96a	4.92 ± 0.13b	0.58 ± 0.09b	9.16 ± 0.10a
Al-WTR + MS	4.86 ± 0.08a	0.52 ± 0.04bc	9.54 ± 0.63a	4.86 ± 0.02ab	0.52 ± 0.04b	9.56 ± 0.03a
Control	4.54 ± 0.09a	0.26 ± 0.04a	18.86 ± 2.35b	4.54 ± 0.08a	0.27 ± 0.02a	12.82 ± 0.03a
Statistical significance§						
	SOC	TN	C/N			
Treatment	*[a]	*	*			
Depth	ns	ns	ns			
Time	ns	ns	ns			
Time × Depth	ns	ns	ns			
Time × Treatment	ns	ns	ns			
Depth × Treatment	ns	ns	ns			
Time × Depth × Treatment	ns	ns	ns			

*[a] significant at 6 WAP; Means that do not differ significantly at $p < 0.05$ contain the same letter according to Tukey's test.

7.4.2 Soil microbial biomass C and N concentration

Both MBC and MBN were significantly greater in the 0-10 cm than the 10 – 20 cm depth ($p < 0.05$) across treatments (**Figure 7.1**). Similarly, both MBC and MBN were significantly ($p < 0.05$) higher at 6 weeks than at 3 weeks after planting (WAP) maize. The highest MBC concentration (190 ± 1.14 mg C kg^{-1}) was recorded for Al-WTR + CM at 3 WAP for the 0-10 cm depth, whereas the least (120 ± 1.58 mg C kg^{-1}) was recorded for the control. At 6 WAP (0-10 cm), both Al-WTR + CM and Al-WTR + MS recorded > 250 mg C kg^{-1} MBC with 265 ± 1.41 mg C kg^{-1} and 251 ± 1.14 mg C kg^{-1}, respectively, while the control had the least with 153 ± 0.71 mg C kg^{-1}. At the same time interval, for a soil depth of 10-20 cm, Al-WTR + CM recorded the highest MBC concentration of 244 ± 1.22 mg C kg^{-1}, whilst the control gave the least of 149 ± 0.95 mg C kg^{-1} (**Figure 7.1b**).

Overall, at 3 WAP, the influence of treatments on MBN concentration was not significant ($p > 0.05$) for both the 0-10 and 10-20 cm soil depths (**Figure 7.1 c, d**). However, the MBN concentration was slightly higher in Al-WTR + CM, which attained a MBN concentration of 11.52 ± 0.44 mg N kg^{-1} whilst standard NPK had the least with 10.10 ± 0.23 mg N kg^{-1} at the 0-10 cm depth (**Figure 7.1**). At 6 WAP, the MBN concentration had significantly ($p < 0.05$) improved and significantly ($p < 0.05$) differed with treatment type for both soil depths. The co-amendment, Al-WTR + CM attained significantly higher MBN of 35.80 ±0.51 mg N kg^{-1} and 30. 14 ± 0.94 mg N kg^{-1} for 0-10 cm and 10-20 cm soil depths, respectively. The control continually attained the least with 10.82 ± 0.34 mg N $kg^{-1}$and 8.72 ±0.35 mg N kg^{-1} for the 0-10- and 10-20 cm depth, in that respective order (**Figure 7.1**). Whilst the single amendment of CM gave a higher concentration of MBC at both soil depths and sampling time frames, compared to the single amendment of Al-WTR, Al-WTR resulted in higher MBN relative to

CM at 6 WAP for both soil depths. (**Figure 7.1**). Relative to the control, Al-WTR + MS attained higher MBN concentration by > 100% for both soil depths at 6 WAP (**Figure 7.1**). Overall, results indicated that treatment type, soil depth and time of sampling significantly ($p < 0.001$) influenced MBC and MBN concentrations (**Figure 7.1**).

