Water Treatment Residual: Potential Amendment to a Sandy Soil

By

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DECLARATION

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ABSTRACT

Water treatment residual (WTR) is a waste product generated during the water treatment process. This study assesses the potential of using WTR as a potential amendment or co-amendment with commercial compost, to the sandy soils common in the Cape Town metropolitan area.

The study set out to: i) characterise the Alum-WTR collected in 2019 and Ferric-WTR collected in 2018 and 2019, a sandy topsoil and compost through mineralogical and chemical characterization, ii) determine the soil-water interactions of Ferric-WTR (2018) single amendment and co-amendment with compost at application rates of 10% w/w (225 tons/ha) and 20% w/w (450 tons/ha), iii) conduct a greenhouse experiment on Swiss Chard (*Beta vulgaris* cicla.) growth in a sandy topsoil with 10% and 20% single amendments of compost and Ferric-WTR (2018) and a WTR-compost co-application (20%) under water and nutrient-induced stress, and iv) investigate the effect of the Ferric-WTR (2018) amended sandy topsoil on trace element plant availability and phytotoxicity.

The properties of the Alum-WTR (2019), Ferric-WTR (2018 and 2019) samples was characterised in terms of morphology, mineralogy, specific surface area, EC, pH, aqua regia extractable elements, exchangeable cations and acidity and ammonium oxalate extractable Al, Mn and Fe. The adsorption of phosphate to the WTR was fitted to Langmuir and Freundlich isotherm models. The analysed WTRs exhibit irregular surface morphology and a large specific surface area (84.80 – 144.13 m^2/g). The X-ray diffraction results showed that the crystalline phases from the raw water are quartz, muscovite, kaolinite and feldspar, while the Al and Fe derived from the treatment process is mainly held in poorly crystalline phases. The WTR from both water treatment plants (WTP) contained Al, Fe, Cr, Mn, Co, Ni, Cu, Zn, As, and Pb. The EC of the WTRs ranged between 0.24 -0.8 dS/m while the pH (KCl) ranged from 4.7 to 6.6 and the CEC of Ferric-WTR (2018) was the highest at 90 $cmol_c/kg$, followed by 25 $cmol_c/kg$ for the Ferric WTR (2019) and 6 $cmol_c/kg$ for Alum-WTR (2019). The maximum P sorption was 12.62 mg/g and 12.01 mg/g for Ferric-WTR (2019) and Alum-WTR (2019), respectively.

The soil water repellency (SWR) of the Ferric-WTR (2018), compost and WTR-compost co-application was investigated trough a Water Drop Penetration Time test (WDPT). The water retention characteristics of the amendment mixtures were determined with pressure plates. The SWR of the sandy topsoil was significantly reduced from 1661 seconds to 67 seconds by the 20% Ferric-WTR (2018) amendment. The Ferric-WTR (2018) amendment mixtures (10%

and 20%) resulted in an upward shift in the water retention curve, without altering the retention curve shape. The 20% Ferric-WTR (2018) amendment resulted in a 12.5% increase in the total available-water holding capacity (TAWC). The increased water content at all matric potentials is related to water held in the micropores of the WTR.

A 6 x 2 x 2 factorial ANOVA (6 amendment mixtures, 2 water levels and 2 fertiliser levels) on the water use efficiency (WUE) of Swiss Chard was conducted. The unfertilized treatment combinations were analysed colourimetrically for plant available P and N with a Mehlich-3 extract and a 2 M KCl solution and ammonium and nitrate test kits. The factorial ANOVA on WUE resulted in significant interaction. The treatment combinations were subsequently analysed by a single factor ANOVA. The WUE of the unfertilised water-unstressed WTR-compost co-application resulted in a 16-fold increase in WUE relative to the control. The WTR addition to the sandy soil reduced the plant availability of P. The WTR-compost co-application improves Swiss Chard biomass production and WUE under water and nutrient-limited conditions, and it outperformed both the control and the WTR single amendment.

The plant-available trace elements of the unfertilized amendment mixtures was extracted in a Mehlich-3 extract. Both the unfertilised 20% Ferric-WTR (2018) single amendment and the WTR-compost co-amendment, WTR reduced the plant availability of As, Pb, Mo, Cu and Zn, while the Ferric-WTR is a source of Al, Cr, Mn, Fe, Co and Ni in comparison to the sandy topsoil. No treatment combination resulted in Pb, Ni, Mn, Cu and Zn exceeding the Mehlich-3 toxicity threshold.

Land application of a WTR-compost co-application to a poor sandy soil is a viable conduit for diverting waste from landfill into agricultural potential.

OPSOMMING

Waterbehandelingsresidu (WTR) is 'n afvalproduk wat tydens die waterbehandelingsproses gegenereer word. Hierdie studie ondersoek die potensiaal van WTR as 'n moontlike aanvulling of mede-aanvulling te same met kommersieel beskikbare kompos tot die sanderige grond, algemeen in die groter metropool van Kaapstad.

Die studie het ten doel gehad: i) om die Alum-WTR wat in 2019 versamel is, en Ferric-WTR wat in 2018 en 2019 versamel is, 'n sanderige bogrond en kompos deur fisiese en chemiese karakterisering te ontleed, ii) die grond-water-wisselwerking van Ferric-WTR (2018) as enkel aanvulling en mede-anvulling met kompos teen toedieningshoeveelhede van 10% w/w (225 ton/ha) en 20% w/w (450 ton/ha) te bepaal, iii) 'n kweekhuiseksperiment wat die groei van Swiss Chard (*Beta vulgaris* cicla.) in 'n sanderige bogrond met 10% en 20% enkel aanvullings van kompos en Ferric-WTR (2018) asook 'n WTR-kompos mede- anvulling onder water en nutrient spanning te ondersoek, en iv) om die effek van die Ferric-WTR (2018) aanvulling tot `n sanderige bogrond op die beskikbaarheid spoorelementplante en plant toksisiteit te ondersoek.

Die eienskappe van die Alum-WTR (2019), Ferric-WTR (2018 en 2019) monsters is ontleed in terme van morfologie, mineralogie, spesifieke oppervlakte, EC, pH, aqua regia- oplosbare elemente, uitruilbare katione en suurheid en ammoniumoksalaat oplosbare Al, Mn en Fe. Die adsorpsie van fosfaat aan die WTR is gepas op Langmuir en Freundlich isotermmodelle. Die analiese van die WTRs toon onreëlmatige oppervlakmorfologie en 'n groot spesifieke oppervlak (84,80 - 144,13 m^2/g). Die resultate van die X-straal diffraksie toon dat die kristallyne fases, kwarts, muskoviet, kaoliniet en veldspaat is van die rou water, terwyl die Al en Fe wat van die behandelingsproses afkomstig is, hoofsaaklik in swak kristallyne fases gehou word. Die WTR van beide waterbehandelingsaanlegte (WTP) bevat Al, Fe, Cr, Mn, Co, Ni, Cu, Zn, As en Pb. Die EC van die WTR's het gewissel tussen 0,24 -0,8 dS/m, terwyl die pH (KCl) van 4,7 tot 6,6 wissel en die CEC van Ferric-WTR (2018) die hoogste was met 90 $cmol_c$/kg, gevolg deur 25 $cmol_c$/kg vir die Ferric WTR (2019) en 6 $cmol_c$/kg vir Alum-WTR (2019). Die maksimum fosfaat sorpsie was onderskeidelik 12,62 mg/g en 12,01 mg/g vir Ferric-WTR (2019) en Alum-WTR (2019).

Die water hidrophobisteit eienskappe (SWR) van die Ferric-WTR (2018), kompos en WTR-kompos mede- aanvulling is ondersoek deur 'n waterdruppel penetrasie-toets (WDPT). Die water retensie-eienskappe van die aanvulling kombenaies is met drukplate bepaal. Die SWR van die sanderige bogrond is aansienlik verminder van 1661 sekondes tot 67 sekondes deur

die 20% Ferric-WTR (2018) aanvulling. Die Ferric-WTR (2018) aanvulling kombenasies (10% en 20%) het gelei tot 'n opwaartse skuif van die waterretensie-kurwe, sonder om die vorm van die retensie-kurwe te verander. Die Ferric-WTR (20%) aanvulling het gelei tot 'n toename van 12,5% in die totale beskikbare waterhouvermoë (TAWC). Die verhoogde waterinhoud by alle matriekspotensiale hou verband met water wat in die mikropore van die WTR gehou word.

'n 6 x 2 x 2 ANOVA (6 aanvulling kombenasies , 2 water tedienings en 2 kunsmis aanvullings) op die water gebruikseffektiwiteit (WUE) van Swiss Chard is uitgevoer. Die behandelings kombinasies sonder kompos toediening is geanaliseer vir plant beskikbaar P en N met 'n Mehlich-3 uittreksel en 'n 2 M KCl oplossing met ammonium en nitraat toetsstelle. Die faktoriale ANOVA op WUE het beduidende interaksie tot gevolg gehad. Die behandelingskombinasies is vervolgens deur 'n enkele faktor ANOVA geanaliseer. Die WUE van die kunsmis- en water-arm WTR-kompos-toediening het gelei tot 'n 16-voudige toename in WUE in vergelyking met die kontrole. Die toevoeging van WTR tot die sanderige grond het die beskikbaarheid van P verminder. Die WTR-kompos-toediening verbeter die produksie van Swiss Chard-biomassa en WUE onder water- en voedings beperkte toestande, en dit het beter gevaar as die enkele aanvulling van WTR en die kontrole.

Die plantbeskikbare spoorelemente van die kunsmis arm aanvulling kombenasies is met 'n Mehlich-3-ekstrak onttrek. Beide die onbemeste 20% Ferric-WTR (2018) enkel aanvulling en die WTR-kompos mede- anvulling, het WTR die plantbeskikbaarheid van As, Pb, Mo, Cu en Zn verminder, terwyl die Ferric-WTR 'n bron is van Al, Cr, Mn, Fe, Co en Ni is in vergelyking met die sanderige bogrond. Geen behandelingskombinasie het daartoe gelei dat Pb, Ni, Mn, Cu en Zn die Mehlich-3 toksisiteitsdrempel oorskry het nie.

Grondtoediening van 'n WTR-kompos mede-aanvulling, op 'n swak sanderige grond is 'n lewensvatbare alternatief tot stortingsterrein berging, en kan `n afvalproduk omskep in landboupotensiaal.

BIOGRAPHICAL SKETCH

Jan George Steytler was born in Panorama Mediclinic, on 25 June 1995. He began his school career at Welgemoed primary school, and in 2013 matriculated from Paul Roos Gymnasium. In 2014 he enrolled for a BSc (Earth Sciences) degree at Stellenbosch University, which he completed in 2016, after which he completed a BSc (Hons) Geology 2017, also at Stellenbosch University. Thereafter, in 2018, he completed the relevant undergraduate soil science subjects to be legible to enrol for an MSc(Agric) Soil Science at Stellenbosch University, which he started in 2019.

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ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
AC	Activated Carbon
Al	Aluminium
AlWTR	Alum-WTR
As	Arsenic
BDL	Below detection limit
Bo	Boron
Ca	Calcium
CAF	Central Analytical Facility
CEC	Cation Exchange Capacity
cm	Centimetre
Co	Cobalt
Cr	Chromium
Cu	Copper
DAS	Days from sowing
EAWC	Easily available water-holding capacity
EC	Electrical conductivity
FC	Field Capacity
Fe	Iron
FeWTR	Ferric-WTR
FTIR	Fourier transform infrared spectroscopy
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
K	Potassium
LAWC	Least available water-holding capacity
m	Meter
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
N	Nitrogen
Na	Sodium
nd	Not determined
nm	Nanometre
Ni	Nickel

P	Phosphate
Pb	Lead
PWP	Permanent Wilting Point
PZC	Point of Zero Charge
RAW	Readily available water
SOM	Soil Organic Matter
SSA	Specific Surface Area
SWR	Soil Water Repellency
TAWC	Total available water-holding capacity
TMT	Total Maximum Threshold
WDPT	Water Drop Penetration Time
WHO	World Health Organization
WTP	Water Treatment Plant
WTR	Water Treatment Residual
WUE	Water Use Efficiency
XRD	X-ray diffraction
Zn	Zinc

CHAPTER 1. GENERAL INTRODUCTION AND RESEARCH AIMS

1.1 Introduction

Safe, accessible potable water is a cornerstone of modern society. If raw water is adequately treated, it can all but eliminate waterborne diseases like cholera, polio and typhoid fever (Jain, 2012). The global demand for potable water is growing at an astounding rate, driven by rapid population growth and lifestyle changes resulting in higher water demand per capita (Dassanayake *et al.*, 2015; Jain, 2012). The worldwide freshwater demand increases by an estimated 64 billion cubic metres per year (Dassanayake *et al.*, 2015). In order to meet the demand for potable water, large volumes of raw water need to be treated, producing an inevitable Water treatment residual (WTR). This waste product of the drinking water purification process comprises of added chemicals, and flocculated organic and inorganic particles from the raw water (Ackah *et al.*, 2018; Herselman, 2013).

During the water purification process coagulation and flocculation of unwanted material in the raw water is achieved by the addition of an aluminium or iron salt (Dassanayake *et al.*, 2015). Additions such as lime, activated charcoal, polyacrylamide and long-chain organic polymers may be added to aid the coagulation and flocculation process. Such additions, however, are plant and treatment type-specific (Titshall & Hughes, 2005).

The addition of a metal sulfate salt hydrolyses with water to form a metal-oxyhydroxide and sulfuric acid;

$$\mathrm{Al_2(SO_4)_3} + 6H_2\mathrm{O} \rightarrow 2\mathrm{Al(OH)_3} + 3H_2SO_4$$

The acid is then neutralised with the addition of lime;

$$CaO + H_2SO_4 \rightarrow H_2\mathrm{O} + CaSO_4$$

The acid neutralisation results in the coagulation and precipitation of the gelatinous, amorphous metal-oxyhydroxide along with the suspended particles and impurities, forming the WTR (Babatunde & Zhao, 2007; Bugbee & Frink, 1985). The metal hydroxides within the WTR precipitate are not always completely neutralised and can carry a small residual positive charge which plays a significant role in the chemical interaction between WTR and the environment (Bugbee & Frink, 1985).

The global WTR production exceeds 10 000 tons per day (Babatunde & Zhao, 2007; Dharmappa *et al.*,1997), while the Gauteng province of South Africa produces 550 tons per day, which is set to increase as the population of Gauteng grows (Van Rensburg & Morgenthal, 2003). European WTR production is forecasted to double in the next decade. For example; Ireland`s annual WTR production is projected to increase from 15,679 dry tons to 18,000 dry tons of WTR per year (Oh*et al.*, 2010; Zhao *et al.*, 2011). The UK alone produces more than 180 000 dry tons of WTR per year (Keeley, Jarvis & Judd, 2012). The increase in WTR production is also expected within sub-Saharan Africa, with one Water Treatment Plant (WTP) in Rwanda producing more than 450 dry tons per year (Uwimana *et al.*, 2010). Currently, China is the largest producer of WTR at 2.3 million tons per year (Ren *et al.*, 2020).

The financial cost of WTR disposal is also a significant point of concern, with the raw water quality and treatment processes amongst others acting as cost drivers. WTR disposal in the Netherlands cost between 37 - 50 million USD per year and 6.2 million USD per year in Australia (Ren *et al.*, 2020). The transport and landfilling of large quantities of WTR makes up a significant portion of the overall operating costs. In the United States of America the cost of landfilling one ton of WTR was an estimated 59.99 USD (R 910/ton) in 2010 (USEPA, 2011).

Although landfill of WTR is the preferred disposal method of recent years, the decrease in landfill capacity, stricter environmental laws, and the shift towards more environmentally conscious closed-loop waste management strategies has resulted in water purification plants looking for alternative disposal methods (Ackah *et al.*, 2018; Herselman, 2013; Oh *et al.*, 2010; Titshall & Hughes, 2005; Winkler, 2011).

One viable, cost-effective disposal alternative to landfilling is land application (Dassanayake *et al.*, 2015; Zhao *et al.*, 2020). Land application as a disposal mechanism for WTR is not a novel concept. It was proposed as an alternative disposal method in the 1970s, with renewed interest in the 1990s, driven by increased concerns of improper disposal mechanisms (Dempsey *et al.*, 1990; Oh *et al.*, 2010; Russell, 1975).

Land application is the process of mixing wastes into the upper strata of the plant system where microbial stabilisation, adsorption, immobilisation, selective adsorption and crop recovery leads to acceptable assimilation of waste, without adverse effects on soil quality or the environment (O'Connor *et al.*, 2004; Titshall & Hughes, 2005). The inherent non-hazardous, non-pathogenic nature of WTR makes it suitable for this method of disposal if the WTR is applied at an optimum rate (Babatunde & Zhao, 2007; Dassanayake *et al.*, 2015; Lucas *et al.*, 1994; Mahdy *et al.*, 2020; Trollip *et al.*, 2013).

The physiochemical character of WTR is strongly dependant on the water source, character and volume of the raw water, coagulant type, dosage and plant-specific operating conditions

(Ahmad *et al.,* 2016; Babatunde & Zhao, 2007; Dayton & Basta, 2001; Norris & Titshall, 2012; Trollip *et al.*, 2013; USEPA, 2011; Zhao *et al.*, 2011). This inherent variability makes it is essential to characterise the WTR and the soils of the potential land application area before deciding on disposal (Ackah *et al.*, 2018).

The method of residuals handling implemented by the WTP is dependent on the plant operating conditions and the availability of land (Gibbons & Gagnon, 2011). On-site WTR storage in storage ponds does not require any mechanical dewatering (Gibbons & Gagnon, 2011). Storage ponds are periodically cleaned, and the material is then transported to landfill. Alternatively, if no on-site storage is possible, the residual is mechanically dewatered with a press or centrifuge, after which it is directly transported to landfill (Gibbons & Gagnon, 2011).

Dried and crushed WTR resembles a fine-textured soil, depending on the processing methods; the physicochemical nature of the dried WTR makes it not only suitable for land application purposes but creates scope for use as soil amendment (Bayley *et al.*, 2008; Bugbee & Frink, 1985; Dayton & Basta, 2001; Elliott & Dempsey, 1991; Oh *et al.*, 2010; Ye *et al.*, 2001). Apart from the physical nature of the WTR, the chemical interaction with the soil environment should be carefully considered to ensure the WTR application suits the land application scenario.

Amending soil with WTR can introduce elements such as Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Ni, and Zn (Dassanayake *et al.*, 2015; Heil & Barbarick, 1989; Lucas *et al.*, 1994; Novak *et al.*, 2007; Trollip *et al.*, 2013; USEPA, 2011). The introduction of trace metals can be detrimental to the soil and can potentially be phytotoxic; thus, great care should be taken prior to land application. Apart from being a potential source of trace elements, the ability of WTR to sorb oxyanions such as phosphate is another major factor to consider before land application, adding WTR in high loadings can potentially limit the plant available phosphate, which is detrimental to plant growth (Bugbee & Frink, 1985; Dayton & Basta, 2001; Heil & Barbarick, 1989; Ippolito *et al.*, 2002; Kim *et al.*, 2002; Oh *et al.*, 2010; Rengasamy *et al.*, 1980; Skene *et al.*,1995).

For successful land application of WTR, both the soil and WTR should be characterised and studied beforehand, to ensure that the WTR amended soil system is not detrimental to the environment. Various studies suggest that a poor soil, with respect to its nutrient status and physical nature, is the most suitable candidate for WTR application (Clarke *et al.*, 2019; Park *et al.*, 2010; Titshall & Hughes, 2005). Furthermore, for a soil to be earmarked for land application of WTR, it should be economical and practical (Figure 1.1). For land application of WTR to be viable, the processing, transport and the land application cost of WTR should be comparable, or less than the current landfill waste management strategy currently implemented by the WTP. In addition to the economical aspect, the land application strategy should be practically feasible, with respect to WTR volume, potential co-application candidates and land application method.