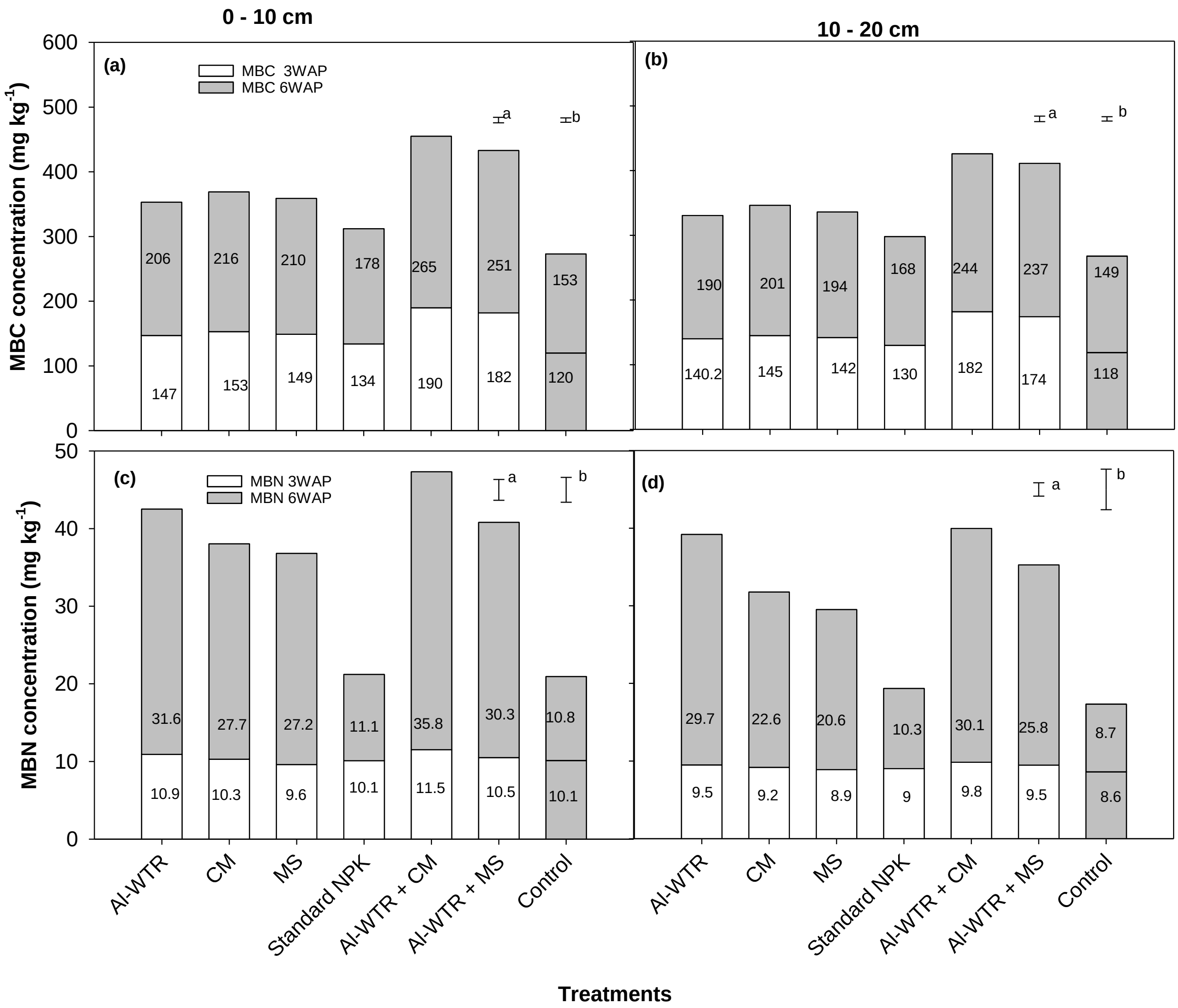

Figure 7.1: Soil microbial biomass C and N due to different soil fertility management at 3- and 6-WAP maize at Domboshava, Zimbabwe. Error bars represents least significant differences of means (lsd) ($p < 0.05$) at a = 3 WAP and b = 6 WAP for both MBC and MBN.

7.4.3 MBC/SOC and MBN/TN ratios under different soil fertility management options

The MBC to SOC ratio significantly ($p < 0.001$) differed with treatment, soil depth and sampling time (**Table 7.2**). Across treatments, higher MBC/SOC ratios were recorded for the 0 – 10 cm depth at 6 WAP whilst the least were recorded for the 10-20 cm at 3 WAP (**Table 7.2**). The co-amendment of Al-WTR + CM consistently recorded a higher MBC/SOC ratio ranging from 3.26 ± 0.08 (3 WAP; 10 – 20 cm) to 5.37 ± 0.03 (6 WAP; 0 - 10 cm). The control, on the other hand, consistently gave the lowest MBC/SOC ratio ranging from 2.12 ± 0.03 (3 WAP; 10-20 cm depth) to 3.36 ± 0.03 (6 WAP; 0-10 cm depth). Compared to the single amendments of CM, MS or Al-WTR, the co-amendments (Al-WTR + CM and Al-WTR + MS) attained at least > 0.5% in MBC/SOC ratios across all soil depths and sampling time frames.

Comparable to TN and the MBN/TN ratio, although not significantly ($p > 0.05$) different was lower for the 10 -20 cm soil depth compared to 0-10 cm. Treatment type, soil depth or the interaction of treatment × depth had no significant ($p > 0.0.5$) influence on the ratio of microbial biomass N to total N (**Table 7.2**). However, time of sampling and treatment × time interaction, significantly ($p < 0.05$) influenced MBN/TN ratio. Thus, the ratio of MBN to TN across most treatments except standard NPK increased by more than 50% from 3- to 6- WAP for all soil depths (**Table 7.2**). For example, the MBN/TN for CM (6 WAP; 0-10 cm depth) rose 2.5 times attaining an MBN/TN ratio of 7.4 ± 0.18 compared to an MBN/TN ratio of 2.80 ± 0.14 for the same depth at 3 WAP (**Table 7.2**).

Table 7.2: Soil organic C, Total N and the MBC/SOC and MBN/TN ratios under different soil fertility management options at 3 and 6 weeks after planting maize at Domboshava Training Centre, Zimbabwe

	3 WAP		6 WAP	
Sampling depth/Treatment	MBC/SOC (%)	MBN/TN (%)	MBC/SOC (%)	MBN/TN (%)
0 – 10 cm				
Al-WTR	3.11 ± 0.06bc	2.30 ± 0.09ab	4.35 ± 0.02bc	5.9 ± 0.31ab
CM	3.23 ± 0.06c	2.80 ± 0.14ab	4.61 ± 0.09c	7.4 ± 0.18b
MS	3.16 ± 0.05bc	2.44 ± 0.29ab	4.46 ± 0.06c	6.96 ± 0.22ab
Standard NPK	2.93 ± 0.08b	2.80 ± 0.21ab	4.06 ± 0.08b	2.80 ± 0.22a
Al-WTR + CM	3.85 ± 0.07d	2.18 ± 0.14ab	5.37 ± 0.13d	6.44 ± 0.10ab
Al-WTR + MS	3.73 ± 0.06d	1.88 ± 0.14a	5.14 ± 0.06d	5.44 ± 0.11ab
Control	2.46 ± 0.03a	3.36 ± 0.09b	3.36 ± 0.07a	3.82 ± 0.12ab
10 - 20 cm				
Al-WTR	2.63 ± 0.03bc	2.10 ± 0.22a	3.96 ± 0.04b	5.86 ± 0.25b
CM	2.73 ± 0.08c	2.28 ± 0.20ab	4.13 ± 0.05b	5.20 ± 0.23ab
MS	2.67 ± 0.06c	2.46 ± 0.27ab	4.07 ± 0.04b	5.42 ± 0.26ab
Standard NPK	2.39 ± 0.04b	2.78 ± 0.29ab	2.77 ± 0.13a	3.18 ± 0.25a
Al-WTR + CM	3.26 ± 0.08d	1.80 ± 0.23a	4.56 ± 0.10c	5.56 ± 0.27ab
Al-WTR + MS	3.15 ± 0.03d	1.90 ± 0.15a	4.47 ± 0.03c	5.08 ± 0.12ab
Control	2.12 ± 0.03a	3.61 ± 0.29b	2.62 ± 0.03a	3.26 ± 0.26a
Statistical significance§				
	MBC/Organic C	MBN/TN		
Treatment	*	*		
Depth	*	ns		
Time	*	*		
Time × Depth	*	ns		
Time × Treatment	*	*		
Depth × Treatment	*	ns		
Time × Depth × Treatment	*	ns		

Means that do not differ significantly at $p < 0.05$ contain the same letter according to Tukey's test.

7.4.4 Soil CO_2-C emission and metabolic quotient due to different soil fertility management

Across treatments, basal respiration was higher in soils sampled from the 0 – 10 cm depth than the 10 – 20 cm depth (**Figure 7.2**), indicating high microbial activity in the topsoil layer. In the 0-10 cm depth, Al-WTR + CM (165 ± 3.76 mg CO_2-C kg^{-1} soil) and Al-WTR + MS (167 ± 3.44 CO_2-C kg^{-1} soil) gave the highest CO_2-C emissions, whilst the unamended control gave the least of 112 ± 1.80 mg CO_2-C kg^{-1} soil (**Figure 7.2 a**). In the 10-20 cm depth, Al-WTR + CM gave the greatest CO_2-C emission of 133.20 ± 2.43 mg CO_2-C kg^{-1} soil, whilst the control consistently emitted the least with 110 ± 0.85 mg CO_2-C kg^{-1} soil (**Figure 7.2 b**). The single amendment of Al-WTR also released significantly higher CO_2-C compared to both the control and standard NPK by 36% and 28%, respectively, for the 0-10 cm soil depth and 20.6% and 17% for the 10-20 cm depth.

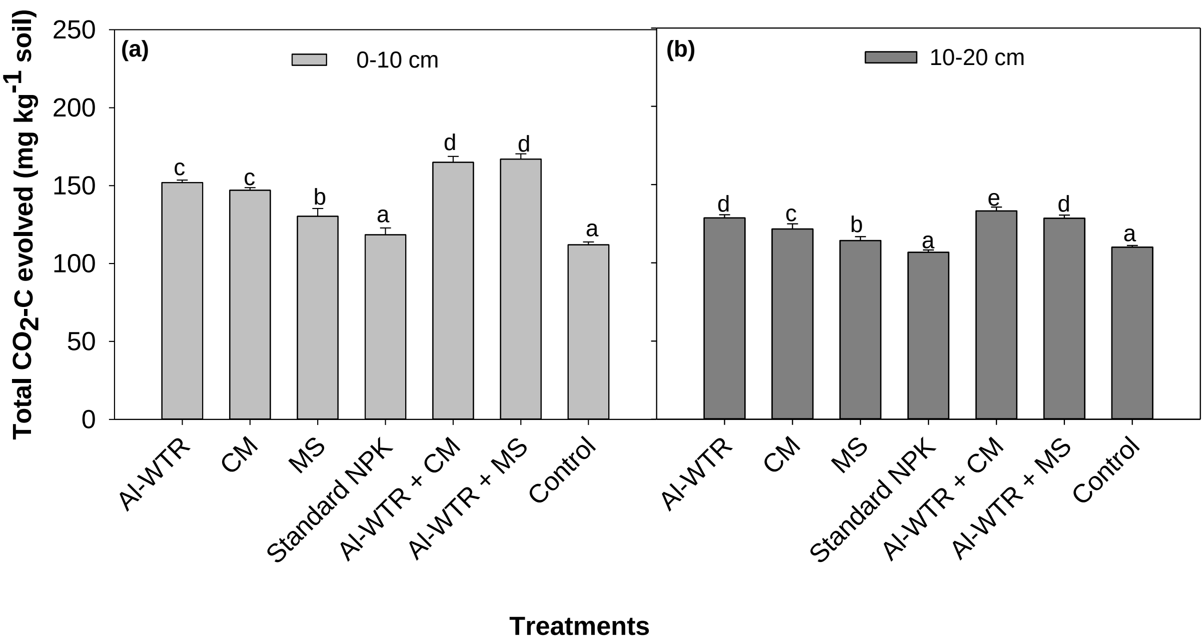

Figure 7.2: Total CO_2-C released from sandy soils under different soil fertility management options sampled at 6 WAP maize at (a) 0-10 cm and (b) 10-20 cm at Domboshava, Zimbabwe. Data and error bars represent mean ± SE (*N*= 3). Means that do not differ significantly at $p < 0.05$ contain the same letter according to Tukey's test.