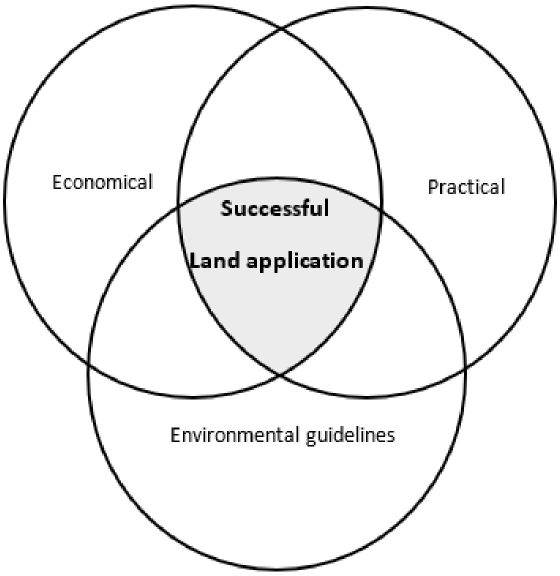

Figure 1.1 Venn diagram of successful WTR land application. The land application solution must be practical and economically feasible, whilst being beneficial to the new, man-altered environment.

The Cape Town metropolitan area, has all the components for viable land application of WTR; The sandy soil of the Cape Flats is nutrient-poor and has a low water-holding capacity, which is a severe limitation to vegetable crop yield in this area (Clarke *et al.*, 2019; Ghodrati *et al.*, 1995). Secondly, the proximity of this sandy soil to various water treatment plants makes it an ideal candidate for using the WTR residual in terms of land application (Figure 1.2). Finding alternative ways of disposing of material in a way that may be economically and environmentally beneficial is vital in moving towards a more sustainable future. One such strategy is to divert waste from landfill and turning it into agricultural potential. Disposing of WTR through land application is one such possibility. In-depth knowledge of the interaction between the waste and soil-plant system it is added to is critical for successful long-term disposal through land application.

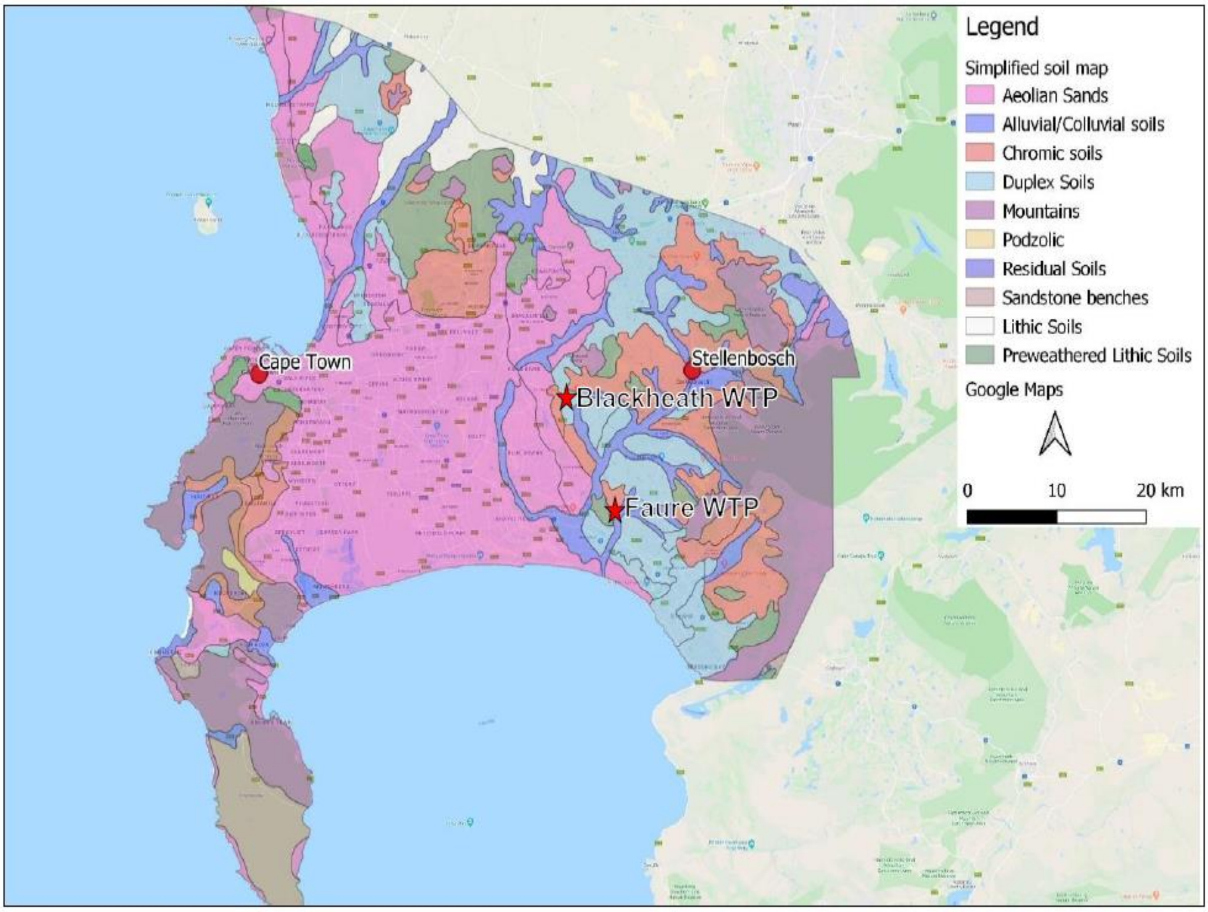

Figure 1.2 The location of two water treatments plants that provide potable drinking water to the greater Cape Town metropolitan area. The pink shades are surface covering of aeolian sand. Source Agricultural Research Council, Institute for Soil, Climate and Water (1976).

1.2 Aims and Objectives

This study aims to establish the risks and benefits of applying WTRs generated in the Cape Town metropolitan area to the surrounding sandy soils. In order to achieve this aim, the study is divided into four objectives:

1) Mineralogical and chemical characterisation of the WTR generated by two water treatment plants (Fe- and Al-based), the receiving soil and compost for potential co-application.

2) Determination of the soil-water interactions of a sandy soil at various application rates of Ferric-WTR (FeWTR), compost and WTR-compost co-application.

3) A greenhouse study investigating the potential risks and benefits of FeWTR and FeWTR-compost addition on Swiss Chard (*Beta vulgaris* cicla.) with respect to water and nutrient-induced stress.

4) To determine whether the trace element loading introduced by FeWTR to the soil can result in toxic levels within the soil and leaves of Swiss Chard tissue and whether they are safe for human consumption.

1.3 Thesis structure

This thesis consists of a further five chapters. Chapter 2 addresses the first objective of the study, which is the characterisation of WTR from two different WTPs, a commercially available compost that can be utilised as a possible co-amendment to the WTR and the sandy soil. Chapter 3 is focused on the second research objective, which investigates the soil-water interactions of a sandy soil amended with FeWTR, compost and a FeWTR-compost co-application. In Chapter 4, the third objective, which explores the effect of FeWTR and FeWTR-compost co-application on the growth of Swiss Chard in response to water and nutrient stress, is investigated. The fourth objective (Chapter 5), investigates the soil toxicity of FeWTR amended sand and the foliar trace element of Swiss Chard and whether it is safe for human consumption. The final chapter (Chapter 6) contains the general conclusions and further research recommendations.

CHAPTER 2. **MINERALOGICAL AND CHEMICAL CHARACTERISATION OF FERRIC-WTR, ALUM-WTR, SOIL AND COMPOST**

2.1 Introduction

Successful land application of waste requires an understanding of both the receiving soil and the waste. The properties of the waste and soil should be characterised and studied beforehand, to assess whether the waste amended soil system is detrimental to the environment, neutral or beneficial. Moreover, successful land application is critical for a more sustainable future and can provide a crucial stepping stone towards a more sustainable community, conscious of their environmental legacy. The waste, water treatment residual (WTR), generated by water treatment plants (WTP), is one such waste stream that can be diverted from landfill and used for land application.

Water treatment residual, an inevitable by-product of the drinking water purification process, has interested environmental scientists since the early 1970s (Russell, 1975). This material, which resembles coarse sand when crushed and dried, is inherently non-pathogenic and non-hazardous, which are critical factors to consider before land application (Dassanayake *et al.*, 2015; Lucas *et al.*, 1994; Trollip *et al.*, 2013; USEPA, 2011). However, the capacity of WTR to interact with oxyanions, enhance the cation exchange capacity (CEC) and buffer changes in pH, amongst others, are of key interest (Caporale, *et al.*, 2013; Kim *et al.*, 2002; Makris *et al.*, 2004; McKeague & Day, 1965; Novak & Watts, 2004; Park *et al.*, 2010; Titshall & Hughes, 2005; Wang *et al.*, 2011). Complete chemical characterisation will ensure that the WTR is not detrimental to the environment (Lucas *et al.*, 1994). Moreover, understanding how WTR will respond to drying, storage and ageing is also of critical importance (Agyin-Birikorang & O'Connor, 2009; Dempsey *et al.*, 1990; Wang *et al.*, 2015).

In order to maximise the amount of material disposed through land application without detrimental environmental effects, characterisation of the waste and receiving soil is critical. This chapter reviews some aspects of WTR from two different WTPs with respect to their chemical character, mineralogy and surface morphology to determine which WTR is best suited for plant growth promotion in the target receiving soil. Furthermore, the impact of the freeze-drying and air-drying on the crystallinity of the WTR will also be assessed. Sand from a potential land application site as well as commercial compost, which may be used as a potential co-application to the WTR, will also be characterised.

2.1.1 Chemical characterisation

The nature of WTR is strongly dependant on the water source, character and volume of the raw water, coagulant type, dosage and plant-specific operating conditions. (Ahmad *et al.*, 2016; Babatunde & Zhao, 2007; Dayton & Basta, 2001; Norris & Titshall, 2012; Titshall & Hughes, 2005; Trollip *et al.*, 2013; USEPA, 2011). This inherent variability makes it is essential to characterise the WTR of the WTP in question, comparing and contrasting it with published literature (Ackah *et al.*, 2018).

The pH of the resulting WTR will be dependent on the operating conditions of the plant (Ippolito *et al.*, 2011; Titshall & Hughes, 2005). Two temporally spaced samples from the Faure WTP had different pH values of 6.56 and 7.84 in KCl (Titshall & Hughes, 2005). Furthermore, differences in the coagulant type can also influence the pH, with Alum-WTR (AlWTR) having an average pH of 6.5 in comparison to 7.0 for a Ferric-WTR (FeWTR) (Ippolito *et al.*, 2011). Dayton *et al.* (2003) reported that the average pH of 21 AlWTR is 7.24. The point of zero charge (PZC), is the pH where a particle with amphoteric properties, such as metal hydroxides will have no net surface charge (McBride, 1994). The PZC for FeWTR is established at a pH of 7.5 and 6.85 for AlWTR (Castaldi *et al.*, 2015; Ociński *et al.*, 2016).

Similarly, the electrical conductivity (EC) will exhibit a wide range reflecting the water source, WTP operating conditions as well as chemical additions (Dayton *et al.*, 2003; Titshall & Hughes, 2005). The EC of 21 AlWTR samples ranged between 0.22 dS/m and 1.09 dS/m, well below the salinity threshold of 4.0 dS/m (Dayton *et al.*, 2003; McBride, 1994). Similarly, Ippolito *et al.* (2011) reported 1.6 dS/m for AlWTR and 0.2 dS/m for FeWTR. Two temporally spaced samples from the Faure WTP had different values of 0.16 and 0.4 dS/m, respectively (Titshall & Hughes, 2005).

The cation exchange capacity (CEC) of the WTR is a key factor in the ability to interact and absorb cations and trace metals. Castaldi *et al.* (2015) reported 61.98 $cmol_c$/kg and 55.45 $cmol_c$/kg for Fe- and AlWTR respectively. The CEC of 5 South African WTRs ranged from 15.85 to 35.79 $cmol_c$/kg, which is similar to the median value of 30 $cmol_c$/kg reported by Dayton and Basta (2001) (Titshall & Hughes, 2005). On average, the WTRs CEC is higher than a typical soil (3.5 - 35.6 $cmol_c$/kg) (Dayton & Basta, 2001). The addition of WTR to a sandy soil can therefore improve the CEC of the WTR amended soil system, which can have a major effect on how the soil interacts with the environment (Kim *et al.*, 2002; Park *et al.*, 2010). An increase in CEC can greatly enhance the capacity of a WTR amended soil to sorb and interact with nutrients and trace metals; however, other sorption dynamics are also involved, most notably the capacity of the metal oxides of the WTR to take part in ligand exchange (Warwick *et al.*, 1998).

2.1.1.1 WTR sorption mechanisms

The high phosphate fixation capacity of WTRs is one primary concern for potential land application (Bugbee & Frink, 1985; Elliott & Dempsey, 1991; Ippolito *et al.*, 2011; Norris & Titshall, 2012). Dayton and Basta (2005) reported that for 21 AlWTR samples, the mean maximum P sorption is 9.68 g/kg. This extraordinary capacity of WTR to sorb P can be detrimental or beneficial, depending on the land application scenario; Within constructed wetlands, the P sorption can be beneficial by reducing the P in runoff from agricultural lands, whilst the P absorption capacity of WTR may result in deficiencies in plants grown in a WTR amended soil (Ahmad *et al.*, 2016; Bugbee & Frink, 1985; Dayton & Basta, 2001; Heil & Barbarick, 1989; Ippolito *et al.*, 2002; Kim *et al.*, 2002; Lucas *et al.*, 1994; Oh *et al.*, 2010; Park *et al.*, 2010; Rengasamy *et al.*, 1980; Skene *et al.*, 1995). WTR can absorb various other oxyanions with similar chemical nature to that of phosphate, most notably is As and Pb (Finlay *et al.*, 2021; Gibbons & Gagnon, 2011; Ippolito *et al.*, 2011; Ren *et al.*, 2020; Shen *et al.*, 2019; Zhao *et al.*, 2020).

It is proposed that ligand exchange is the dominant short term P adsorption mechanism (Babatunde & Zhao, 2007; Makris *et al.*, 2004). The ligand exchange reaction occurs when P replaces functional groups on the surface of the WTR particles (Agyin-Birikorang & O'Connor, 2009; Babatunde & Zhao, 2007; Dassanayake *et al.*, 2015). The sorption of P to WTR is biphasic, with the first adsorption phase being a fast-forming, outer-sphere complex, followed by a slower adsorption inner-sphere complex, the latter may last for weeks until equilibrium is reached (Agyin-Birikorang & O'Connor, 2009; Evans & Smillie, 1976; Ippolito *et al.*, 2011; Makris *et al.*, 2006; Ociński *et al.*, 2016). Makris *et al.* (2004) proposed that P moves in a three-dimensional fashion toward the interior of the WTR particles rather than accumulating on the particle surface by precipitation. This P migration may block micropores, reducing the absorption capacity. However, more than one sorption mechanism can co-exist, such as inner-sphere or surface complexes (Arai & Sparks, 2001; Makris *et al.*, 2004, 2006).

Experiments have suggested that desorption of P was minimal for both Al- and FeWTR, reflecting the increased micropore energy potentials, due to pore geometry and the hysteric nature of the sorbed P as well as the stable nature of the inner-sphere complexes (Agyin-Birikorang & O'Connor, 2009; Makris *et al.*, 2004; Makris*et al.*, 2009). Micropore bound P will not be released under pH conditions in the range of 5 - 7 if the structural integrity of the WTR particle stays sound (Makris *et al.*, 2004). Incubation studies on artificially aged WTR suggest that P will remain fixed under field conditions for extended periods (Agyin-Birikorang & O'Connor, 2007). Makris *et al.* (2005) found that WTR with a limited capacity to sorb P may desorb the P easier.

The capacity of WTR to act as an adsorbent is partly dependant on the molar amount of the primary elements it contains WTR(Gibbons & Gagnon, 2011; Hou *et al.*, 2018; Makris *et al.*, 2004). Gibbons and Gagnon, (2011) found FeWTR to be a stronger absorbent of P than AlWTR, due to the higher molar concentration of the primary oxide. In contrast, Caporale *et al.* (2013) found AlWTR to be a better absorbent of arsenic than FeWTR, which was attributed to a higher degree of crystallinity of the latter. The nature of the oxides within WTR influences the absorption capability as crystalline oxides will adsorb less than amorphous oxides (Elliott *et al.*, 2002; Evans & Smillie, 1976). The capacity of a metal oxide to absorb oxyanions such as P is correlated with the amount of oxalate extractable Fe and Al; hence, the reactivity of WTR can be related to the amorphous oxide fraction rather than the total oxide content (Evans & Smillie, 1976; Makris *et al.*, 2005).

2.1.1.2 Ageing and drying

One of the main points of interest surrounding the use of WTR in various environmental roles is its capacity to sorb and control oxyanions, such as phosphate (Agyin-Birikorang & O'Connor, 2009). This sorption capacity is vital in determining how the WTR will be used; whether it is to control the mobility of oxyanions or in a land application scenario where the sorption capacity of WTR must be counterbalanced with the addition of fertiliser, compost or biosolids to prevent P deficiencies within plants. Therefore, determining whether the sorption capacity of WTR changes in response to dewatering and drying is key.

The amorphous metal-hydroxide that forms and acts as flocculation agent is deemed to be the main sorbent for oxyanions (Agyin-Birikorang & O'Connor, 2009). The amorphous Al or Fe that is oxalate- extractable is deemed to be the fraction of the total metal oxide that is the main contributing factor to the effectiveness of oxyanion sorption (Agyin-Birikorang & O'Connor, 2007; Dayton & Basta, 2005). The amount of oxalate extractable Al or Fe can be used as an indication of the capacity of WTR to act as a sink to oxyanions (Agyin-Birikorang & O'Connor, 2007; Dayton & Basta, 2005).

Agyin-Birikorang & O'Connor, (2009) determined the amount of 5 mM oxalate extractable Al in freshly generated AlWTR and that of a moisture-controlled incubation sample of the same WTR representing the 'aged' sample. The oxalate extractable Al showed a decrease with an increase in age, up to six months, after which the oxalate extractable Al was constant (Agyin-Birikorang & O'Connor, 2009). The metal mobility and toxicity of the WTR may decrease with increased storage period and drying (Agyin-Birikorang & O'Connor, 2009; Dempsey *et al.*, 1990; Gibbons & Gagnon, 2011; Wang *et al.*, 2015). Drying and storing for at least six months before using WTR for land application purposes is recommended (Agyin-Birikorang & O'Connor, 2009). The drying and ageing process increases the stability of organic phases within the WTR aggregate and reduces the bioavailability of associated metals (Agyin-Birikorang & O'Connor, 2009). Irrespective of age, WTR is classified as non-hazardous in the USA and can be used for land application (Agyin-Birikorang & O'Connor, 2009).

2.1.2 Mineralogical characterisation

The WTR particles consist of flocculated material from the raw water and the coagulants used. Various authors attributed the high sorption and immobilisation capacity of the material to its irregular structure with an extensive surface area and microporosity (Babatunde*et al.*, 2008; Gibbons & Gagnon, 2011; Kim *et al.*, 2002; Makris *et al.*, 2004; Morris *et al.*, 2009; Wai *et al.*, 2012; Wang *et al.*, 2011; Wang, *et al.*, in press).

Mineralogical characterisation, along with the chemical characterisation, will give a better understanding of how the physical nature of the WTR interacts and influences the chemical character.