The unamended control consistently gave significantly ($p < 0.05$) higher metabolic quotients (qCO_2) compared to all the other amendments at both soil depths with 0.15 mg CO_2-C microbial C day^{-1} for both 0-10 cm and 10- 20 cm soil depths (**Figure 7.3**). The co-amendment of Al-WTR + CM had the least metabolic quotient with 0.13 ± 0.003 mg CO_2-C microbial C day^{-1} and 0.11 ± 0.006 mg CO_2-C microbial C day^{-1} corresponding to the 0 -10 cm and 10-20 cm soil depths (**Figure 7.3**). Whilst the metabolic quotients for the rest of the treatments declined with soil depth, the control remained unchanged. (**Figure 7.3**).

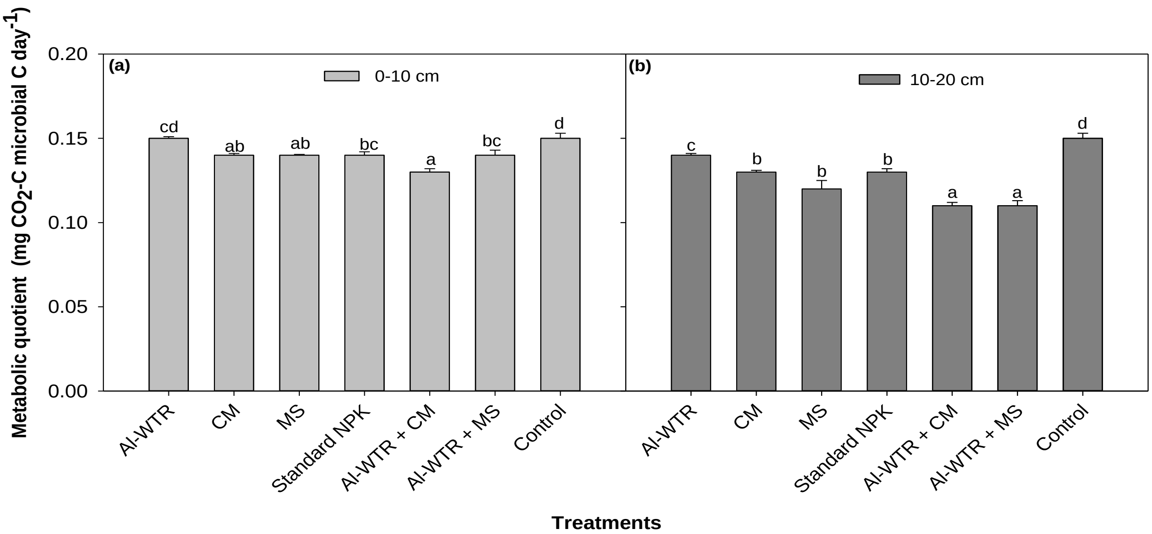

Figure 7.3: Soil metabolic quotient (qCO_2) under different soil fertility management options taken at 6 WAP maize at (a) 0-10 cm and (b) 10-20 cm at Domboshava, Zimbabwe. Data and error bars represent mean ± SE (N = 3). Means that do not differ significantly at $p < 0.05$ contain the same letter according to Tukey's test.

7.5 Discussion

7.5.1 The influence of co-amendments on microbial biomass C and N, MBC/SOC and MBN/TN indices in relation to the concentration of SOC and total N

Soil microbial biomass (SMB) has been used to give a more sensitive appraisal and indication of OM dynamics in the short term (Nilsson, 2005; Nunes *et al*., 2012; Jenkinson and Ladd., 2021). Although SMB constitutes about 1 - 4% of total organic C (Jenkinson and Ladd, 2021), it has a turnover time of less than a year and reacts quickly to environmental and management changes that affect SOC levels, and therefore serves as an early indicator of SOC degradation (Zornoza *et al*., 2009; Singh and Gupta, 2018). Results from this study clearly revealed significant changes in microbial biomass compared to SOC, confirming that microbial biomass is a better and more rapid indicator of soil quality than SOC. From the results, there were no treatment effects in SOC with depth and time of sampling (**Table 7.1**), but both microbial biomass C and N significantly differed with soil depth and time of sampling (**Figure 7.1**).

The high microbial biomass C and N attained for the co-amendments compared to the single amendments of their constituents suggest a synergistic effect of Al-WTR and other organic amendments in the provision of labile C and N to stimulate microbial activity. This is partly attributable to the high organic C and total N contents in the co-amendments compared to the single amendments (**Table 7.1**). However, it is also suggested that zinc (Zn), due to its structural and regulatory function is essential for the development of microorganisms at a certain concentration (Liu *et al*., 2020). Al-WTR co-amendments have been associated with increased plant and soil Zn levels (Gwandu *et al*., 2022). Soil microbial biomass C and N are directly impacted by changes in SOC and TN levels, which are frequently regarded as crucial indications of substrate availability and stoichiometry (Yang *et al*., 2010; Ren *et al*., 2019). As such a decrease in SOC results in a decline in SMB, as evidenced by the decrease in both microbial biomass C and N with decrease in SOC e.g., in the unamended control (**Table 7.1**). This was also possibly enhanced by their low C to N ratios which aided decomposition, providing nutrients to support a high microbial biomass concentration (Horwath, 2017). While the application of maize stover, cattle manure and inorganic fertilisers are known to improve soil microbial biomass (Heinze *et al*., 2011; Yang *et al*., 2017; Ren *et al*., 2019), there is also evidence to show improvements in microbial biomass C following co-application of WTR with other organic or mineral amendments. For example, Hsu and Hseu (2011) reported increased levels of microbial biomass C when Al-WTR was co-applied with compost. Similarly, Mahmoud et al. (2021) reported higher microbial biomass C when WTR was co-applied with inorganic N fertiliser. Results from this study are consistent with Stone et al. (2021), who observed improved microbial concentrations in addition to microbial diversity in a nutrient-deficient sandy soil after co-applying Al-WTR and compost. Although, according to Stone et al. (2021), the single amendment of compost had a greater influence than sole WTR on the receiving soil microbiome diversity; in this study, the high nutrient levels in Al-WTR (see Chapter 5, section 5.4) and other improved soil properties such as improved soil aggregation and water holding capacity in co-amended soils (see Chapter 4, section 4.7.2), likely provided a conducive environment for improved microbial growth and conversion of soluble C into microbial C (Li *et al*., 2015; Ren *et al*., 2019) hence improved soil quality in co-amended soils. Lower values of microbial biomass C and N in the unamended soil indicate a very small labile pool, which is often linked with soil degradation (Nuenes *et al*., 2012). Sandy soils in Domboshava are classified as degraded and are characterised by low SOC (Nyamapfene, 1991; Mtangadura *et al*., 2017) and thus low microbial biomass.

In this study, there were fluctuations in the concentration of microbial biomass C and N with depth and time of sampling. Both microbial biomass C and N were higher at 6 WAP maize compared to 3WAP and decreased with depth (**Figure 7.1**). Microbial biomass corresponds more with soil organic C and N concentrations (Ren *et al*., 2019; Gąsiorek and Halecki, 2022), hence the higher biological activities observed for the top 10 cm, which contained more organic C and N in most treatments. Other factors such as temperature, soil moisture, pH and texture also play a role in the dynamics of soil microbial biomass (Chen *et al*., 2005; Singh and Gupta, 2018; Gąsiorek and Halecki, 2022). The variations in both microbial biomass C and N with sampling time reflects immobilisation and mineralisation dynamics of soil C and N (Yang *et al*., 2010). At early stages of the growing cycle, SMB is low, which can potentially result in nutrient mineralisation (conversion of OM to mineral nutrients). When SMB increases, immobilisation (uptake of mineral nutrients by soil microbes and ultimate conversion to OM) of nutrients can occur (Horwath, 2017). The differences could also have come about due to differences in soil moisture content. At 6 WAP, soil moisture content was high, partly owing to the higher rainfall received at 6 WAP compared to 3 WAP (see Chapter 3, **Figure 3.1**). Results from this study showed higher microbial biomass with increased rainfall events. High soil moisture content promotes rapid mineralisation of soil nutrients, which contributes more to soil microbial growth (Serna-Chavez *et al*., 2013).

In essence the MBC/SOC ratio measures the proficiency of conversion of exogenous C inputs into MBC (Sparling, 1992; Ren *et al*., 2019). The MBC/SOC ratios were high for the co-amendments relative to the unamended control by ranges of 49 to 60%, whilst the MBN/TN ratio of the co-amendments was 55.5% to 69% higher than the unamended control but only at 6 WAP (see **Table 7.2**). Although the reason for a lower MBN in the co-amendments relative to the control at 3 WAP could not be ascertained, findings point to high biological activities suggestive of a high turnover potential of the co-amendments in rebuilding soil health. Co-amendments can thus be used to sustain soil fertility and enhance microbial growth, which is a key component in rebuilding soil health.

7.5.2 Influence of Al-WTR co-application on basal respiration (CO_2-C emission) and metabolic quotient (qCO_2)

Consistent with soil microbial biomass C and N, the co-amendments resulted in higher basal respiration, owing to their higher amounts of organic C. An increase in SOM and nutrients in soils contributes to increased microbial biomass, thus leading to increased rates of respiration (Leita *et al*., 1999; Mahmoud *et al*., 2020). In addition, the co-amendments resulted in relatively higher amounts of total N (> 0.50 g kg^{-1} compared to < 0.35 g kg^{-1} for the control) (see **Table 7.1**), and their C:N ratios are also low (ranging from 8.7:1 to 9.5:1), which favours rapid microbial decomposition. Although it is well known that OM added in the form of manure contains high amounts of labile C, which can enhance CO_2-C emission (Rahman, 2013), the higher CO_2-C emissions by the co-amendments or by the single amendment of Al-WTR compared to single amendments of MS or CM (**Figure 7.2**) was rather unexpected. It is envisaged that the Al/Fe oxides organo-mineral associations that are formed when Al-WTR is added to the soil would protect the C from microbial mineralisation (Novak and Watts, 2004; Kögel-Knabner *et al*., 2008), resulting in less CO_2-C emission from the co-amendments. These findings might point out to the presence of labile C in Al-WTR or alternatively because of the shorter time frame from additions of Al-WTR to soil sampling and measurements, no effective contact would have been made between the Fe/Al oxides and OM. It is not known how much time is taken for these strong mineral bonds to form and stabilise soil C. Basal respiration was higher in the top 10 cm compared to the 10-20 cm soil depths corresponding to changes in microbial biomass which also declined with soil depth. Literature suggests that there is a linear relationship between microbial respiration and biomass (Grayston *et al*., 2001; Fang and Moncrieff, 2005).