2.1.2.1 Surface morphology

Scanning electron microscope (SEM) can be used to investigate the surface morphology of a material. SEM imaging of WTR show that the shape and surface morphology of both FeWTR and AlWTR is variable; with substantial variability in shape and surface roughness, ranging from smooth to rough (Babatunde *et al.*, 2008; Gibbons & Gagnon, 2011; Ippolito *et al.*, 2011; Kim *et al.*, 2002; Makris *et al.*, 2004; Morris *et al.*, 2009; Wai *et al.*, 2012; Wang *et al.*, 2011, 2015, in press). Two separate studies found that FeWTR exhibits more surface roughness and cracks than AlWTR under the same magnification (Gibbons & Gagnon, 2011; Makris *et al.*, 2004). The irregular shapes and surface morphology of WTR particles are attributed to the poorly crystalline, amorphous nature of the material which consists of coagulants and particles from the raw water (Ippolito *et al.*, 2011; Kim *et al.*, 2002; Makris *et al.*, 2004; Wang *et al.*, 2015).

2.1.2.2 Brunauer-Emmett-Teller specific surface area

A large specific surface area (SSA) allows for a greater surface area to absorb and immobilise various trace elements and macronutrients like phosphate (Arai & Sparks, 2001; Makris *et al.*, 2004, 2006). The porosity and surface area character of WTR may be the result of entrapment of air within the amorphous coagulating sludge during the flocculation process (Moodley *et al.*, 2004). Furthermore, it is hypothesised that organic components trapped within the pore network influence and regulate the diffusion of water and chemical substances (Makris *et al.*, 2005).

The Brunauer-Emmett-Teller specific surface area (BET-N_2 SSA) of the WTRs may be underestimated due to the amorphous nature and significant carbon content (Makris *et al.*, 2004). Ociński *et al.* (2016) obtained a BET-N_2 SSA of 120 m^2/g for a FeWTR, while Makris *et al.* (2005) reported an SSA of 100 m^2/g for AlWTR. Moreover, the adsorption of P within micropores can restrict solute movement since the ionic diameter of P is similar to that of some micropores (Makris *et al.*, 2004, 2005). The meso- and macropores will not be affected by P adsorption; however, the majority of pores in a WTR particle are micropores (Makris *et al.*, 2004, 2005).

2.1.2.3 XRD and FTIR analysis of WTR

X-ray diffraction analysis (XRD) can verify the presence of mineral phases as well as the degree of crystallinity (Ackah *et al.*, 2018; Ahmad *et al.*, 2016; Bai *et al.*, 2014; Finlay *et al.*, 2021; Ociński *et al.*, 2016; Tay *et al.*, 2017; Wang *et al.*, 2015). XRD analysis of both Fe- and AlWTR shows that the WTR contain amorphous metal hydroxides and crystalline hydroxides, the later being absent in some cases (Ackah *et al.*, 2018; Ahmad *et al.*, 2016; Bai *et al.*, 2014; Finlay *et al.*, 2021; Ociński *et al.*, 2016; Tay *et al.*, 2017; Wang *et al.*, 2015). A higher degree of crystallinity can decrease the capacity of WTR to absorb oxyanions (Finlay *et al.*, 2021; Hou *et al.*, 2018; Makris *et al.*, 2005). The XRD results can be used to compare and contrast WTR from different plants and ages with respect to their crystallinity and their mineral composition. Comparing rapid freeze-drying with air drying with respect to crystallinity will indicate whether the rate of drying effects the degree of crystallinity (Kondo & Domen, 2008). Similarly, Fourier transform infrared (FTIR) spectroscopy can be used to analyse the type of bonds and the degree of crystallinity of the WTR (Caporale *et al.*, 2013; Castaldi *et al.*, 2015; Jouraiphy *et al.*, 2005; Morris *et al.*, 2009; Ociński *et al.*, 2016; Wang *et al.*, in press).

2.2 <u>Materials and Methods</u>

2.2.1 Material background

2.2.1.1 Sand

The sandy soil used in this study forms part of the Cenozoic Sandveld Group sediments (Roberts *et al.*, 2006). This aeolian derived sandy soil covers an area of 620 km^2 around the Cape Town metropolitan area (Figure 1.2) (Adelana & Jovanovic, 2006; Adelana *et al.*, 2010). This low lying area covered by Cenozoic deposits is known as the Cape Flats, and the land use of this area varies considerably from residential and, industrial to agricultural (Adelana & Jovanovic, 2006). The sand is deposited by aeolian mechanisms, resulting in a well-sorted, poorly graded matrix (Hillel, 2004; Koster, 2009; Schloemann, 1994).

2.2.1.2 Compost

Reliance Compost Company, established in 2001, makes compost from green refuse originating from various sources (Reliance Compost, 2019). The fate of trace metals with regards to composting of green refuse with variable sources is extensive and unpredictable, and using more than one source also makes it difficult to trace back the origin of trace elements. Furthermore, associated volume reductions from the composting process also lead to higher concentrations of trace elements in the final product in comparison to the starting material (Brinton, 2000; Reliance Compost, 2019). Using compost produced from green refuse is not only an economic consideration but also utilises a resource created from a waste product, underpinning the shift towards a closed-loop economy where a potential waste is turned into a valuable resource.

2.2.1.3 FeWTR production by Faure WTP

Faure WTP was first operated in 1994. Faure WTP receives water from the Theewaterskloof and Steenbras dams. The plant uses $Fe_2(SO_4)_3$, lime, activated carbon (AC) and polyacrylamide within the water treatment process (Table 2.1). The plant uses mechanical means (centrifuge) to dewater the WTR before transporting it to the landfill site (Figure 2.1). Fe-based water treatment residuals are more suitable than Al-based residuals for mechanical dewatering due to Fe`s higher specific gravity (USEPA, 2011).

$Fe_2(SO_4)_3$ is the preferred flocculation agent due to the raw water from the Palmiet River having a high humic acid concentration; Fe^{3+} is more effective in removing humic substances than Al^{3+}(Edzwald, 1993).

2.2.1.4 AlWTR production by Blackheath WTP

Blackheath WTP started operations in 1983. Blackheath WTP receives water from the Theewaterskloof dam via the Kleinplaas levelling dam. $Al_2(SO_4)_3$, lime and AC is used within the water treatment process (Table 2.1). The AC is only added during summer months to control blue-green algal blooms. The WTRis pumped to on-site lagoons for long term storage and non-mechanical drying, which does not require the use of polyacrylamide (Figure 2.1). The WTR from the dams is landfilled every 3-5 years.

Table 2.1 Summary of the treatment process at Blackheath and Faure WTP

	Blackheath WTP	**Faure WTP**
Plant Influent source	Theewaterskloof dam	Theewaterskloof dam, Steenbras dam, Palmiet river system
Treatment Steps	Lime and activated carbon	Activated carbon, polyacrylamide and lime
Coagulant type	$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$
Residuals treatment	Non- mechanical dewatering	Centrifuge
Residuals handling	On-site pond storage (3-5 years) and landfilling	Direct landfilling

Table modified after Gibbons & Gagnon (2011)

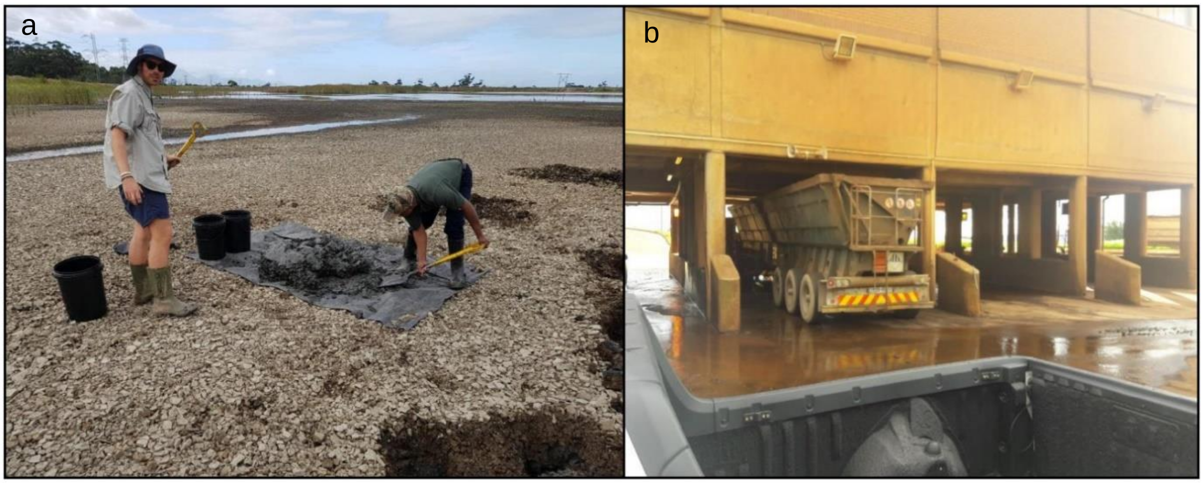

Figure 2.1 a) A storage pond of Blackheath WTR, b) direct collection of mechanically dewatered WTR produced by Faure WTP.

2.2.2 Collection and preparation

2.2.2.1 Sand

The sand was collected in March 2019 from Jacobsdal Farm, Kuilsrivier, South Africa (-33.967350 S,18.717388 E). The sample site is covered in sparse natural vegetation and has not been utilised in any agricultural capacity in the recent past. Only the top 30 cm of the soil was sampled. After collection, the sand was air-dried and mixed to homogeneity. The sand was sieved to a < 2 mm fraction and stored in a cool, dry room.

2.2.2.2 Compost

The compost from Reliance Compost is store-bought and used without any alteration. Two 30-litre bags were mixed to homogeneity and stored in a sealed bin.

2.2.2.3 Water treatment residuals

The WTR from Faure WTP was collected directly after mechanical dewatering of the WTR by means of a centrifuge. Two batches were collected in June 2018 and March 2019 (Figure 2.1). WTR collected from Faure WTP in 2018 will be referred to as FeWTR (2018) and the 2019 collected sample as FeWTR (2019). After collection of FeWTR (2019) a subsample of the wet WTR was freeze-dried, representing a fresh, unaged sample, after freeze-drying, the material was sieved to a < 2 mm fraction. The remaining FeWTR (2019) was allowed to air dry in a temperature-controlled (25 °C) room for one week. After the FeWTR (2019) was dried, the large aggregates were crushed and milled with a disk mill. The milled material was sieved to < 2 mm (Figure 2.2). Material (> 2 mm) was milled in multiple passes to achieve the required size. The sieved material was stored in a plastic container in a temperature-controlled environment. The FeWTR (2018) was air-dried and processed following the same procedure.

The WTR from Blackheath WTP was collected from one of the storage ponds (Figure 2.1). The exact age of the material is unknown. The material was collected in March 2019 (Figure 2.1). WTR collected from Blackheath WTP in 2019 will be referred to as AlWTR (2019). The material was collected at a distance from the side of the pond to get an undisturbed sample. The top 15 cm of the was not collected; the material of four sample sites was mixed to homogeneity on site prior to transport in sealed containers. After collection, a subsample of the wet AlWTR (2019) was freeze-dried, representing a fresh, unaged sample, after freeze-drying, the material was sieved to a < 2 mm fraction. The remaining AlWTR (2019) was allowed to air dry in a temperature-controlled room for one week. After the AlWTR (2019) was dried, the large aggregates were crushed and milled with a disk mill. The milled material was sieved to < 2 mm (Figure 2.2). Material (> 2 mm) was milled in multiple passes to achieve the required size. The sieved material was stored in a plastic container in a temperature-controlled environment.

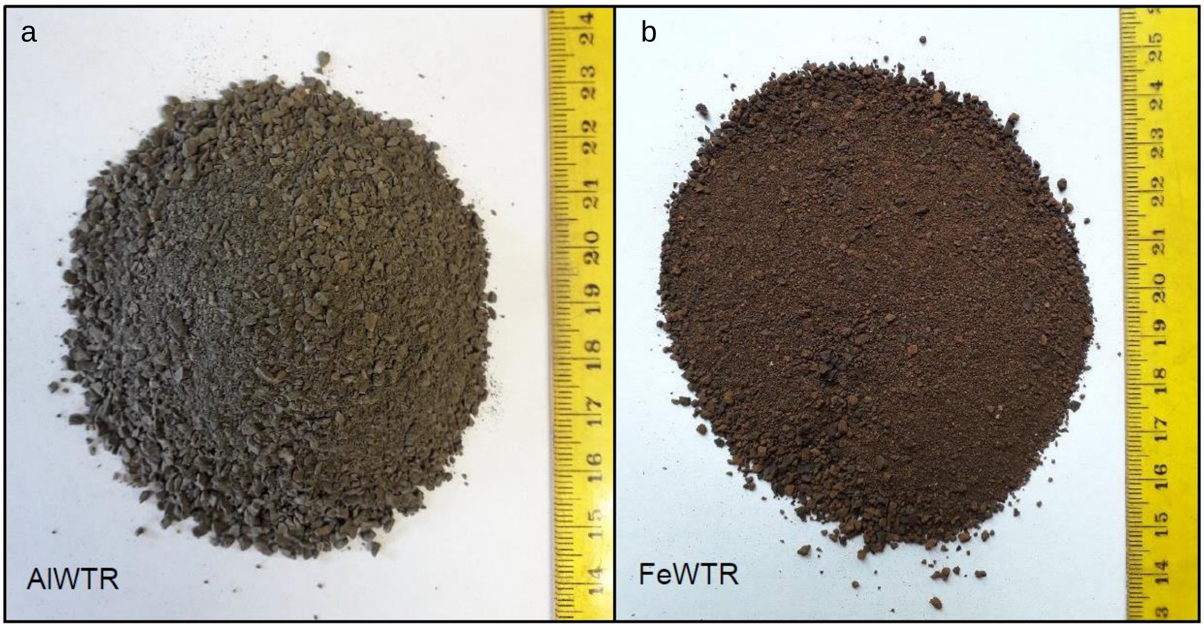

Figure 2.2 The WTR after air drying and milling to a < 2 mm size fraction. a) AlWTR from Blackheath WTP (left) dark greyish-brown (2.5Y 4/2). b) FeWTR from Faure WTP (right) dark reddish-brown (5YR 3/3).

2.2.3 Mineralogical characterisation

2.2.3.1 Brunauer-Emmett-Teller specific surface area

The Specific surface area (SSA) of the different WTR was measured with the BET-N_2 adsorption method using the Micrometrics 3Flex (version 4.00) Physisorption instrument at Department of Process Engineering, Stellenbosch University. BET-N_2 SSA was conducted on one air-dried and sieved WTR sample from Faure WTP- FeWTR (2018) and FeWTR (2019) and the Blackheath WTP- AlWTR (2019).

2.2.3.2 Scanning electron microscope (SEM)

The air-dried and sieved FeWTR (2018) and (2019) from Faure WTP and the AlWTR (2019) from Blackheath WTP, were studied under a scanning electron microscope (SEM). The Zeiss MERLIN SEM was used with energy-disperse X-ray spectroscopy (EDS) to determine the composition and relative distribution of elements on the surface of the material investigated. Samples were mounted on aluminium stubs with conductive double-sided carbon tape to ensure samples adhere to the stub. After mounting, the samples were dried at 70 °C for 24 h before being coated with an 8 nm gold coating to make the specimen conductive and emit secondary electrons.

2.2.3.3 X-ray diffraction (XRD)

Air-dried FeWTR (2018), (2019) and AlWTR (2019) as well as freeze-dried FeWTR (2019) and AlWTR (2019) were subjected to XRD analysis at iThemba labs, Cape Town. The measurements are performed using a multipurpose X-ray diffractometer D8-Advance from Bruker. Operated in a continuous ɵ - ɵ scan in locked coupled mode with Cu-Ka radiation.

The > 2 mm WTR samples were further ground by mortar and pestle after which it is mounted on a glass slide. The measurements run within a range in 2ɵ step size of 0.034°. A position sensitive detector, Lyn-Eye, is used to record diffraction data at a speed of 0.5 sec/step (iTHEMBALabs, 2019). All samples was measured with the same parameters.

Data are background subtracted so that the phase analysis is carried out for diffraction pattern with zero background after the selection of a set of possible elements from the periodic table. Phases are identified from the match of the calculated peaks with the measured ones until all phases have been identified within the limits of the resolution of the results (iTHEMBALabs, 2019).

2.2.3.4 Fourier transform infrared spectroscopy (FTIR)

Air-dried FeWTR (2018), (2019) and AlWTR (2019) as well as freeze-dried FeWTR (2019) and AlWTR (2019) were subjected to Fourier transform infrared (FTIR) spectroscopy. The (> 2 mm) WTR samples were analysed without any further processing. The Nicolet iS10 FTIR instrument (optimised for mid-infrared with a KBr detector) at the Department of Polymer Science, Stellenbosch University, were used. The WTR samples were analysed between 4000 and 500cm^{-1} with the DRIFT-FTIR technique. The measurements were corrected against the ambient background spectrum.

2.2.4 Chemical characterisation

2.2.4.1 pH and EC determination

The pH of the sand, compost and WTR samples was conducted in a 1:2.5 soil: solution ratio in a 1 M KCl with a Metrohm 827 pH meter (The Non-Affiliated Soil Analysis Work Committee, 1990). The electrical conductivity was measured in a 1:2.5 soil: solution ratio in 1 M KCl with a Jenway 4510 conductivity meter (Sonmez *et al.*, 2008). All measurements were performed in triplicate.

2.2.4.2 Elemental analysis

The total carbon and nitrogen of the samples were determined through dry combustion. The analysis was performed in triplicate on the sand, compost and air-dried FeWTR (2018), (2019) and AlWTR (2019) samples. Elements were extracted using Aqua Regia digestion by the Central Analytical Facility (CAF) of Stellenbosch University. The concentrations of the elements Al, Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Mo and Pb in the samples were determined through Inductively coupled plasma atomic emission spectroscopy (ICP-AES) utilising a Thermo ICap 6200 ICP-AES instrument.

2.2.4.3 Adsorption characteristics of phosphate

The adsorption of P to the WTR samples was conducted following the method of Bai *et al.* (2014). The initial P concentrations, P_o, (0, 25, 50,75, 100 mg/l) were prepared by dissolving predetermined amounts of KH_2PO_4 in a 0.01 mol/l KCl solution. The batch experiments were conducted on 1:100 soil: solution ratio of the different P_o solutions in a 50 ml falcon tube. The samples were shaken for 48 hours at 200 rpm to attain equilibrium after which samples were centrifuged at 3500 rpm for 5 minutes in a Zonkia SC-3612 low-speed centrifuge prior to filtration with a 45 µm syringe filter.

The P concentration was colorimetrically determined at 880nm with the molybdenum blue method using a Jenway 7315 spectrophotometer (Myers & Pierzynski, 2000). The amount of P adsorbed (P_{max}) was determined using the following equation:

$$P_{max} = \frac{(P_0 - P_e)V}{m}$$

Where the initial and final phosphate is indicated as P_o (mg/l) and P_e (mg/l), respectively, V (L) is the solution volume, and m (g) is the mass of the WTR.

2.2.4.4 Acid ammonium oxalate extraction

Acid ammonium oxalate extractable Mn, Fe and Al was determined on the WTR samples. Acidified (3.0 pH) ammonium oxalate (0.2 M) in a 1:100 soil: solution ratio was allowed to equilibrate in a 50 ml tinfoil covered falcon tube for four hours, shaken at 350 rpm to attain equilibrium after which samples were centrifuged at 3500 rpm for 5 minutes in a Zonkia SC-3612 low-speed centrifuge prior to filtration with a 45 µm syringe filter (AgroEcoLab, 2018; McKeague & Day, 1965). Fe, Mn and Al were measured with Atomic Absorption Spectrometry (AAS). The Acid ammonium oxalate method extracts very little of the crystalline Fe, Mn and Al, and will give a clear indication of the amount of Fe, Mn and Al held in amorphous phases (McKeague & Day, 1965).

2.2.4.5 Exchangeable cations (Ca, Mg, Na and K) and exchangeable acidity

The exchangeable cations (Ca, Mg, Na and K) of the sand, compost and WTR samples were extracted with ammonium acetate (NH_4OAc, pH = 7.0) in a 1:10 soil: solution ratio after which it was analysed using AAS (The Non-Affiliated Soil Analysis Work Committee, 1990). Exchangeable acidity was determined in a 1 M KCl solution by 0.01 M NaOH titration (The Non-Affiliated Soil Analysis Work Committee, 1990).

2.2.5 Grain size distribution

Soil organic matter (SOM) was removed from the sand sample with H_2O_2 prior to the determination of the grain size distribution. The sample was heated in a water bath to accelerate the reaction. The SOM % was determined to be the weight difference of the oven-dried sample before and after SOM removal by H_2O_2. The WTR was not subjected to SOM removal.

The particle size of the crushed and milled air-dried FeWTR (2018), AlWTR (2019) and sand was determined by passing ≈ 100 cm^3 of material through sieve ranges from > 2000; 2000 - 1000; 1000 - 500; 500 - 250; 250 - 125; 125 - 63 µm and < 63 µm. Particles < 63 µm and smaller was collected in the pan. Sieves and pan were mechanically shaken for 5 minutes. The weight of the material in the various sieves are recorded and tabulated. All samples were done in triplicate.

2.3 <u>Results and Discussion</u>

2.3.1 Grain size distribution

2.3.1.1 Sand

The grain size distribution is given in Table 2.2. The medium and fine sand fractions form more than 95% of the total composition, resulting in a well-sorted, poorly graded matrix (Table 2.2). The grain size distribution reflects the aeolian deposition mechanism (Hillel, 2004; Koster, 2009; Schloemann, 1994). The sand contains only 1.04% SOM. This low SOM content is consistent with aeolian deposited sands (Koster, 2009; Schloemann, 1994).

Table 2.2 Grain size distribution of the milled and crushed Ferric- WTR and Alum-WTR and the sandy soil

Wentworth size class	Size Range (µm)	Weight (%)		
		Sand	FeWTR (2018)	AlWTR (2019)
Granule	> 2000	0	1.29	3.06
Very coarse sand	2000 - 1000	0.05	37.3	42.02
Coarse sand	1000 - 500	0.11	21.02	22.06
Medium sand	500 - 250	36.88	21.26	16.08
Fine sand	250 - 125	61.87	15.88	14.48
Very fine sand	125 - 63	0.85	3.16	2.17
Fines (silt and clay)	< 63	0.24	0.09	0.13

2.3.1.2 Water treatment residuals

The WTR grains are angular with irregular shapes, reflecting the crushing and milling process (Figure 2.2). The size distribution of both the FeWTR (2018) and AlWTR (2019) is heterogeneous, poorly sorted and well-graded, with the very coarse sand fraction dominant (Table 2.2).

The size range of the WTR is not a true reflection of the actual mineral grain sizes within the WTR but rather that of the stable aggregates after crushing (Table 2.2) (Ackah *et al.*, 2018; Ippolito *et al.*, 2011). The particle size range of dried and crushed WTR varies considerably throughout the literature. It is to some degree dependant on the amount and type of sediment from the raw water. The crushed size range represented in Table 2.2, is therefore for this specific batch and a result of the interaction between the WTR and the crushing and milling process (Dassanayake *et al.*, 2015; Kim *et al.*, 2002; Oh *et al.*, 2010; Park *et al.*, 2010; Titshall & Hughes, 2005, 2009). Moreover, decreasing the particle size may significantly increase the ability of the WTR to interact and absorb phosphate and trace elements (Caporale *et al.*, 2013; Dayton & Basta, 2005).

The procedures taken to prepare WTR for potential land application, like milling can result in variations in grain size, which can influence how the WTR interacts with the soil environment. However, the residuals handling by the WTP will determine some inherent properties of the WTR.

The residuals handling can introduce a large variability to the WTR. The direct collection, as in the case of Faure WTR, limits the inherent variability to the raw water quality and the type and quantity of chemicals used in the treatment process. The material and trace elements within the WTR can originate from two possible sources; the raw water from the catchment or the chemicals used to treat the water.

The pond storage of the Blackheath WTR for extended periods creates additional variability (Figure 2.1). The pond can be seen as a closed lacustrine system that interacts with the environment (Figure 2.1). The ponds are lined with reeds which attract birds, while the lack of proper fencing results in free-roaming livestock from a nearby village. Aeolian derived sediments also enter the storage pond. Cyclic addition of new WTR, as well as wetting and drying can also affect the final WTR -product that is collected after the 3 to 5-year storage period.

The method of residuals handling implemented by Faure WTP is more suitable for land application than that of Blackheath. The direct collection of smaller batches makes it easier to characterise, monitor and control the inherent chemical nature of the WTR, which is essential for successful land application.

2.3.2 Mineralogical characterisation

2.3.2.1 Surface morphology

Figure 2.3 shows the air-dried FeWTR (2019) and AlWTR (2019). The SEM images show similar morphology for both FeWTR (2019) and AlWTR (2019) particles. Both WTRs show irregular shapes and sizes with smaller particles on to the surface of larger particles. The lack of distinct shapes and structures may be attributed to the flocculation and coagulation of WTR out of suspension, forming an shapeless material (Ippolito *et al.*, 2011). The AlWTR (2019) has a more irregular surface morphology than the FeWTR (2019) (Figure 2.3). The surface

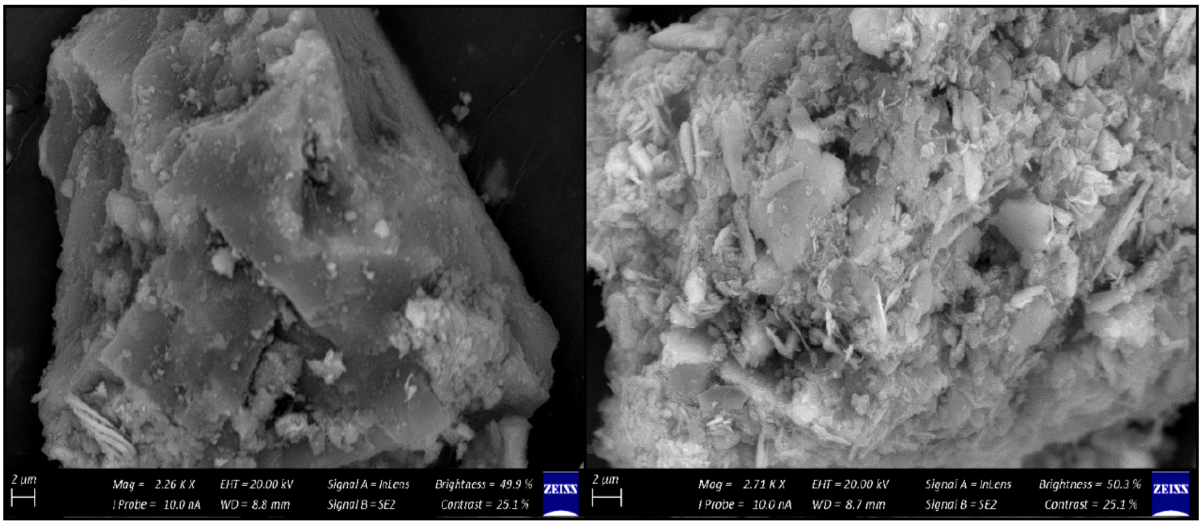

Figure 2.3 a) SEM image of FeWTR (2019) from Faure WTP, b) SEM image of AlWTR (2019) from Blackheath WTP.

morphology of AlWTR (2019) show irregular platy structures with no preferred orientation, shape or size. In contrast, the FeWTR (2019) has fewer small particles on to the surface of the larger particles, which exhibit an irregular shape and irregular surface topography. The platy structures observed in Figure 2.3 may be flocculated clay particles from the raw water.

In contrast to the findings of Gibbons & Gagnon (2011), who found FeWTR sludge to be more amorphous with more surface roughness, the SEM images show that the AlWTR has more variable surface topography over the FeWTR (Figure 2.3). The difference in observed surface roughness may be influenced by the treatment process rather than the primary flocculation agent. The AlWTR investigated by Gibbons & Gagnon (2011) was dewatered with mechanical mechanisms, while the FeWTR was without mechanical aids. In this study, the FeWTR (2019) derived from Faure was subjected to mechanical dewatering by centrifuge while the AlWTR (2019) from Blackheath was dewatered without mechanical aid. The mechanically dewatered FeWTR (2019) showed less morphology than the passively dewatered AlWTR (2019) (Figure 2.3). Thus, the effect of the dewatering mechanism, storage methods, must be considered along with the amount of coagulant and raw water quality.

The EDS results show the relative composition of the major elements from the ablated surface. Complete EDS results are presented in Appendix 2.3.2, ablation spots are chosen to give a representation of the whole sample. The metal sulfate salt used by the two WTPs is reflected in the mineral composition of the WTR. The WTR from Faure, which uses an iron sulfate salt, is dominant in Fe over Al in the composition, while the WTR from Blackheath, which utilises aluminium sulfate is dominant in Al over Fe. In all the WTRs carbon is present in significant proportions, since both plants use AC during the treatment process. The C % of the AlWTR (2019) is much higher than that of the FeWTR (2018), (2019). The two samples from Faure, separated by a year in collection dates, differ significantly in composition; with FeWTR (2018) containing notably more Ca and Mn, while FeWTR (2019) contains more Fe (Table A 2.3.2.3 and Table 2.3.2.6). The variability in composition reflects the variability introduced by the raw water quality and the amount of treatment chemicals used in response to water quality (Ahmad *et al.*, 2016; Babatunde & Zhao, 2007; Dayton & Basta, 2001; Norris & Titshall, 2012; Titshall & Hughes, 2005; Trollip *et al.*, 2013; Zhao *et al.*, 2011).

The presence of higher concentrations of Mn and Ca in the 2018 Faure sample probably reflects a higher dosage of lime for that particular time period. The introduction of Mn into the WTR through the lime used was also noted by Titshall & Hughes, (2005) and Trollip *et al.* (2013). Mn phytotoxicity in WTR amended soil systems can have a negative environmental impact and should be monitored closely (Novak *et al.*, 2007).

2.3.2.2 Specific Surface Area

The BET specific surface area (SSA) is shown in Table 2.3. The SSA of the AlWTR (2019) is the highest followed by FeWTR (2019) and FeWTR (2018). Various authors note the significant SSA of WTR (Bai *et al.*, 2014; Caporale *et al.*, 2013; Makris *et al.*, 2004, 2005; Ociński *et al.*, 2016; Wai *et al.*, 2012). The high SSA indicates that the material has an extensive network of micropores and an irregular surface morphology. The higher SSA of the AlWTR (2019) in comparison to FeWTR (2019) is also exhibited in the SEM images (Figure 2.3). Similar to these, Caporale *et al.* (2013) found AlWTR to have a greater SSA than FeWTR, 312.8 m^2/g and 80.3 m^2/g, respectively, these variations in SSA may be related to the total carbon content.

The SSA of WTRs is attributed to the amorphous nature of the metal oxides used in the flocculation process as well as the AC used in the treatment process (Bai *et al.*, 2014; Caporale *et al.*, 2013; Kaiser & Guggenberger, 2003; Makris *et al.*, 2004). Activated carbon has an extensive heterogeneous micropore structure with a large specific surface area, and the presence of AC significantly increases the specific surface area of metal oxides (Li, Quinlivan & Knappe, 2002; Schwickardi *et al.*, 2002). The AC within the structure prevents the formation of more crystalline structures, attributing to the formation of an amorphous metal oxide, and ultimately an increased SSA (Schwertmann, 1966; Schwickardi *et al.*, 2002). Re-arrangement of the atoms or molecules to a crystalline form under ambient pressure and temperature, in the presence of organic matter, is unlikely (Kondo & Domen, 2008; Schwertmann, 1966). The SSA of WTR allows for a large surface area to absorb and immobilise various trace metals and macronutrients like phosphate. Furthermore, the extensive micropore network may play a role in water retention.

Table 2.3 Specific surface area (BET-SSA) (m^2/g) of different air-dried WTR samples

Sample	WTP	Primary coagulant	Specific surface area (m^2/g)
FeWTR (2018)	Faure	Iron sulfate	84.82
FeWTR (2019)	Faure	Iron sulfate	110.17
AlWTR (2019)	Blackheath	Aluminium sulfate	144.13

2.3.2.3 X-ray diffraction (XRD)

The XRD results of the five samples showed sharp peaks well defined peaks separated by low crystalline intensities (Figure 2.4, Figure 2.5). The XRD results indicate that both poorly crystalline phases and crystalline phases are present in the WTR, with the crystalline phases most likely derived from the raw water sediment (Figure 2.4, Figure 2.5) (Ackah *et al.*, 2018; Ahmad *et al.*, 2016; Bai *et al.*, 2014; Finlay *et al.*, 2021; Ociński *et al.*, 2016; Tay *et al.*, 2017; Titshall & Hughes, 2005; Wang *et al.*, 2015). The stronger quartz peaks in the AlWTR sample may also be of aeolian derived sand that was blown into the storage pond (Figure 2.1). The XRD pattern of the WTR sludge derived from two different WTP plants, Blackheath and Faure, differ from each other, with the FeWTR samples having a lower overall intensity Figure 2.4, Figure 2.5). Freeze drying did not result in any changes in crystallinity for both AlWTR and FeWTR samples; similarly, Wang *et al.* (2015) and Ahmad *et al.* (2016) found no changes in the degree of crystallinity between fresh and air-dried WTR.

The XRD verified the presence of quartz, kaolinite, muscovite and feldspar. These minerals are derived from the raw water suspended sediments, and the minerals are consistent with the geology of the drainage areas that feed both WTPs (Tamm & Johnson, 2006). However, the poorly crystalline phases show different patterns, which can be attributed to the two WTP using two different metal salts for flocculation. Faure being iron-based and Blackheath being aluminium based. The differences in XRD patterns from different plants are also reported by Hou *et al.* (2018).

The AlWTR derived from the Blackheath WTP did not show any identifiable crystalline aluminium $Al(OH)_3$ phases. The lack of any crystalline aluminium in AlWTR was also reported by Ackah *et al.* (2018), Ahmad *et al.* (2016), Hou *et al.* (2018) and Ippolito *et al.* (2011).

All three FeWTR samples from Faure WTP contain goethite FeO(OH). Finlay *et al.* (2021) also noted that FeWTR contains some crystalline phases derived from the iron-oxyhydroxide precipitate. However, the vast majority of the Fe is held in poorly crystalline phases, such as ferrihydrite and feroxyhyte (Finlay *et al.*, 2021; Ociński *et al.*, 2016; Wai *et al.*, 2012). The SEM EDS elemental composition indicates that Fe makes up a large portion of the elemental composition, furthermore Fe is not a major element within any of the XRD identified crystalline phases, suggesting that the majority of the Fe is held in poorly crystalline, amorphous phases.

Samples taken from the Faure WTP in 2018 and 2019 differ slightly. The FeWTR (2018) sample contains a peak indicating the presence of calcite while it is absent from FeWTR (2019). The differences between FeWTR (2018) and FeWTR (2019) are due to changes in the chemical additions during the water treatment process, with the FeWTR (2018) sample containing unreacted lime from the water purification process (Figure 2.5). The presence of calcite in WTR were also reported by Ippolito *et al.* (2011).

The XRD pattern reflects both the raw water source and the added chemicals during the water treatment (Figure 2.4, Figure 2.5). The material inherited from the raw water will have a crystalline nature, defined by clearly identifiable peaks. These minerals will always be present-as long as the same raw water source is used. The poorly crystalline phases within WTR, will to some extent be dependent on the WTP specific conditions. Different WTPs will result in different XRD patterns due to the utilisation of different flocculation agents and differences in plant operation. Furthermore, the same plant can result in changes in the XRD patterns due to changes in added chemicals, in response to water quality changes, as seen with the differences in the 2018 and 2019 Faure WTR samples.

Both FeWTR and AlWTR holds most of its Al or Fe derived from the treatment process chemicals in poorly crystalline phases (Figure 2.4, Figure 2.5). However, the AlWTR had no crystalline Al phases like gibbsite $Al(OH)_3$ present, while the FeWTR contains some crystalline Fe in the form of goethite, which is similar to the findings of Ackah *et al.* (2018), Ahmad *et al.* 2016), Finlay *et al.*(2021), Hou *et al.* (2018), Ippolito *et al.*(2011), Ociński *et al.* (2016) and Wai *et al.* (2012). The SEM imaging of the FeWTR showed less surface roughness in comparison to the AlWTR; furthermore, the BET-SSA of the FeWTR was lower than that of the AlWTR (Table 2.3). This may be due to the presence of crystalline phases derived from the water treatment process which can reduce and influence the BET-SSA, as well as surface morphology as observed through SEM imaging. The SEM-EDS data show that the AlWTR contains a more significant proportion of carbon than the FeWTR, AC plays a crucial role in the crystallinity of metal oxides, and the higher proportion of carbon in the AlWTR may completely prohibit the formation of crystalline phases. The primary flocculation agent may not the only contributing factor, dosage, raw water quality and the method of dewatering can also influence the aforementioned factors.

The lack of any change between the fresh (freeze-dried) and air-dried WTR with respect to crystallinity, as indicated by the XRD patterns (Figure 2.4, Figure 2.5), may be attributed to the complex nature of the WTR, which contains a large range of materials (Bolanz *et al.*, 2013; Hou *et al.*, 2018; Schwertmann, 1966; Wang *et al.*, 2015). Furthermore, recrystallization requires an input of energy to rearrange the crystal lattice, which is unlikely with a soil environment (Kondo & Domen, 2008). The presence of crystalline phases can have enormous effects on the ability of WTR to absorb anions (Finlay *et al.*, 2021). However, freeze-drying or air drying over a more extended period does not affect the degree of crystallinity.

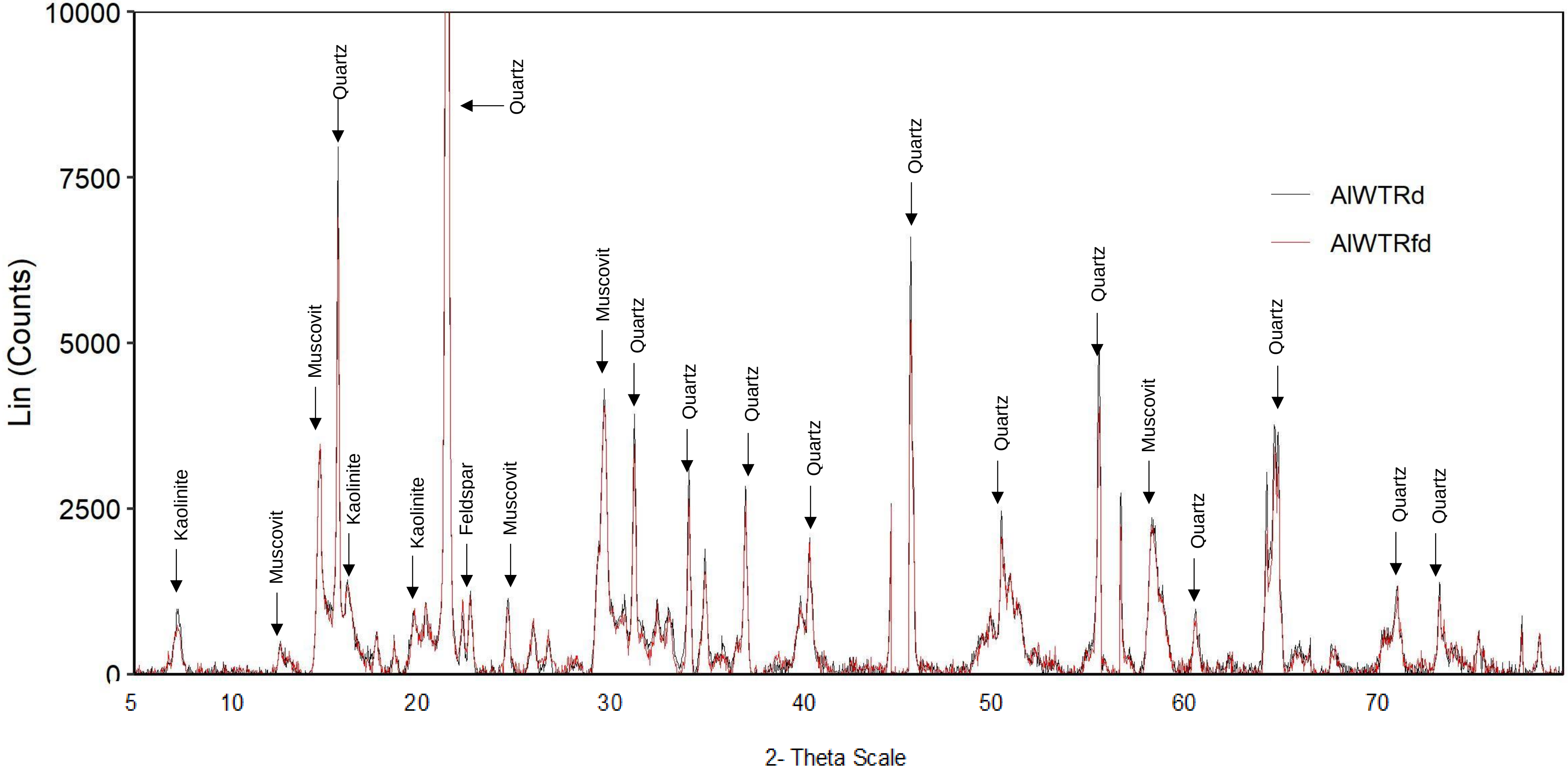

Figure 2.4 XRD graph of the AlWTR collected from Blackheath WTP, the freeze-dried (AlWTRfd) and air-dried (AlWTRd) samples show no differences in the XRD pattern.