The metabolic quotient (respiration rate versus microbial biomass), qCO_2, represents the ability of the microbial community to utilise the substrate that is available (Fang and Moncrieff, 2005). Soil qCO_2 is also used as an indicator of the microbial response to soil degradation (Sawada *et al*., 2009; Nunes *et al*., 2012), hence it is expected that a higher qCO_2 in disturbed/degraded soils compared to natural undisturbed soils (Nunes *et al*., 2012). In nutrient-deficient/degraded soils, microbes divert energy from biomass accumulation to cellular maintenance (Sawada *et al*., 2009; Hu *et al*., 2011). For instance, as earlier on highlighted, research has shown that Zn, due to its structural and regulatory function is necessary for the development of microorganisms at a particular concentration (Liu *et al*., 2020), but excess Zn can be toxic to microorganisms through the displacement of essential metals from their native binding sites or through ligand interactions (Bruins *et al*., 2000). In this study, the unamended control, which is deficient in Zn (see Chapter 5) recorded higher qCO_2 at both soil depths compared to the co-amendments (**Figure 7.3**). This indicated more available C in the co-amendments in addition to the conducive environment proffered by Zn availability (Gwandu *et al*., 2022) and therefore less microbial stress compared to the unamended soil.

7.6 Conclusions

In this study, laboratory experiments were conducted on soils sampled from two soil depths at 3 and 6 WAP maize to investigate the influence of different soil fertility amendments on soil C and N concentration, microbial biomass, basal respiration, and metabolic quotient. Soil organic C and total N was significantly ($p < 0.05$) higher in the co-amendments which attained > 4.90 g kg^{-1} SOC and > 0.50 g kg^{-1} TN across soil depths. However, variations in both SOC and TN were not associated ($p > 0.05$) with soil depth and time of sampling. The observed variations in the concentration of microbial biomass C and N were associated with depth and time of sampling. Both microbial biomass C and N were higher at 6 WAP maize compared to 3WAP and decreased with depth. The co-amendments (Al-WTR + CM and Al-WTR + MS) recorded higher microbial biomass C and N and basal respiration and a lower metabolic quotient across all depths and time frames relative to the unamended control, indicating more available C in the co-amendments. The co-amendments also attained higher microbial biomass

C and N compared to the single amendments of their constituents, suggesting a synergistic effect of Al-WTR and other organic amendments in the provision of labile C and N to stimulate microbial activity. The MBC/SOC and MBN/TN ratio of the co-amendments were ~50% higher relative to the unamended soil. Overall, findings show a higher biological activity reminiscent of the high turnover potential of the co-amendments for restoring soil health. It is concluded Al-WTR co-amendments can be used to sustain soil fertility and enhance microbial growth, which is a key component in rebuilding soil health in line with sustainable development goal number 15 of restoring degraded lands and soils. Further research could be done to investigate dynamics in situ-CO_2 emission measurements (in field or laboratory-based) in co-amended soils over a long growing period e.g., 120 days from Al-WTR incorporation.

Chapter 8

8.0 Overall discussion, conclusions, and recommendations

8.1 Introduction

This study explored the co-application of aluminum water treatment residual (Al-WTR) with other sources of organic matter and mineral fertiliser as ‘co-amendments’ to improve the health of a sandy soil. Aluminium water treatment residual is an organo-mineral containing variable amounts Al and Fe oxides, clay, and organic matter sediments from the raw water (Matilainen *et al.*, 2010). The use of Al-WTR for land application is an alternative disposal route (Turner *et al*., 2019) for this by-product. The following discussion summarises the study's key findings in relation to the four study objectives and their implications for use of Al-WTR co-amendments for rebuilding soil health in urban agroecosystems in Zimbabwe and other similar agro-ecologies.

8.2 Can we use Al-WTR co-amendments to increase crop productivity and rebuild sandy soils?

8.2.1 Co-application of Al-WTR and other organic nutrient sources contributes to improved soil organic carbon concentration, soil physical characteristics and maize grain yield

The use of Al-WTR coamendments (i.e., Al-WTR + CM; Al-WTR + MS) resulted in increased SOC in soils (Chapter 4 and Chapter 7). The improvements in SOC in the co-amendments in comparison to the single amendments of either cattle manure or maize stover were linked to the Al-WTR component. Water treatment residual can contribute to increased soil C through several mechanisms (i) by directly contributing to soil C due to their high C content

(Dassanayake *et al*., 2015; Kerr *et al*., 2022), (ii) the Al and Fe oxides on the surface of WTR can form strong inner sphere complexes with OM through various OM functional groups (Yang *et al*., 2019) and (iii) due to their high surface area and active adsorption sites, the Al and Fe oxides in the WTR matrix also adsorb OM molecules, protecting them from microbial destruction (Kögel-Knabner *et al*., 2008). As a result, they can aid in long-term C storage (Chadwick and Kramer, 2018; von Fromm *et al*., 2021). The improvements in SOC by the co-amendments in turn led to reduced soil bulk densities in Al-WTR co-amended soils. Additionally, because WTRs are highly porous with characteristically low bulk densities, they are expected to lower the receiving soils' bulk density when added for soil improvement (Dayton and Basta, 2001; Babatunde *et al*., 2008).