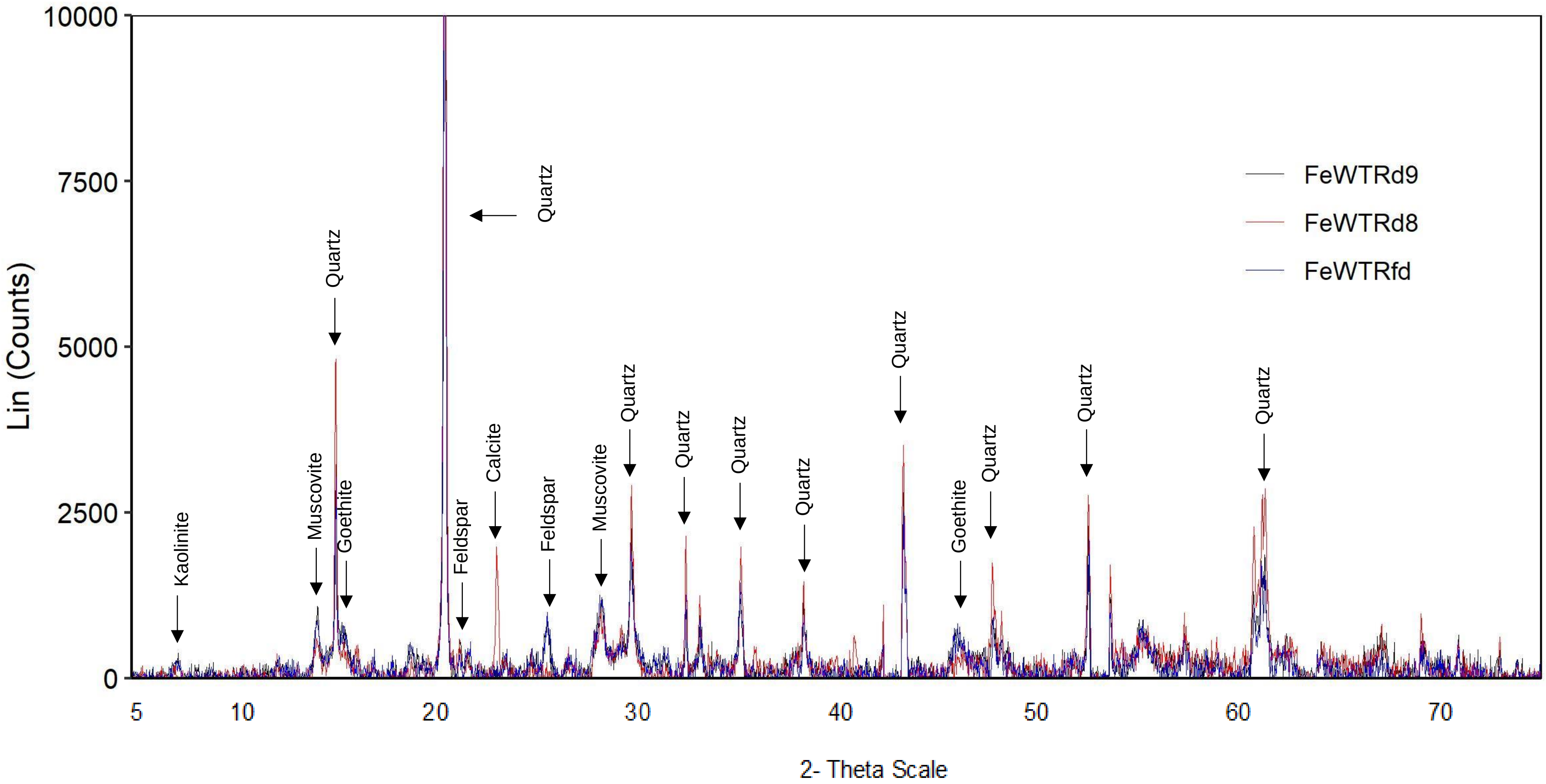

Figure 2.5 XRD graph of the FeWTR collected from Faure WTP in 2019 shows no difference in XRD pattern between the freeze-dried (FeWTRfd) and air-dried (FeWTRd9), FeWTRd8, show slight differences in the XRD pattern.

2.3.2.4 Fourier transform infrared spectroscopy (FTIR)

The poorly crystalline nature of WTR and the presence of inorganic and organic substances results in the superposition and masking of various FTIR peaks, making clear identification of peaks difficult (Caporale *et al.*, 2013; Castaldi *et al.*, 2015; Jouraiphy *et al.*, 2005; Morris *et al.*, 2009; Ociński *et al.*, 2016; Wang *et al.*, in press). The FeWTR (2018 and 2019) and AlWTR (2019) show peaks in the same ranges with varying intensity; the effect of freeze-drying of the WTR did not result in any shift in the peaks (Figure 2.6).

Peaks at 3615 cm^{-1} and 3640 cm^{-1} indicate hydroxyl groups. These hydroxyl groups may be associated with kaolinite (Saikia & Parthasarathy, 2010). The hydroxyl groups (~ 3620 cm^{-1}) were also observed in AlWTR analysed by Wang *et al.* (2020) (Figure 2.6). A broad peak at 3217 cm^{-1}, associated with O-H stretching vibrations of surface water molecules on the WTR particles is present in all the analysed samples (Figure 2.6) (Ociński *et al.*, 2016; Wang *et al.*, in press). The intensity of the broad peak associated with surface water molecules is lower in certain samples, which may indicate less surface water molecules (Figure 2.6). Two broad peaks at 1565 cm^{-1} and 1393 cm^{-1} can be associated with the asymmetrical stretching of C=O carbonate groups (Figure 2.6) (Castaldi *et al.*, 2015; Jouraiphy *et al.*, 2005; Wang, Wang, Lin, *et al.*, 2012). The carbonate groups can either be from the added AC, lime or the organic matter from the raw water. The peaks associated with the carbonate groups are more pronounced for the FeWTR samples. The Faure WTP treats water from the Palmiet River as well, which is high in humic compounds (Figure 2.6), (Table 2.1).

The peaks at 1025 cm^{-1} and 912 cm^{-1} are associated with the bending of Fe(Al)-O molecules while bending of the same molecule results in a peak at 750 cm^{-1}. However, the identification of Fe-O and Al-O related bands in the lower spectra can be problematic due to a high degree of overlapping and the possibility of it rather being a result of Mn-O (Castaldi *et al.*, 2015; Ociński *et al.*, 2016). The strong peak at 1000 cm^{-1} is associated with quartz (Figure 2.6) (Castaldi *et al.*, 2015; Ociński *et al.*, 2016). A small peak at 860 cm^{-1} may be associated with calcite (Jouraiphy *et al.*, 2005). The peak at 777 cm^{-1} can be associated with Si-O-Al compounded vibrations, characteristic of feldspar (Ghale *et al.*, 2019). However, Wang *et al.* (2012), associated a peak at 780 cm^{-1} in FeWTR with the oxalate functional group, which can bind various trace metals as well as phosphate (Kim *et al.*, 2013).

The peak of certain spectra can shift and vary in intensity due to the presence of other bond interactions with trace elements and phosphates (Castaldi *et al.*, 2015; Li *et al.*, 2019). The presence of trace metals can also alter and prohibit the formation of more crystalline phases by occupying positions which prohibit the formation of more crystalline variants of the oxides;

furthermore, changes in pH can alter the speciation, bonds and co-existence between various oxides and metals (Arai & Sparks, 2001; Bolanz *et al.*, 2013). The FTIR shows the added chemicals of the water treatment process and the raw water. Quartz, kaolinite and feldspar originated from the raw water sediments.

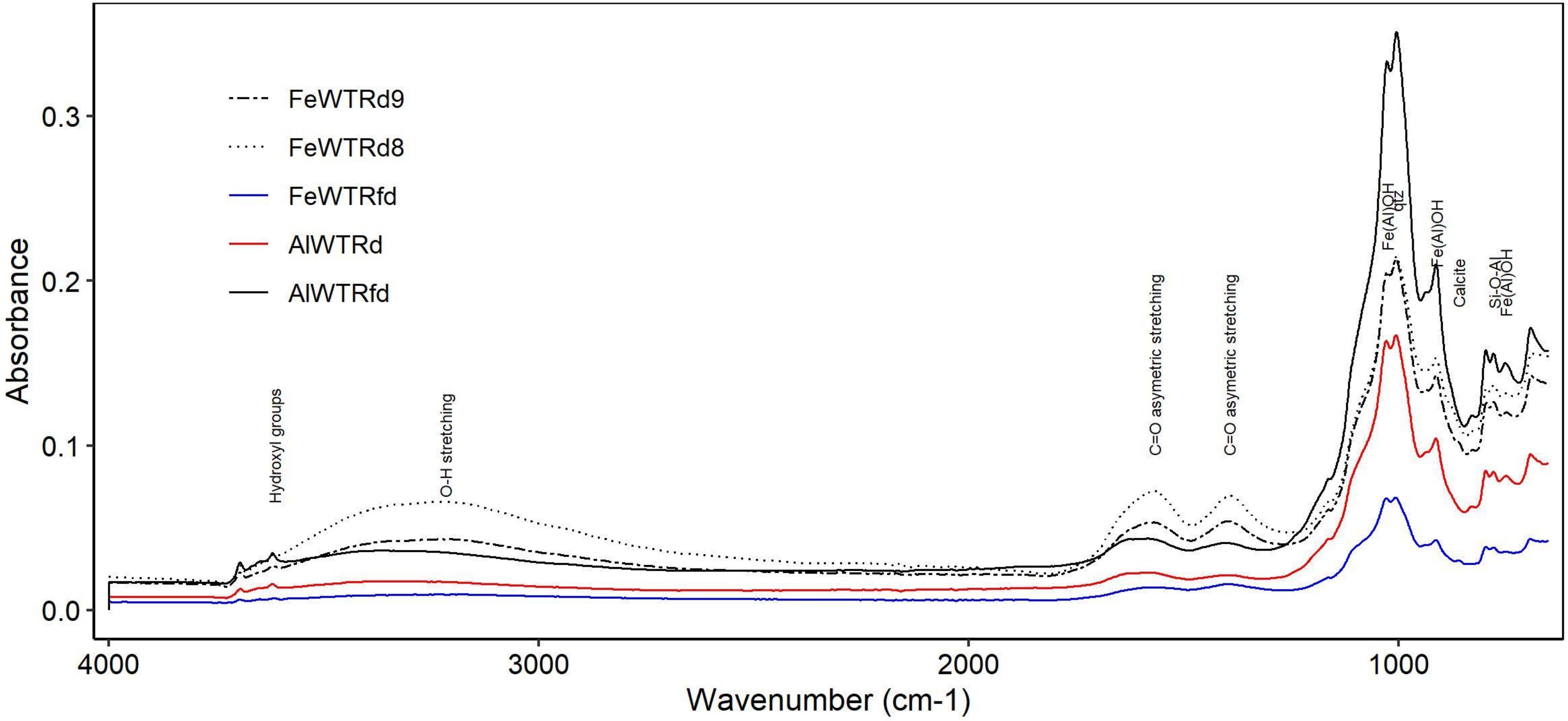

Figure 2.6 The FTIR spectra of the WTR from Blackheath and Faure WTP. The freeze-dried (AlWTRfd) and air-dried (AlWTRd) samples show no shifts in the FTIR pattern. Similarly, the freeze-dried (FeWTRfd) and air-dried (FeWTRd9), and the sample collected a year prior FeWTRd8 show slight differences in peak intensity, but no shifts within the spectra.

2.3.3 Chemical characterisation

The chemical characterisation results are given in Table 2.4. The pH of the samples collected from Faure WTP show an almost two-unit difference (Table 2.4). The FeWTR (2018) sample correlates well with the ranges of Titshall & Hughes (2005), while FeWTR (2019) sample falls below this range at 4.7, which is similar to the lowest pH reported by Norris and Titshall (2012). The pH of AlWTR (2019) from Blackheath WTP falls within established ranges (Castaldi *et al.*, 2015; Dayton *et al.*, 2003; Ippolito *et al.*, 2011; McBride, 1994; Ociński *et al.*, 2016).

The EC of the WTR samples conforms to the low EC values reported by previous studies (Dayton *et al.*, 2003; Ippolito *et al.*, 2011; Titshall & Hughes, 2005). The two temporally spaced samples from Faure show some variation, which is consistent with Titshall & Hughes (2005).

The average C % of the WTR samples are in excess of 10%, while the average N % is less than 1%, resulting in a C/N ratio exceeding 20/1 (Table 2.4). The high carbon content is a result of the AC that is added during the water treatment process (Table 2.1) (Bai *et al.*, 2014; Kaiser & Guggenberger, 2003; Makris *et al.*, 2004). The low N % results from a water source relatively unaffected by nitrogen fertiliser pollution. The C/N ratio will affect the rate of nitrogen mineralisation. At a C/N ratio higher than 20, the rate of immobilisation of N is high, and competition between plants and microorganisms can result in nitrogen deficiencies (Bengtsson *et al.*, 2003). The WTR samples have a C/N ratio greater than 20 and would result in the nett immobilisation of the limited available N, the C/N ratios concur with the WTR C/N ratios reported by Kerr (2018). Despite a C/N ratio that will promote N mobilization the total N% of the compost falls below the 1% threshold recommended in composts intended for fertiliser use (Table 2.4) (Baker, 1997; Bengtsson *et al.*, 2003).

The CEC of the WTR samples showed a wide range of 5.94 - 90.40 ($cmol_c$/kg) (Table 2.1). These values correlate well with Castaldi *et al.* (2015), Dayton & Basta (2001) and Titshall & Hughes (2005). However, the amount of exchangeable Ca^{2+} for the FeWTR samples may be an overestimation due to the addition of lime in the water treatment process, which may result in free lime within the WTR. The greater amount of Ca^{2+} within FeWTR (2018) may also explain the higher pH obtained (Table 2.1). The ammonium acetate extraction method may also have resulted in the high Ca^{2+} extraction. Adding any amount of WTR to the sandy soil will increase the CEC of the soil (Table 2.1). This increase in CEC can significantly enhance the ability of the soil to sorb and interact with nutrients, and trace metals. However, other sorption dynamics are also involved, most notably the capacity of the metal oxides of the WTR to take part in ligand exchange (Warwick *et al.*, 1998). The CEC of the soil will increase with WTR loading (Rosalina*et al.*, 2019).

Table 2.4 Chemical properties of the WTRs, sandy soil and compost of air-dried samples

Parameter	Sand	FeWTR (2018)	FeWTR (2019)	AlWTR (2019)	Compost
pH KCl	4.3	6.6	4.7	6.1	7.5
EC (dS/m)	0.01	0.80	0.35	0.24	5.8
N (%)	0.03	0.41	0.5	0.55	0.54
C (%)	0.46	9.08	11.35	14.13	8.46
C/N	17	22	23	26	16
Fe_{ox} (g/kg)	nd	176.30	210.64	9.92	nd
Al_{ox} (g/kg)	nd	2.80	3.64	32.02	nd
Mn_{ox} (g/kg)	nd	0.72	0.42	0.18	nd
Crystallinity index[a]	nd	0.89	nd	0.29	nd
P_{max} (mg/g)	nd	5.83	12.62	12.01	nd
K ($cmol_c$/kg)	< 0.001	0.027	< 0.001	< 0.001	4.787
Na ($cmol_c$/kg)	0.028	0.433	0.256	0.298	4.185
Ca ($cmol_c$/kg)	0.551	85.585	23.044	5.041	35.130
Mg ($cmol_c$/kg)	0.264	4.209	1.852	0.494	6.085
Acidity ($cmol_c$/kg)	0.133	0.150	0.200	0.108	0.083
CEC ($cmol_c$/kg)	0.977	90.404	25.352	5.940	50.271

[a] crystallinity index calculated as: Fe_{ox}/Fe_{total} and Al_{ox}/Al_{total}

nd: Not determined

The sand is almost devoid of any trace elements (Table 2.5). The primary component of soils derived from the Sandveld Group is quartz, which has limited capacity to absorb or to supply nutrients and trace elements, and the association of trace elements might be to the organic matter rather than the mineral sand grains (Herselman, 2007; Koster, 2009; Schloemann, 1994). The sandy soil is acidic, with a pH of 4.3 (Table 2.4). The soil acidity may be due to the low buffering capacity of the quartz dominant sand. The CEC of the sand is also low due to the limited sorption capacity of the sand; the majority of the basic cations are lost through leaching (Rosalina *et al.*, 2019). In contrast to the low salinity of the sand, the compost (5.8 dS/m) exceeds the salinity threshold of 4.0 dS/m (Table 2.4). The CEC of the compost is 50.271 ($cmol_c$/kg), with Ca^{2+} being the dominant cation. The pH of the compost is 7.5 (Table 2.4).

Both the FeWTR and AlWTR contain Al, Fe, Cr, Mn, Co, Ni, Cu, Zn, As, and Pb (Table 2.5). The amount of Fe or Al within the WTR is dependent on the metal sulfate salt used by the WTP. Faure WTP uses an iron sulfate salt, while Blackheath WTP uses an aluminium sulfate. The Al-based coagulants are more effective in removing particulates from suspension and require a lower dosage than an Fe-based coagulant to remove the same amount of material from suspension (Kerr, 2018). This difference in effectiveness is also observed in the amount of primary flocculant within the FeWTR from Faure and AlWTR from Blackheath (Table 2.1, Table 2.4, Table 2.5).

AlWTR exceeds the Al concentration range for typical soils while FeWTR exceeds the range for Fe (Table 2.5) (Herselman, 2013). Furthermore, both WTRs exceeds the Total Maximum Threshold (TMT) for As (Herselman, 2013). In order to successfully utilise WTR for land application, without exceeding the TMT, it should be applied as a percentage of the total soil mass earmarked for land application. Mixing WTR into the soil will ensure that the WTR amended soil does not exceed the TMT, despite the WTR exceeding the TMT limit. The higher amount of Mn in the FeWTR in comparison to the AlWTR may be a result of the quality of the lime used by the two WTPs (Titshall & Hughes, 2005; Trollip *et al.*, 2013). The fate of the various trace elements will be discussed in Chapter 5.

The amount of Fe, Mn and Al are also reflected in the oxalate extractable fraction of each within the WTR (Table 2.4). The crystallinity index, Fe_{ox}/Fe_{total} for the FeWTR and Al_{ox}/Al_{total} for AlWTR can be used to evaluate the amount of the primary flocculant that is in an amorphous state. The majority, 89%, of the Fe within FeWTR is held in amorphous coordination while the amorphous Al in AlWTR is only 29%. Despite the lower crystallinity index of the AlWTR (2019) sample it has a higher SSA and does not contain any XRD identifiable crystalline phases from the added treatment chemicals.

The age of the WTR can influence the oxalate extractable metal fraction (Agyin-Birikorang & O’Connor, 2009; Dempsey *et al.*, 1990; Gibbons & Gagnon, 2011; Wang *et al.*, 2015). The age or duration between flocculation and sample collection of WTR from Blackheath is not known, and storage periods can be as long as five years (Table 2.1). In contrast, Faure WTP makes use of mechanical dewatering and direct landfilling, resulting in a shorter duration between flocculation and sample collection. The sum of the oxalate extractable Fe and Al of Faure WTP is much greater than that of Blackheath WTP (Table 2.4). This can be due to different plant operating conditions, with Faure WTP requiring greater amounts of iron sulfate to achieve purification (Kerr, 2018). The XRD indicated that the FeWTR from Faure WTP does contain crystalline phases derived from the added chemicals. The effect of age on sorption capacity and crystallinity should be measured from the flocculation date to be able to directly compare between various WTRs, to exclude the possible influence of storage and drying methods implemented by the different WTP. The role of the AC within the WTR deserves further study, especially with respect to the role of AC in the crystallinity of the WTR. Unaltered air-dried WTR should be compared to WTR with the AC removed, following the rationale of Schwertmann (1966).

The Fe_{ox} and Al_{ox} can be related to the capacity to sorb phosphate and trace elements (Dayton & Basta, 2005; Evans & Smillie, 1976; Norris & Titshall, 2012). The P sorption to the WTR was fitted to Langmuir and Freundlich isotherm models. The Langmuir model showed a better fit for all three WTR samples with R^2 values of 0.91 (FeWTR 2018), 0.98 (FeWTR 2019) and 9.9 (AlWTR 2019). The maximum P sorption was calculated as 5.83 mg/g for FeWTR (2018), 12.62 mg/g for FeWTR (2019) and 12.01 mg/g for AlWTR (2019) (Table 2.4). Both the AlWTR and FeWTR 2019 exceeded the mean maximum P sorption of 18 AlWTR samples of 9.68 mg/g (Dayton & Basta, 2005). However, FeWTR (2018), FeWTR (2019) and AlWTR (2019) al fall within the range of 1.84 – 29.5 mg/g reported by Dayton & Basta (2005). The adsorption curves of the WTR are L-shaped, indicating that the sorption sites become increasingly occupied (McBride, 1994). The L-shaped adsorption curves correspond well to the biphasic adsorption of P to WTR, where the initial sorption phase is fast, followed by slower, inner-sphere adsorption until equilibrium is reached (Appendix 2.3.3) (Agyin-Birikorang & O'Connor, 2009; Evans & Smillie, 1976; Ippolito *et al.*, 2011; Makris *et al.*, 2006; Ociński *et al.*, 2016).

Despite the significantly lower total oxalate extractable Fe, Al and Mn of the AlWTR (2019) sample, the maximum absorption of P was comparable to that of FeWTR (2019). This may indicate that factors other than the amount of the primary oxide contribute to the P adsorption capacity of WTR. The AC within the WTR, which plays a role in surface area, crystallinity and absorption of ions, can contribute to the sorption of P, along with the total amount of amorphous Al and Fe (Dayton & Basta, 2005).

Table 2.5 Aqua Regia extractable elements of the sand, WTRs and compost in relation to the recommended limits for WTR amended soils and normal soil ranges

Parameter	**Sand**	**FeWTR (2018)**	**AlWTR**	**Compost**	**Normal soil ranges [b]**	**TMT [a]**
Al (g/kg)	0.80	39.07	110.18	< 0.001	10 - 40	-
Fe (g/kg)	0.34	196.81	38.06	0.01	1 - 100	-
Cr (mg/kg)	0.78	86.17	60.02	4.46	-	350
Mn (mg/kg)	6.52	897.23	270.60	4.47	10 - 9000	-
Co (mg/kg)	0.09	11.11	9.39	6.08	-	-
Ni (mg/kg)	0.27	39.61	25.33	6.08	-	150
Cu (mg/kg)	0.80	26.81	16.22	6.08	-	120
Zn (mg/kg)	2.82	64.41	43.80	6.09	-	200
As (mg/kg)	0.29	8.32	11.68	6.09	-	2
Mo (mg/kg)	BDL	3.90	0.81	BDL*	-	-
Pb (mg/kg)	1.58	15.36	26.08	BDL	-	100

*BDL below the detection limit
[a] Total Maximum Threshold (Herselman, 2013)
[b] Normal soil ranges (Herselman, 2013)

2.4 Conclusions

The WTP and temporal differences in the plant operating conditions and raw water quality will affect the properties of the WTR. The surface morphology, specific surface area, XRD and FTIR results indicate that the WTR contain some poorly crystalline phases. The SSA differ between samples of Al and Fe- WTR. This may be a result of raw materials, chemical dosage and processing. Most notably the amount AC and the primary metal oxide. The crystallinity is unlikely to change due to the complex chemical nature of the WTR. WTR from Faure WTP, rather than Blackheath WTP should be considered for land application; based on residuals handling and storage methods. Although none of the chemical parameters (pH, EC, CEC) limit WTR in terms of land application, the WTR is inherently variable, and the pond storage method of Blackheath WTP may significantly increase the variability, which should ideally be easily monitored for matching waste to receiving soils with analytics.

Constraining the variability of the WTR from a specific WTP is key for monitoring for land application. Establishing a possible range of parameters is critical if WTR is used for land application on a large scale. Parameters of interest should be measured at regular intervals over an extended period of time, along with the factors such as raw water quality, volume and plant-specific operation conditions, all of which may influence the WTR characteristics. The data can then be integrated as part of a multivariate regression model to narrow down the main driving forces behind the character of the WTR and to define the inherent variability of WTR within a statistical framework. The established ranges can be used to guide land application of the WTR from that specific WTP; such a guideline range will be invaluable with relation to toxic trace elements that may be contained within the WTR.

Any addition to the receiving nutrient-poor sandy soil will alter the overall chemical characteristics. However, the effect of WTR is limited to the solid itself; better mixing, and finer WTR will maximise the effect of the WTR; moreover, the loading of the WTR is of crucial importance. Increasing the WTR loading will increase the contribution of WTR to the amended soil system; however, if the loading is too great, the WTR can be detrimental to the soil environment. Furthermore, the addition of compost, biosolid or fertiliser can have a significant effect on the performance of the WTR amended system. FeWTR (2018) was used in all subsequent application trials.

CHAPTER 3. **SOIL - WATER INTERACTIONS OF A SANDY SOIL AMENDED WITH WTR, COMPOST AND WTR-COMPOST CO-APPLICATION**

3.1 Introduction

A water deficit reduces crop growth and yield more than all other plant stress factors combined (Kirkham, 2005; Kramer, 1983; Russell, 1973; Zhang, 1997). The risk of a water deficit increases in a soil medium with a low water-holding capacity, such as a sandy soil (Hillel, 2004; Sims *et al.*, 2013; Sivapalan, 2006). Furthermore, the high hydraulic conductivity of sandy soils leads to leaching of fertilisers, further decreasing the crop yields (Hillel, 2004; Sivapalan, 2006).

Increasing productivity of a sandy medium, by adapting the irrigation method to suit the low water-holding capacity of the sandy soil is one possibility. However, agriculture already accounts for 70% of the global water consumption (Basso *et al.*, 2013). Furthermore, worldwide, more than 200 million people in rural communities are relying on rainfall for agriculture and do not have access to irrigation schemes (Govindaraj, Kannan, Arunachalam, *et al.*, 2011).

Alternatively, to offset the water-holding capacity shortfalls of a sandy medium, soil amendments such as polyacrylamide can be added. These commercial products are expensive at AU$ 8/ kg (R 90/ kg) (Sivapalan, 2006). The use of biochar and waste products, such fly ash and WTR show potential as an alternative soil amendment to increase the soil water retention (Ahmad *et al.*, 2016; Basso *et al.*, 2013; Bugbee & Frink, 1985; Sims *et al.*, 2013; Skene *et al.*, 1995).

Dried and crushed WTR resembles a fine-textured soil; the physicochemical nature of the dried WTR makes it not only suitable for land application purposes but creates scope for use as a soil amendment (Bayley *et al.*, 2008; Bugbee & Frink, 1985; Dayton & Basta, 2001; Dempsey *et al.*, 1990; Elliott & Dempsey, 1991; Johnson & Johnson, 2017; Oh *et al.*, 2010; Ye *et al.*, 2001). The soil physical improvements, in texture and water-holding capacity, related to WTR amendment of soils is believed to be advantageous enough to offset the potential P deficiencies at low application rates (Ahmad *et al.*, 2016; Bugbee & Frink, 1985; Skene *et al.*, 1995). This chapter reviews some aspects of soil-water interactions that affect especially sandy soils and then will focus on the potential of WTR to improve the soil-water dynamics of a sandy soil.

3.1.1 Soil water repellency

Water repellency or hydrophobicity is a surface property of some soils that reduces the initial wettability of the soil. Soil water repellency (SWR) is a major problem, and it can lead to significant losses in crop production (Doerr *et al.*, 2000). In the Netherlands, 75% of the agricultural land exhibits some degree of SWR, and Australia has 5 million hectares of land affected by hydrophobicity (Doerr *et al.*, 2000; Hall *et al.*, 2010). Reducing SWR of sandy soils can lead to an increase in crop yield and profitability (Hall *et al.*, 2010). The sandy soils around Cape Town exhibit SWR properties. Increasing crop yield through reducing SWR in a manner that is practical, economically feasible and not detrimental to the environment is of great interest.

SWR can have significant influences on germination, plant growth, water infiltration, increased surface runoff and soil erosion (Doerr *et al.*, 2000; King, 1981; Müller & Deurer, 2011). This surface phenomenon is more prominent in coarse-grained sandy soils with a clay percentage of less than 10% (Dekker *et al.*, 2000; Doerr *et al.*, 2000; González-Peñaloza *et al.*, 2013; Müller & Deurer, 2011; Quyum, 2000). Although no solid is inherently hydrophobic, coarser particles with a small specific surface area are more prone to hydrophobicity, as a thin layer of a hydrophobic substance can coat the particle to render it hydrophobic (Bisdom *et al.*, 1993; Doerr *et al.*, 2000; González-Peñaloza *et al.*, 2013; Ma'Shum *et al.*, 1989; Quyum, 2000). The origin of these hydrophobic compounds is derived soil organic matter (SOM), specifically from plant material that contains waxes, resins and other hydrophobic substances (Doerr *et al.*, 2000; Müller & Deurer, 2011; Quyum, 2000). Not all SOM leads to hydrophobic coatings on mineral grains. One hypothesis postulates that an accumulation of poor quality SOM, rich in aliphatic hydrocarbons, waxes and resins that are resistant to microbial breakdown form hydrophobic films (Müller & Deurer, 2011). Bisdom *et al.*, (1993) observed that the water repellency decreased significantly if the organic matter is removed from the sand particle, supporting the role of SOM in soil water repellency. Bushfires, certain fungi and microbes can also lead to alterations in the SOM nature and lead to an increase in hydrophobicity (Doerr *et al.*, 2000).

The soil moisture state influences the severity of the hydrophobicity of soils; the hydrophobicity of a soil decreased with an increase in soil moisture. Soil moisture fluctuations can result in a seasonal cycle of hydrophobicity (Dlapa*et al.*, 2004; Doerr *et al.*, 2000; González-Peñaloza *et al.*, 2013).

Water infiltration into initially dry soil is retarded, leading to surface ponding and increased overland flow (Quyum, 2000). Prolonged periods of contact between water and the hydrophobic layer leads to a decrease in hydrophobicity, ultimately resulting in a wettable soil

(Doerr *et al.*, 2000). Hydrophobic soils tend to have unstable wetting fronts with preferential flow paths facilitated by less water repellent areas (Doerr *et al.*, 2000). The unequal wetting can lead to poor seed germination, and reduced plant growth as certain areas receives less water into the root zone, affecting nutrient uptake (González-Peñaloza *et al.*, 2013). Maintaining a high topsoil moisture content through frequent irrigation is one possible solution to SWR (Müller & Deurer, 2011; Quyum, 2000).

Various approaches and strategies for mitigating SWR have been implemented. Strategies can be direct, focusing on the hydrophobic components of the soil environment, or indirect where the soil environment or management strategies change the whole soil environment (Müller & Deurer, 2011). Direct amelioration approaches include liming, slow-release fertilisers, fungicides, bioremediation, irrigation and earthworms; these strategies aim to decrease the pool of the SOM that leads to SWR (Müller & Deurer, 2011). Indirect strategies aim to mitigate the SWR without changing the hydrophobic soil organic matter but instead change the overall water soil interaction (Müller & Deurer, 2011). Indirect SWR strategies include surfactants, claying, cultivation practices and soil aeration (Müller & Deurer, 2011).

Increasing the topsoil clay content by 1 - 2% can significantly decrease the SWR (Doerr *et al.*, 2000; González-Peñaloza *et al.*, 2013; Müller & Deurer, 2011; Quyum, 2000). High specific surface area and a net negative charge are two characteristics of clay that mitigate the soil hydrophobicity (González-Peñaloza *et al.*, 2013; Müller & Deurer, 2011; Quyum, 2000). Clay can be brought in from a different source or brought to the surface, through deep ploughing (Müller & Deurer, 2011). The clay masks soil hydrophobicity by coating the hydrophobic compounds and the mineral sand grains (Quyum, 2000). The addition of clay to the rooting zone of sandy soils in Australia resulted in a marked increase in crop yield (Hall *et al.*, 2010). Ma'Shum *et al.* (1989) decreased the SWR of a sandy soil significantly by adding a fine silica powder with a 380 m^2g^{-1} specific surface area at a 0.1% weight/weight (w/w) application rate (Ma'Shum *et al.*, 1989). The same study achieved a completely wettable soil with 1% w/w loading of clay (Ma'Shum *et al.*, 1989). Increasing the clay application rate will lead to more significant reductions in SWR (Mckissock *et al.*, 2000). However, not all clays are equally effective; kaolinite and illite are more effective than smectite, despite smectite`s higher specific surface area and cation exchange capacity (CEC). The clays effectiveness in masking hydrophobic particles is attributed to the ability to form micro-aggregates (Ma'Shum *et al.*, 1989; Mckissock *et al.*, 2000). Kaolinite and illite are larger and more readily dispersible than smectite, these attributes are favourable for masking of hydrophobicity on sand grains (Ma'Shum *et al.*, 1989; Mckissock *et al.*, 2000). The amount of $-OH^-$ and polar groups on the clay surface also increases water adhesion, increasing the soil wettability (Dlapa *et al.*, 2004). Clays like kaolinite, with a high density of hydroxyl groups is superior over clays such as Ca-montmorillonite with fewer hydroxyl groups and is more effective in alleviation of SWR (Dlapa *et al.*, 2004).

Adding clay to sandy soils to manage SWR is expensive (100 AU$/ha) (R1150 /ha) (Mckissock *et al.*, 2000). Finding a cheap alternative to clay can be beneficial to farmers. WTR, from nearby WTPs, is one possible alternative as a direct amelioration for SWR.

3.1.2 Saturated hydraulic conductivity

Another severe limitation of sandy soils is their high saturated hydraulic conductivity. The rate of saturated hydraulic conductivity is especially important for irrigation and water management.

Soils from coarse-textured mineral grains tend to be single grained, granular soils without aggregate formation (Hillel, 2004). The resulting porosity is the result of the soil texture rather than intra-aggregate structures (Arthur *et al.*, 2011; Hillel, 2004). The internal packing, particle size and shape of single grain soils depend on the mode of deposition (Hillel, 2004). The two end members of the particle size distribution of granular soils are based on the sorting of grains and the proportion of size fractions. Where the medium consists almost entirely of one size fraction it has a well-sorted, poorly-graded distribution; in contrast to large variations in particle size where the medium is well-graded but poorly-sorted (Bear, 1972; Hillel, 2004). The particle size distribution affects the resulting porosity and the hydraulic nature of the media, decreasing the particle sorting will lower the porosity (Bear, 1972). The porosity of a granular soil will be at its lowest if the fine particle volume equals the pore space of the coarse grains (Barnes *et al.*, 2014). Decreasing particle sorting increases the tortuosity of the pore spaces, decreasing the saturated hydraulic conductivity (Chen *et al.*, 2018; Hillel, 2004). Apart from the grain size, the shape also influences the hydraulic conductivity (Bear, 1972; Sperry & Peirce, 1995). The effect of particle shape is most noticeable in the 295 - 841 µm range conductivity (Sperry & Peirce, 1995). Irregular shapes tend to pack with higher efficiency and further decrease the pore space relative to rounded particles of the same size (Bear, 1972). Furthermore, changes in bulk density can also alter the hydraulic properties of a media, decreasing the bulk density increases the saturated hydraulic conductivity (Barnes *et al.*, 2014; Baronti *et al.*, 2014; Chen *et al.*, 2018; Głąb, 2014; Lei & Zhang, 2013; Tian *et al.*, 2018).

The intrinsic porosity of the added material can also alter the hydraulic properties. The addition of a material with a large specific surface area and high internal porosity can alter the soil physical properties in relation to soil hydraulic properties (Baronti *et al.*, 2014; Lei & Zhang, 2013). Chen *et al.* (2018) found that the effect of biochar addition increases with increasing application rate. Brunauer–Emmett–Teller specific surface area (BET-SSA) analysis of biochar indicates that the structure contains a large proportion of micropores, creating a possible secondary tortuous flow path through the porous structure, assuming that the pores are connected (Barnes *et al.*, 2014; Bear, 1972; Sun *et al.*, 2012). As with biochar, WTR also has a high specific surface area, chapter 2.3.2 and Makris *et al.* (2004).

WTR aggregates have limited potential for swelling, which leads to an increase in the hydraulic conductivity (Moodley & Hughes, 2006; Moodley *et al.*, 2004; Park *et al.*, 2010). Moodley *et al.* (2004) only noted an increase in saturated hydraulic conductivity of Hutton and Westleigh soils (14% sand, 34% silt, 52% clay and 17% sand, 50% silt, 33% clay respectively) under high application rates (1280 Mg/ ha). At lower application rates the addition of WTR did not influence the saturated hydraulic conductivity. Park *et al.* (2010) also concluded that the saturated hydraulic conductivity (K_S) of sand and WTR did not differ significantly. The breakdown of the structural integrity of WTR in the soil can have adverse effects on the hydraulic properties of the soil since the main constituents of WTR are clays and silts from the raw water, which can block soil pores (Moodley *et al.*, 2004).

Studies investigating the effect of amending soil with biochar, fly ash and compost found that the addition influences the soil hydraulic properties (Barnes *et al.*, 2014; Baronti *et al.*, 2014; Chen *et al.*, 2018; Ghodrati *et al.*, 1995; Głąb, 2014; Lei & Zhang, 2013). The studies emphasised that the resulting change is related to the physical properties of both the receiving soil and the soil amendment (Lei & Zhang, 2013). If the resulting treatment combination decreases the overall porosity by decreasing the particle sorting, a decrease in saturated hydraulic conductivity was observed (Barnes *et al.*, 2014; Chen *et al.*, 2018; Ghodrati *et al.*, 1995; Lei & Zhang, 2013). Furthermore, the addition of material to a sandy soil that decreased the bulk density increased the overall porosity and resulted in an increased saturated hydraulic conductivity (Głąb, 2014).

3.1.3 Water retention

How a soil interacts with water at unsaturated soil conditions is critical for soil management applications. These characteristics are key to implementing optimal irrigation and soil water management strategies. A major limitation to crop yields is water , and sandy soils with low moisture-holding capacity are especially vulnerable to water induced stress (Ghodrati *et al.*, 1995).