Results from this study have shown the importance of SOC in improving aggregate stability and soil water holding capacity (Chapter 4). Although research has consistently demonstrated the value of combining OM and inorganic fertilisers to improve soil aggregate stability and water-holding capacity (Zhao *et al*., 2017; Gautam *et al*., 2020), this study revealed the significance of combining OM and soil mineral components (Al and Fe oxides) to enhance aggregate stability and increase the soil's water holding capacity. The stable organo-mineral complexes formed when Fe and Al oxides binds with OM proffers high tensile strength that aids in aggregate stability. This is evidence to show that Al-WTR co-amendments have the potential to build and stabilise soil structure in the long-term leading to improved soil water-retention capacity of sandy soils and therefore their drought resilience.

The improved soil physical conditions contributed to improved soil biological properties (Chapter 7) and crop yields Chapter 4 and 5). Improvements in soil physical conditions can have multiplier effects to soil biological properties and crop yields (Oldfield *et al*., 2018). In this study, the increments in maize grain yield could be attributed to the improved soil conditions and the enhanced soil fertility benefits (Chapter 5) due to co-application of Al-WTR and other organic amendments (Clarke *et al*., 2019; Ibrahim *et al*., 2020).

8.2.2 Co-amendments positively impact on the soil chemical environment leading to higher maize dry matter yield, and nutritional quality.

Findings from this study have shown improved soil chemical properties in co-amended soils to include both macro- and micro- nutrients (Chapter 5 and Chapter 7), which was attributed to the synergy in nutrient supply between Al-WTR and compost (Clarke *et al*., 2019). There were also improvements in soil pH in Al-WTR co-amended soils (Chapter 5), which is essential to decrease the bioavailability of heavy metals such as Pb and Ni and to reduce Al toxicity which can be problematic in sandy soils. Apart from influencing the availability of nutrients, favourable soil pH maintains high biological activity in the soil, leading to better nutrient cycling (Sawada *et al*., 2009). While the application of Al-WTR as a single amendment has for long been associated with P sorption by the Fe and Al oxides (Silveira *et al*., 2013; Novak and Watts, 2014), this study has demonstrated that co-application of Al-WTR and compost in a 1:1 ratio of 5% (5% co-amendment) enhanced the availability of P in Al-WTR amended soils (Chapter 6). This led to reductions in crop P fertiliser requirements in co-amended soils compared to the single amendment of Al-WTR across different pH and particle sizes (Gwandu *et al*., 2023), thus providing scope for use of Al-WTR in rebuilding soil health. Increasing soil P availability for plant uptake enhances plant root development, which boosts their capacity to take up nutrients from the soil, leading to improved plant growth and overall crop quality (Malhotra *et al*., 2018).

In Chapter 5, results from both field and greenhouse experiments demonstrated improvements in the uptake of both macro- and micro- nutrients by maize and a reduction in heavy metal uptake due co-application of Al-WTR and either compost, cattle manure or maize stover and

P fertiliser. The co-amendment of Al-WTR + CM attained higher Zn and Cu grain concentration relative to the unamended control, providing an entry point for alleviating micronutrient deficiency in cereal-based diets in SSA (Gwandu *et al*., 2022). Apart from increasing maize productivity and grain yield (as shown by both greenhouse and field experiments), this study also revealed the important role of P fertiliser in rebuilding soil health to enhance crop yield. For example, in Chapter 5, the co-amendment (10% Al-WTR+10% compost) produced maize shoot biomass of 3.92 ± 0.16 g at 5 weeks after emergence, out-yielding the unamended control which yielded 1.33 ± 0.17 g. However, the addition of P fertiliser to the co-amendment further increased maize shoot yield by about two-fold (7.23 ± 0.07 g) emphasising the important role of P fertiliser in the predominantly sandy soils of SSA. The improvement in maize grain yield observed for the co-amendments was attributed to an improved soil chemical, biological and physical environment in the soil (Chapters 4, 5, 6 and 7), which in turn are key steps towards reversing soil degradation in urban croplands in Zimbabwe (Lal, 2015).

8.2.3 Al-WTR co-amendments proffer opportunities for enhancing soil quality

Soil Organic C is often regarded as an important indicator for monitoring soil quality/health (Obalum *et al*., 2017; Singh and Gupta, 2018). Soil biological characteristics such as microbial biomass C and N, basal respiration and metabolic quotient that rapidly responds to changes in SOC are often used as indicators of soil degradation or improvements in soil health restoration. Findings from this study have demonstrated higher microbial biomass and basal respiration by the co-amendments relative to the unamended control, suggesting a synergy between Al-WTR and other organic amendments in the provision of labile C and N to stimulate microbial activity. Results also show a lower metabolic quotient by the co-amendments, implying low microbial stress and thus a high turnover potential for restoring soil health. Overall, findings suggest that Al-WTR co-amendments are an entry point for re-building soil health in sandy soils.