Soil pore space and soil water content are mutually interactive, any changes due to the addition of compost, biochar, fly ash or WTR to the soil that can lead to a change in the soil pores which will affect the hydraulic properties of the soil (Głąb, 2014; Greenland & Pereira, 1977; Moodley & Hughes, 2006; Stange & Horn, 2005). The addition of microporous biochar to a sandy soil increased the water content at permanent wilting point (PWP); however, the increase in water-holding capacity due to biochar addition was predominantly attributed to the increase in macropores resulting from the increase in grain size heterogeneity brought on by the addition of biochar (Abel *et al.*, 2013; Basso *et al.*, 2013; Hardie *et al.*, 2014). Similarly, the application of WTR can change the soil texture and possibly the water-holding capacity of the amended media.

A study by Park *et al.* (2010) that investigated the water retention curve pattern of fine, medium and coarse WTR, found that it is similar to that of sand of the same size fraction, but it has higher water contents at any matric potential. The water retention curve of WTR decreased rapidly with the decrease in matric potential until -13 kPa, after which the decrease was more gradual (Park *et al.*, 2010). Addition of WTR shifted the entire water retention curve to higher water content, with a slightly increased water retention at low matric potentials (0 to -100 kPa); however, the readily available water content (0 to -100 kPa) of the soils remained unchanged, implying that there is no increase in water availability to crops (Moodley *et al.*, 2004).

Moodley and Hughes (2006) also observed this shift in water retention curve without any change in the shape of the curve. The total available water-holding capacity (TAWC) and easily available water-holding capacity (EAWC) of the WTR treated soils (14% sand, 34% silt, 52% clay and 17% sand, 50% silt, 33% clay respectively) were not significantly different from the control despite the water content of the WTR treated soil being higher at all matric potentials. Moodley and Hughes (2006) concluded that this upwards shift might result in some additional benefit to crops, while Dayton and Basta (2001) concluded that despite the higher water-holding capacity of WTR, the plant-available fraction is lower than that of an average soil. A greenhouse study conducted by Mahdy *et al.* (2009) showed an increased dry matter production with soils amended with WTR, which the study attributed to increased water-holding capacity; however, the water-holding capacity was calculated from the amount of water 100 cm^3 of the WTR amended soil can hold against gravity, following the method of Skene *et al.* (1995). The changes in water retention due to the addition of WTR is related to the physical properties of WTR, rather than the interaction between the WTR and soil; changes, therefore, are proportional to the WTR loading (Moodley & Hughes, 2006). The WTR water-holding capacity is attributed to the clay particles within the aggerates and the WTRs larger number of intra-aggregate pores (Mahdy *et al.*, 2009; Oosterveld & Chang, 1980; Park*et al.*, 2010; Skene *et al.*, 1995).

This chapter investigates the effect that adding WTR to a sandy soil will have on the soil-water interaction with relation to the soil water repellency, saturated hydraulic conductivity and water retention. Literature suggests that land application of WTR with a co-amendment of compost will be more beneficial than a WTR single amendment (Bayley *et al.*, 2008; Clarke *et al.*, 2019; Hsu & Hseu, 2011; Ippolito *et al.*, 2002; Johnson & Johnson, 2017; Mahdy *et al.*, 2009).

Therefore, WTR as a single amendment and WTR-compost co-application were investigated. Understanding the soil-water interactions of a WTR amended sandy soil is of benefit to the management of irrigation on areas where WTR may be added to the soil system.

3.2 Materials and Methods

The FeWTR (2018), compost and sand used in this chapter is described and characterised in Chapter 2.

3.2.1 Saturated hydraulic conductivity

The saturated hydraulic conductivity (K_s) was determined with the KSAT® instrument and software from METER. The K_s was determined with the falling head method on the treatments (Table 3.1). All samples were measured in triplicate.

Table 3.1 Amendment mixture ratios

Amendment mixture	Material and mixing ratio w/w%	Ton/ha of amendment mixture
Control sand	100% aeolian sand	0
10% Compost	90% sand + 10% compost	225
20% Compost	80% sand + 20% compost	450
10% WTR	90% sand + 10% FeWTR (2018)	225
20% WTR	80% sand + 20% FeWTR (2018)	450
WTR-compost	80% sand + 10% compost + 10% FeWTR (2018)	450

[a] Based on an incorporation depth of 15 cm, and a bulk density of 1.5 g/cm^3

The granular nature of all three components made effective mixing and homogeneous packing possible. The weight (g) of each treatment loading were calculated based on the w/w % ratio, the instrument volume, and a bulk density of 1.5 g/cm^3 to ensure the ratios are constant throughout. In order to achieve the optimum porosity and hydraulic properties, the added material should be mixed to homogeneity; otherwise, the hydraulic properties will not be uniform throughout the treated sample (Barnes *et al.*, 2014; Moodley & Hughes, 2006).

The samples were saturated in a water bath for 6 hours before measurement. Each treatment was performed in triplicate and measured three times to ensure consistent readings from the probe. When describing the hydraulic movement of a fluid through a medium some of the flow characteristics are a result of the fluid properties, such as density, viscosity and polarity amongst others (Bear, 1972), in this study only the effect of the medium is discussed and considered, and the fluid, water is kept constant with regards to density and viscosity. The readings were recorded at the room temperature water (20 - 25 °C) and converted with the KSAT® software to 10 °C since the K_s is dependent by the fluidity (f) of the liquid and the intrinsic permeability of the soil medium (k) hence; K=kf (Hillel, 2004).

The soil exhibited water repellant behavior; however, SWR does not influence a fully saturated medium (Quyum, 2000). Statistical analysis was performed on the temperature corrected saturated conductivity with the RStudio statistical Package.

3.2.2 Soil water repellency

The Water Droplet Penetration Time test (WDPT) was used to measure the degree of soil water repellency of the sand with various amendment mixtures of FeWTR (2018) and compost (Table 3.1). The compost from Reliance was used without alterations. Samples were dried at 65°C for 24 h and allowed to reach room temperature before the WDPT experiment (Abel et al., 2013). The time (in seconds) for a distilled water droplet (40 µl) to infiltrate the medium was measured (King, 1981). The water repellence was classed based on Dekker *et al.* (2000). The classification has two main classes; non-hydrophobic (< 5 s), and hydrophobic (> 5 s). The latter is further subdivided into lightly water repellent (5 - 60 s), strongly water repellent (60 - 600 s), severely water repellent (600 - 3600 s) and lastly extremely water repellent (> 1 h). The WDPT test method results are relative and cannot be directly compared to other studies (Dekker *et al.*, 2000). This test aimed to investigate the effect of the addition of WTR, compost or a co-amendment, on the hydrophobic nature of the control sand. Three aluminium rings (with an internal diameter of 4.6 cm and a height of 3.0 cm) of each treatment were prepared (Table 3.1). The WDPT of 10 drops per disk was recorded in seconds. The temperature of the water (20 °C) used for the experiment was kept constant since the surface tension decreases with increasing temperature (Doerr *et al.*, 2000).

3.2.3 Soil water retention

The soil water retention was determined on each treatment by using a pressure plate system. Aluminium rings with an internal diameter of 4.6 cm and a height of 3.0 cm were used. A filter paper was glued to one side of the ring. Each treatment was conducted in quadruplicate. Poor contact between the plate and the ring may result in inaccurate readings, if the ring weight is greater than the previous pressure, and vastly different from the replicates, the value were not considered. The samples were saturated in a water bath along with the pressure plate before each pressure was applied. Three pressure pots were used in this experiment; a low-pressure pot (1-100 kPa) with a 1 bar plate, medium pressure pot (100 kPa) and high-pressure pot (1500 kPa). The medium and high-pressure pots used a 15 Bar plate. The rings were allowed to reach equilibrium for a certain pressure after which the weight was recorded. The process was repeated for the next pressure. The gravimetric ($g.g^{-1}$) and volumetric ($cm.cm^{-1}$) water content was determined at 0, 2, 6, 10, 14, 20, 30, 60, 100 and 1500 KPa.

3.2.4 Statistical analysis

Data were analysed using parametric statistical tests with the RStudio statistical Package. All error bars on graphs are the standard error ($s_{\bar{x}} = s^2/n$). If $p < α$, the result was deemed significant, where alpha is 0.05. A single factor ANOVA on the saturated hydraulic conductivity and WDPT results were performed to investigate the effect of the amendment mixtures. To analyse for significant differences between treatments post hoc Tukey HSD test was performed. The ANOVA validity assumptions of normality and homoscedasticity were visually based on the normal Q - Q plots.

3.3 Results and Discussion

3.3.1 Grain size distribution shifts of WTR amended sand

The grain size distribution of the sand and WTR is shown in Table 2.2. Mixing the material with the sand will change the grain size distribution (Figure 3.1). The WTR amended sand will still reflect the grain size distribution pattern of the sand, which makes up the majority of the mixture by volume. The addition of the WTR does increase the coarse and medium size fractions, shifting the grain size distribution slightly towards the coarser size fractions (Figure 3.1). The change in the grain size distribution will influence the pore space size and distribution which can influence the saturated hydraulic conductivity and water retention characteristics (Abel *et al.*, 2013; Basso *et al.*, 2013; Hardie *et al.*, 2014).

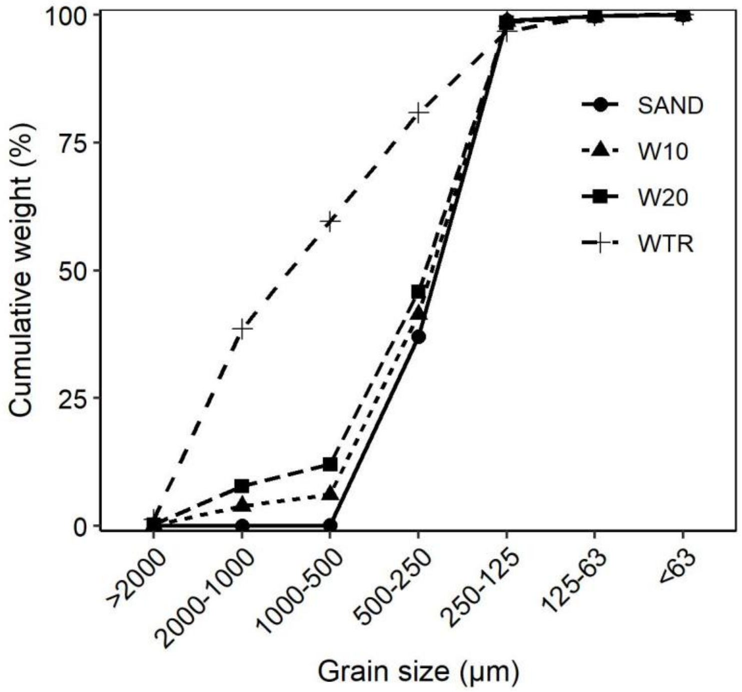

Figure 3.1 Cumulative grain size distribution of FeWTR (2018) and sand and two amendment mixtures of 20% and 10% FeWTR (2018) and sand.

3.3.2 Saturated hydraulic conductivity

A single factor ANOVA was performed on the saturated hydraulic conductivity of the amendment mixtures. The addition of material to the sand influenced the saturated hydraulic conductivity (Table 3.2). However, based on the Post hoc Tukey tests, only the addition of 20% compost resulted in a significant increase in K_s (Table 3.2).

Table 3.2 The mean (n=3) saturated hydraulic conductivity of the amendment mixtures

Amendment mixture t	**Ks (cm.s^{-1}) at 10C° [a]**	**Ks (cm.s^{-1})**	**Significance symbol**
Control sand	0.009	0.013	ac
10% WTR	0.008	0.010	ab
20% WTR	0.007	0.010	a
10% compost	0.012	0.015	c
20% compost	0.016	0.022	d
WTR-compost	0.011	0.013	bc

[a] Used in statistical analysis, conversion by KSAT software. Amendment mixtures that are not significantly different from each other share the same letter. All significance levels are set at $p < 0.05$

The sand is deposited by aeolian mechanisms, resulting in a well-sorted, poorly graded matrix, which conforms well with the results of Schloemann, (1994) (Table 2.2, Figure 3.1). The control sand hydraulic conductivity corresponds well to the typical saturated hydraulic conductivity of aeolian sand (0.001 $cm.s^{-1}$) (Hillel, 2004). The K_s of the 10% WTR amendment decreased with 11% while the K_s of the 20% WTR treatment decreased with 22% (Table 2.2). Although neither WTR amendment resulted in significant changes ($p > 0.05$) in the K_s, it indicates that any change in the grain size and particle distribution will affect the K_s of the medium.

The addition of material with different grain size and texture increases the heterogeneity of grains, decreasing the well-sorted nature of the sand resulting in a higher packing efficiency which leads to a decrease in porosity (Figure 3.1) (Ghodrati *et al.*, 1995; Głąb, 2014; Greenland & Pereira, 1977; Moodley & Hughes, 2006; Stange & Horn, 2005). The decreased hydraulic conductivity observed with the addition of 10 and 20% of WTR may be a result of increased tortuosity of the water flow paths due to a higher packing efficiency of a polydisperse medium, which in turn decreased the K_s. The irregular, angular shape of the WTR may have also added to the higher packing efficiency and touristy (Bear, 1972).

The K_s of the 10% compost treatment increased with 33%, while the 20% compost treatment resulted in a significant K_s increase of 77% (Table 2.2). The addition of compost which contains a wide variety of material of > 2 mm increased the K_s by creating more interconnected pores despite the polydisperse nature of the treatment mixes. The compost treatment packed to a bulk density of lower than the 1.5 g/cm^3 at which the mixing ratios were calculated. The compost addition lowered the bulk density, which also increased the Ks (Głąb, 2014). The addition of a WTR-compost co-application further decreased the sorting and increases the particle heterogeneity. The large pieces > 2 mm in the compost can help to increase the macropores and the porosity, which will lead to an increase in K_s.

Adding WTR does increase the overall micro-porosity of the treatment; supported by high BET-SSA values (Makris *et al.*, 2005; Ociński *et al.*, 2016). The overall porosity of the system may increase, however, if it is contributing to the effective porosity and hydraulic conductivity is not clear through these results (Barnes *et al.*, 2014; Bear, 1972; Sun *et al.*, 2012). Microporosity introduced through WTR may play a role in hydraulic scenarios where the flow is much lower, in a clay-rich soil, for example.

The results show that any change in the particle size distribution and bulk density will influence the hydrology of the system (Table 3.2) (Blanco-Canqui, 2017; Głąb, 2014). This change is dependent on both the properties of the added material and receiving material, such as particle size and shape (Blanco-Canqui, 2017). Decreasing particle sorting through the addition of WTR decreased the saturated hydraulic conductivity.

3.3.3 Soil water repellency and hydrophobicity

A single factor ANOVA of the amendment mixtures and the infiltration time (s) was conducted. The addition of any material to the soil results in significant changes to WDPT, ($p < 0.05$) (Table 3.3). The addition of WTR resulted in the most significant reduction in penetration time, followed by the co-application of WTR and compost and lastly the compost.

Table 3.3 Mean (n=30) Water Droplet Penetration Time test results of the amendment mixtures

Amendment mixture	**Infiltration time (s)**	**Hydrophobicity class***	**Significance symbol**
Control sand	1661.63	Extremely water repellent	a
10% WTR	215.03	Strongly water repellent	b
20% WTR	67.30	Strongly water repellent	c
10% compost	595.13	Strongly water repellent	d
20% compost	176.50	Strongly water repellent	bc
WTR-compost	156.93	Strongly water repellent	bc

* After (Dekker *et al.*, 2000). Amendment mixtures that are not significantly different from each other share the same letter. All significance levels are set at $p < 0.05$

The control sand contains minimal soil organic matter and silt and clay percentages of less than 1% (Table 2.2). The aeolian deposited sand consists mainly of well-sorted fine-grained mineral quartz particles. These characteristics aid in forming a hydrophobic topsoil (Dekker *et al.*, 2000; Doerr *et al.*, 2000; González-Peñaloza *et al.*, 2013; Müller & Deurer, 2011; Quyum, 2000). The control sand WDPT yielded an average infiltration time of more than 27 minutes (Table 3.3), which is classed as an extremely hydrophobic soil (Dekker *et al.*, 2000). The hydrophobic nature of the soil can be attributed to the soil organic matter, rather than the properties of the mineral quartz (Müller & Deurer, 2011).

The 20% WTR treatment had the most significant effect in reducing SWR by a factor of 24 ($p < 0.05$). Although not significant in all cases, the following trend was observed in the order of decreasing effect on the SWR: 20% WTR > WTR-compost > 20% compost >10% WTR >10% compost >>control sand (Table 3.3).

The addition of both compost and WTR to the sand resulted in a significant decrease in hydrophobicity. Treatments that consisted of a 20% w/w mixing ratio (20% WTR, 20% Compost and WTR-compost) resulted in a more significant reduction in SWR in comparison to the 10% w/w treatments (10% WTR and 10% Compost).

Adding clay to a hydrophobic soil is an effective indirect SWR strategy. Increasing the topsoil clay content by 1 - 2% drastically decreased the SWR (Doerr *et al.*, 2000; González-Peñaloza *et al.*, 2013; Müller & Deurer, 2011; Quyum, 2000). Similarly, Increasing the WTR loading from 10% to 20% decreased the WDPT significantly from 215 s to 67.3 s (Table 3.3).

The addition of WTR increased the clay mineral content of the WTR amended soil; which can reduce SWR through masking (Dassanayake *et al.*, 2015; Kim *et al.*, 2002; Oh *et al.*, 2010; Park *et al.*, 2010; Titshall & Hughes, 2005, 2009). Furthermore, the addition of a material like WTR, with a high specific surface area can also decrease the SWR (Table 2.3) (Makris *et al.*, 2005; Ociński *et al.*, 2016).

The addition of compost also resulted in a significant decrease in SWR and was more effective at mitigating the effect at higher loadings (Table 3.3). The compost reduced the SWR by increasing the total SOM of the compost- amended soil (Müller & Deurer, 2011). The addition of WTR-compost co-application significantly reduced the SWR, compared to the single soil-compost treatment with the same amount of compost added (10%). Although not statistically significant, the co-amendment had a lower WDPT than the 10% WTR treatment. This synergistic effect may result from the two different mechanisms involved; the WTR reduces the SWR by masking the hydrophobic components while the compost dilutes the effect of the hydrophobic SOM of sand.

These initial results of adding WTR to mitigate SWR are promising; however, this study only reported results of a laboratory experiment and did not investigate the long-term effect of these additions on SWR, and how it will respond to repeated cycles of drying and wetting is also not investigated in this study. The decreased SWR due to WTR and WTR-compost co-application may result in more regular infiltration with less preferential flow. This may benefit agriculture on hydrophobic soils, by increasing the irrigation effectiveness, which ultimately increases nutrient uptake and germination.

3.3.4 Water retention characteristics

The control sand showed a steep decrease in gravimetric water content from 0 kPa to -14 kPa, after which it decreased gradually (Figure 3.2). The same retention curve characteristics are observed for 10%, and 20% WTR loadings, however, the whole curve shifted to higher gravimetric water contents for the same KPa values. The 20% WTR treatment shifted to higher kPa values with respect to the 10% WTR treatment. The addition of 10% and 20% compost to the sand resulted in a slight change in slope between -6 and -14 kPa. The slope of the compost treatments is gradual from -20 kPa, with a steeper slope than the control sand. The upwards shift in the water retention curve for the WTR amended soils is similar to that described by Moodley & Hughes, (2006), Moodley *et al.* (2004) and Park *et al.* (2010).

Addition of WTR, compost or WTR-compost co-application to the sand increased the total available water-holding capacity (TAWC) (Table 3.4). The TAWC increases with increasing WTR loading from 10% to 20%. The WTR also increased the least available water-holding capacity (LAWC) (Table 3.4), probably due to micropore bound water within the WTR (Mahdy *et al.*, 2009; Oosterveld & Chang, 1980; Park *et al.*, 2010; Skene *et al.*, 1995).