8.3 The role of Al-WTR co-amendments in improving soil health and addressing sustainable development goals

As an indicator for soil health, soil organic C is of major significance for its contribution to food production, climate change mitigation and adaptation, and the achievement of Sustainable Development Goals (SDGs) (FAO, 2017). Soil health is linked to many SDGs (Keesstra *et al*., 2016; Lal, 2019). In this study, Al-WTR co-amendments enhanced soil chemical, physical and biological properties, and crop yields (Chapters 4, 5, 6 and 7), which could partly address SDGs 2 (zero hunger), 15 (protect and restore degraded land and soil) and contribute to SDG 13 (climate action) through improvements in SOC. Also, the re-use of Al-WTR, a by-product of the drinking water treatment process, is a welcome development for most Water Treatment Plants, which are looking for sustainable ways for its re-use in line with SDG 12 that relates to responsible production and consumption. In Chapter 5, the use of Al-WTR and compost enhanced micronutrient uptake to improve maize grain Zn, which could potentially improve human nutrition for the urban population of SSA, partly addressing SDG3 of improving diets.

8.4 Recommendations

The research on use of Al-WTR as a soil improvement technology has been conducted for more than 40 years (e.g., Rengasamy *et al*., 1980). One drawback that has been highlighted for its use is its ability to fix soil P, a nutrient that is critical in plant production (Penn and Camberato, 2019; Mahmoud *et al*., 2020). This study contributes to the ongoing research by finding ways to enhance P availability in Al-WTR amended soils through combining Al-WTR with other organic nutrient sources and P fertiliser. In addition, there is now ample evidence to show that

Al-WTR co-amendments improve soil physical properties, water holding capacity and biological properties and plant yield (Hsu and Hseu, 2011; Clarke *et al.*, 2019; Mahmoud *et al.*, 2020; Stone *et al.*, 2021; Kerr *et al.*, 2022). Emerging evidence has also shown that Al-WTR co-amendments can enhance P availability (Gwandu *et al.*, 2023) and improve micronutrients Zn and Cu in maize and help alleviate hidden hunger (Gwandu *et al.*, 2022). Considering these findings, the following recommendations are made from this study:

- To maintain yield stability, integrated use of Al-WTR, OM and P fertiliser is recommended.
- It is necessary to determine P levels of organic amendments before they can be co-applied with Al-WTR. Organic amendments with P levels > 3% can be co-applied with Al-WTR (**Figure 6.6**).
- The initial Al-WTR particle size should be > 0.5 mm for use as soil improvement, otherwise it can be used for environmental remediation.
- To maintain the pH of soils above 5.5 to reduce P sorption in Al-WTR amended soils.

8.5 Areas for further research

This study provided experimental evidence that Al-WTR co-amendments can be used to rebuild the health of poor sandy soils and enhance their nutrient and water holding capacity. The following knowledge gaps still exist:

- Further research should investigate potential for increasing Al-WTR application rates for field trials from the current recommendation of 2 t ha^{-1} to 5 t ha^{-1} or more and investigate how such increases can impact on maize yield and P availability.
- Further studies to determine: (i) the rate of breakdown of Al-WTR in sandy soils, (ii) how often it might be required to add fresh compost to provide more P, and (iii) how

many of the newly exposed sorption sites will be used up with stronger carboxyl bonds in existing or freshly added organic matter over time, providing scope for specific recommendations on P fertilisation strategies in Al-WTR amended soils.

- Further research could be done to investigate in situ-greenhouse gas (GHG) emissions, in particular CO_2 in Al-WTR co-amended soils over a long growing period e.g., 120 days from Al-WTR incorporation.

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Appendix 1

Table 1: Statistical significance of the effects of different organic amendments (treatments), P concentration, pH, particle size and their interaction on P adsorption based on a split-split plot analysis of variance using GENSTAT 21st Edition (VSN International, 2022)

Factors/ interactions	p value
Treatment (A)	< 0.001
P concentration (B)	< 0.001
A × B	< 0.001
pH (C)	<0.001
A × C	<0.001
B × C	< 0.001
A × B × C	< 0.001
Particle size (D)	<0.001
D × A	< 0.001
D × B	< 0.001
A × B × D	< 0.001
C × D	< 0.001
A × C × D	< 0.001
B × C × D	< 0.001
A × B × C × D	< 0.001

Appendix 2

Trainings

The following courses and training were offered by the Durham Centre for Academic Development (DCAD)

1. An introduction to descriptive statistics (June 2019)
2. Choosing the right statistical test for your data (June 2019)
3. Best practices in designing questionnaires and survey instruments (June 2019)
4. Overcoming hurdles in the research process (June 2019)
5. Introduction to Endnote (June 2019)
6. Long documents in word (July 2019)
7. Hands on project management-creating your doctoral work Ghantt chart in excel (September 2019)
8. Introduction to R for quantitative analysis (September 2019)
9. The PhD research process (GCRF CDT Post graduate training course) (March 2019)
10. The PhD examination process and the viva (GCRF CDT Post graduate training course Nov 2021)

Conference Presentations

1. Aluminium water treatment residual for rebuilding soil health in urban agroecosystems in Zimbabwe. Department of Engineering Post graduate Research Day (July 2022).
2. From a waste to a valuable resource: Combined application of water treatment residual and compost improves maize productivity. Goldschmidt 2020.

Seminars

1. Innovations in soil and plant nutrient management (22 October 2022) (online)
2. Nutrient management for smallholders in Sub-Saharan Africa. International Fertilizer Society (June 2021).