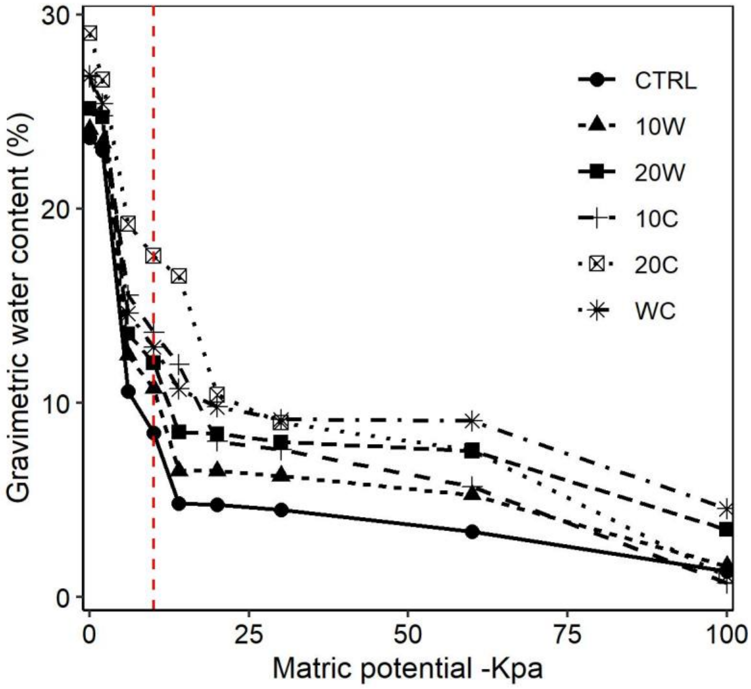

Figure 3.2 Water retention curve for the Easily available water-holding capacity (EAWC) for the treatments. The red dooted line is taken as field capacity (-10 kPa). CTRL-control sand; 10W- 10% WTR; 20W – 20% WTR; 10C - 10% compost; 20C – 20% compost; WC - WTR-compost co application.

Table 3.4 Available water content of the amendment mixtures

Amendment mixture	**AWC (cm^3.cm^{-3})**		
	TAWC [a]	**EAWC** [b]	**LAWC** [c]
Control sand	0.111	0.107 (96.7 %)	0.004 (3.2 %)
10% WTR	0.124	0.119 (96.1 %)	0.005 (3.9 %)
20% WTR	0.127	0.116 (91.6 %)	0.011 (8.4 %)
10% Compost	0.196	0.190 (96.6 %)	0.007 (3.4 %)
20% Compost	0.250	0.244 (97.7 %)	0.006 (2.3 %)
WTR-compost	0.141	0.124 (88.2 %)	0.017 (11.8 %)

[a] Total available water-holding capacity -10 KPa to -1500 KPa
[b] Easily available water-holding capacity -10 KPa to -100 KPa
[b] Least available water-holding capacity -100 KPa to -1500 KPa

The TAWC of the compost treatments also increased with increasing compost loading. However, the effect of compost addition is only visible in the EAWC fraction; the LAWC of the compost-amended soils are comparable to the control sand (Table 3.4). The compost does not contain as many micropores as the WTR; thus its effect is limited to the EAWC.

The addition of material changes the grain size distribution and by implication the porosity and the amount of macro- and mesopores all of which will influence the TAWC (Głąb, 2014; Greenland & Pereira, 1977; Moodley & Hughes, 2006; Stange & Horn, 2005). The effect of porosity changes by adding predominantly coarse material will result in limited changes in LAWC water retention. However, the intrinsic micropores of the WTR do affect the fraction of water held in the LAWC section, and this fraction is directly related to the loading of WTR (Moodley & Hughes, 2006).

The WTR-compost co-application also resulted in an increase in the TAWC, more so than the single amendment 20% WTR but lower than the 20% compost treatment (Table 3.4). The effect of the WTR-compost co-application on the LAWC was greater than that of the 20% WTR. The increase in LAWC may be of benefit to plants under water-limited conditions, the addition of 20% WTR or WTR-compost co-application may be of benefit with respect to drought resilience- if the plant can access the micropore bound water. Critically, this assumption is only based on the available water and does not account for the effect of nutrient availability or the interaction between nutrient- and water availability. In order to obtain strong measurable results, the study utilised high /ha. Land application of WTR to increase the water retention of the soil is impractical due to the high loadings that are required, and at lower loading rates the water retention benefits of WTR addition will be minimal.

Similarly, Moodley & Hughes (2006) concluded that higher loadings of WTR resulted in more significant changes in water retention capacity of WTR treated soils. Moodley & Hughes (2006) postulated that the increase in water retention capacity is due to the physical properties of the material rather than the interaction between the WTR and soil. Similarly, studies on biochar treatment of soil concluded that the change in grain-size distribution affected the water-holding capacity rather than the intrinsic microporosity of the biochar (Hardie *et al.*, 2014).

Based on the presented results, the effect of WTR addition to sandy soil is proportional to the amount of WTR added, and that the gains in EAWC are limited, however, it does increase the fraction of LAWC, which may be a result of micropore bound water within the WTR. The upwards shift may be due to the microporosity of the WTR, while the shape of the curve is dependent on the grain size distribution and macropores of the WTR amended sand. Park *et al.* (2010) showed that the WTR behaves similarly to that of sand of the same grain size, highlighting the importance of WTR particle size. The effect of WTR addition to the soil water-holding capacity is not only influenced by the added microporosity of the WTR but also by the particle size of the WTR aggregates, which will be determined by the milling and crushing of the dried WTR. The co-amendment of compost and WTR may increase the EAWC more than that of WTR single amendments; however, these changes might be a result of the compost rather than the WTR.

These changes are not unique to WTR. Studies investigating amending soils with biochar, compost and fly ash found similar changes in the water dynamics of the amended soils (Arthur *et al.*, 2011; Barnes *et al.*, 2014; Baronti *et al.*, 2014; Chen *et al.*, 2018; Ghodrati *et al.*, 1995; Lei & Zhang, 2013). The resulting changes are a product of the interaction between the physical properties of the soil and the added material. The primary factor will be the interaction of particle shape and size; the effect of the intrinsic physical properties of the material is secondary.

3.4 Conclusions

The significant decrease in SWR by the addition of WTR from Faure WTP to the sandy soil of the Cape flats is promising. The 20% WTR reduced SWR 24-fold through masking the hydrophobic substances associated with the SOM of the sand. Further studies investigating the practical use of WTR in SWR mitigation strategies should be conducted.

Both the saturated hydraulic conductivity and water retention is dependent on both the properties of the added material and the sand. The effect of the added material will increase with an increase in loading, at higher loadings intrinsic properties such as the microporosity of the WTR plays a larger role.

Decreasing particle sorting through the addition of WTR decreased the saturated hydraulic conductivity of the sand, however it was not statistically significant. Only the addition of 20% compost significantly increased the saturated hydraulic conductivity of the sandy soils by 77%, likely due to large interconnected pores. The water retention of the sand is increased with the addition of WTR, compost and a WTR-compost co-application. The WTR addition resulted in an upward shift in the water retention curve, without altering the retention curve shape. The increased water content at all matric potentials is related to water held in the micropores of the WTR. This may be of benefit to plants under water-limited conditions.

Adding WTR as a single amendment or as co-application to a soil-system will have a multitude of effects- intentional and unintended. Understanding each effect on its own is key in managing practices of land to which WTR is added. The combined effect should be optimised so that the potential gains of adding WTR to the soil is maximised.

CHAPTER 4. INVESTIGATING THE POTENTIAL OF WTR AND COMPOST AS CO-AMENDMENT TO A SANDY SOIL ON THE GROWTH OF SWISS CHARD (*BETA VULGARIS* CICLA.) UNDER WATER AND NUTRIENT STRESS

4.1 Introduction

Successful long-term disposal of any waste products through land application requires in-depth knowledge of the interaction between the waste and the soil-water-plant system. One method of studying the waste amended soil-plant interactions is through controlled greenhouse experiments. Greenhouse studies have been successfully used to explore the effect of water treatment residual (WTR) on the chemical and physical properties of the soil-plant system (Dassanayake *et al.*, 2015; Lucas *et al.*, 1994; Trollip *et al.*, 2013).

The majority of the studies focus on the chemical effects of WTR addition to soil and the resulting plant response. Two studies Skene *et al.* (1986) and Dayton and Basta (2001) concluded that WTR is a poor soil substitute. Focus shifted to using WTR in combination with fertilisers, biosolids and most recently compost at different loadings (Bayley *et al.*, 2008; Clarke *et al.*, 2019; Hsu & Hseu, 2011; Ippolito *et al.*, 2002; Johnson & Johnson, 2017; Mahdy *et al.*, 2009). Furthermore, to maximise the potential benefit of WTR addition to soils, a low nutrient status soil with poor soil physical properties should be utilised (Clarke *et al.*, 2019; Park *et al.*, 2010; Titshall & Hughes, 2005).

Numerous studies found that the addition of WTR can benefit plant growth if added in low loadings, at high loadings phosphate becomes deficient which is detrimental to plant growth (Bugbee & Frink, 1985; Dayton & Basta, 2001; Heil & Barbarick, 1989; Ippolito *et al.*, 2002; Johnson & Johnson, 2017; Kim *et al.*, 2002; Mahdy *et al.*, 2009; Oh *et al.*, 2010; Park *et al.*, 2010; Rengasamy *et al.*, 1980; Skene *et al.*, 1995; Walpole & Johnson, 2012; Yiping, 2016). Apart from the chemical and nutrient considerations of WTR application, WTR can change the physical nature of the amended soil. The benefits of WTR amendment to physical improvements are in some cases more beneficial than the inherent nutrient gains of WTR addition (Ahmad *et al.*, 2016; Bugbee & Frink, 1985; Skene *et al.*, 1995). A greenhouse study conducted by Mahdy *et al.* (2009) reported an increase in dry matter production with soils amended with WTR, which the study attributed to increased water-holding capacity. Water, unlike plant nutrients which can be stored and retained, water-use is a continuous, one-way flow through the plant. The water use is driven by transpiration; if the addition of WTR can increase the water-holding capacity of a soil, it will be of tremendous benefit to crop production and irrigation management (Russell, 1973).This chapter reviews some aspects of simulated drought trough chronic water stress conditions that can be utilised in studying the response of Swiss Chard grown in a WTR amended sand.

4.1.1 Simulated drought conditions

A plant growing with a water deficit, in which the transpiration rate exceeds the water absorption by the roots, reduces growth and crop yield more than all other plant stress factors combined. Water stress influences all plant metabolic processes and will reduce the plant size, leaf thickness, leaf area and ultimately crop yield, despite sufficient nutrients (Kirkham, 2005; Kramer, 1983; Russell, 1973; Zhang, 1997). The effect of a water deficit can be less pronounced under nutrient limiting conditions; a moderate water deficiency under low nutrient supply on crop yield is not as pronounced since the nutrient supply is limiting growth rather than water supply (Russell, 1973). Being able to differentiate whether reduced plant growth is in response to a water deficit or limited nutrients is a key outcome of this study; thus, a parameter influenced by both factors needs to be used.

Water use efficiency (WUE) is the relationship between water consumption by the plant as a function of evapotranspiration (ET) and biomass yield (Y) in WUE=Y/ET(Gregory *et al.* .2000; Hatfield *et al.,* 2001). Plant growth, being an irreversible increase in size by mechanisms of cell enlargement and division amongst others, can be used as a proxy for drought conditions, since plants experiencing water-stressed conditions will have limited plant growth (Zhang, 1997). If plant growth is used as a primary indicator for water stress, the water use efficiency (WUE) can be used to relate the water stress response between plants grown in different treatments (Hatfield *et al.*, 2001; Zhang, 1997). Furthermore, the nutrient status of the soil can also influence the WUE efficiency. A study by Hatfield *et al.* (2001) which investigated chickpea growth in phosphorus-deficient soils, concluded that the addition of a phosphorus fertiliser increased WUE. Similarly, Leskovar & Piccinni (2005) showed that the WUE of spinach (*Spinacia* oleracea) grown under various deficient irrigation conditions could be used as a measure of plant performance with respect to water application.

In simulating long-term environmental water-deficient conditions, chronic water stress should be developed over an extended period. If water stress is introduced too rapidly, the results will not be comparable to long term environmental water-deficient conditions (Hsiao, 1973; Kramer, 1983). Wilting of leaves should not be used as primary indictor for chronic water stress; leaves can wilt during periods of high transpiration in soils with readily available soil water. In response to short periods of increased evapotranspiration (mid-day), the plants can recover without permanent effects during periods of reduced evapotranspiration periods (Kirkham, 2005).

For accurate and precise results from greenhouse trials, where relatively large plants are grown in small containers, a failure to maintain control over environmental conditions undermines the experiment (Kramer, 1983). With respect to irrigation, this is especially important if a consistent water level lower than field capacity needs to be maintained for different soil amendments (Kramer, 1983).

Three different approaches to evaluating drought responses in plants can be followed; 1) varying irrigation intervals, 2) irrigating gravimetrically to different water content levels, and 3) measuring survival duration (days) after irrigation termination.

One method of introducing water-deficient conditions is by irrigating the pots at different time intervals to field capacity, whereby the irrigation interval is increased to simulate periods of water stress in a drying cycle (Kramer, 1983). The short irrigation cycle is the water-unstressed control, and the longer irrigation cycles are the water-stressed experiment. This irrigation interval approach to water stress greenhouse studies was used by Ogbonnaya *et al.* (1998), Kirkham (2005) and Agaba *et al.* (2010).

A second approach is to water the control and treatments gravimetrically to different fractions of field capacity. In the control group, referred to as 'water-unstressed', the soil water content is maintained at high field capacity % (FC) range (i.e. 90% to 70%) while in the 'water-stressed' groups the water content is maintained at a lower FC % range, (i.e. 60% to 40%) (Gavili *et al.*,2018; Kammann *et al.*, 2011; Nyathi *et al.*, 2016; Zhang *et al.*, 2005). The pots are then allowed to dry out to the minimum of each range in repeated cycles of moderate water stress (Gavili *et al.*, 2018; Kammann *et al.*, 2011; Zhang *et al.*, 2005).

A third method is to grow plants under favourable environmental conditions with sufficient water until the desirable plant size, after which all irrigation is suspended and the treatments are allowed to dry until permanent wilting occurs (Agaba *et al.*, 2010; Clarke & Stone, 2018; Mulcahy *et al.*, 2013). This method utilises the differences in plant-available water due to different amendment mixtures , where a longer survival duration is interpreted as an increase in drought resistance. Clarke *et al.* (2018, unpublished) utilised this method to investigate the effect of WTR amendment to a sandy soil on the drought resilience of spinach. Despite apparent visual differences between treatments, none of the parameters measured a drought response.

This study will follow the approach of irrigating to different water levels; the method will allow for chronic water stress development of a fast-growing crop under greenhouse conditions. The amount of irrigation water added for each water level (water-stressed and water-unstressed) will be based on the field capacity of that particular soil amendment mix, rather than that of the control, allowing the plants to utilise the potential increase in plant-available water as a result of the soil amendment (Hansen *et al.*, 2016; Kammann *et al.*, 2011).

Both nutrient and water availability will have profound effects on the root architecture and growth (Ekinci *et al.*, 2015; García *et al.*, 2008; Hansen *et al.*, 2016; Williamson *et al.*, 2001). Limited P availability, which is immobile within the soil, reduces root cell elongation and will favour lateral root growth over primary root growth. The availability of immobile nutrients tends to decrease with soil depth (Williamson *et al.*, 2001). Similarly, in response to limited N, the plant may increase root growth to sustain nitrogen uptake for photosynthesis (Bonifas *et al.*, 2005). Water availability will influence plant root development (Ekinci *et al.*, 2015; García *et al.*, 2008; Hansen *et al.*, 2016). Experiments on trefoil (*Lotus tenuis*) showed that water stress decreased both shoot and root growth, which in turn alters the nutrient uptake (García *et al.*, 2008).

The partitioning of biomass between the roots and shoots will also change in response to nutrient and water availability (Bonifas *et al.*, 2005; Johnson & Johnson, 2017; Kramer, 1983). The root: shoot ratio is severely affected by nutrient supply, the ratio will increase in response to limited nutrients, as the plant physiology responds to access the limited nutrient supply (Bonifas *et al.*, 2005; Johnson & Johnson, 2017). Root development is less affected by water stress than that of shoot growth, increasing the root: shoot ratio (Kramer, 1983).

In-depth knowledge of the interaction between WTR and the soil-plant system is critical. Knowing whether the WTR-amended soil system will predominantly be influenced by the soil physical or soil chemical changes due to WTR application to sandy soil is crucial. Furthermore, investigating whether the co-application of WTR and compost will be more beneficial than a single amendment of WTR with respect to WUE and biomass production.

To determine whether the effect of WTR addition results in a predominantly soil physical or soil chemical change, a greenhouse experiment with two water application levels and two fertiliser application levels were conducted. The water-deficient treatment is referred to as water-stressed, which will be an analogue for drought conditions, while water-unstressed will be the analogue for optimal water application.

4.2 <u>Materials and Methods</u>

4.2.1 Greenhouse study

The greenhouse study was designed as a 2 x 2 x 6 factorial ANOVA to investigate the growth of Swiss Chard (*Beta vulgaris* cicla.) in a sandy soil amended with compost, WTR and a WTR-compost co-amendment (Table 4.1) in response to water and nutrient-induced stress. The greenhouse experiment also investigated the soil physical and soil chemical effects of the treatment combinations.

Table 4.1 Amendment mixture ratios

Amendment mixture	**Material and mixing ratio w/w% [a]**
Control sand	100% aeolian sand
10% compost	90% sand + 10% compost
20% compost	80% sand + 20% compost
10% WTR	90% sand + 10% FeWTR (2018)
20% WTR	80% sand + 20% FeWTR (2018)
WTR-compost	80% sand + 10% compost + 10% FeWTR (2018)

[a] The weight (g) of each amendment mixture were calculated based on the w/w % ratio, based on the container volume, and a bulk density of 1.5 g/cm^3 to ensure the ratios are constant throughout

4.2.1.1 Crop selection

Swiss Chard Charsano RZ F1 (69-600) from Rijk Zwaan South Africa (Pty) Ltd. was used for the greenhouse experiment. This variety is fast growing and has low genetic diversity among seeds and will yield uniform growth between seeds (“Rijk Zwaan”, 2019). Swiss Chard is an annual short-season leafy vegetable with a shallow root system and is sensitive to water stress (Ekinci *et al.*, 2015; Stanley & Maynard, 1990; Vittum & Flocker, 1967). The leaves of Swiss Chard are consumed, and there is no other biological structure apart from the roots and leaves that trace elements can accumulate within. Metal analysis of the leaves is, therefore, an accurate approximation of potential plant toxicity and nutrient deficiencies.It is therefore is ideal for a short duration study investigating the effects of water-deficit conditions, nutrient availability and trace metal toxicity in response to the application of WTR, compost and WTR-compost co-application.

4.2.1.2 Amendment mixture

The FeWTR was collected from Faure WTP (June 2018), air dried, crushed and sieved to < 2 mm. The compost from Reliance Compost is store-bought and used without any alteration. The sand was collected from Jacobsdal Farm, Kuilsrivier, South Africa (-33.967350 S,18.717388 E) air-dried and sieved to < 2 mm. The sand, compost and FeWTR (2018) are described and characterised in Chapter 2.2.1. Henceforth, WTR will refer to FeWTR (2018), if not explicitly stated otherwise.

The method of WTR application will dramatically influence the plant WTR interaction, since the effect of WTR is limited to the solid itself and not the liquid leachate thereof (Cox *et al.*, 1997; Geertsema *et al.*, 1994; Moodley *et al.*, 2004). The treatments (Table 4.1), with a total mass of 4.5 kg, were mixed to homogeneity in a plastic bag after which they were transferred to 6-litre pots with a 1 mm plastic mesh screen and glass wool in the base of the container to retain the mixtures while allowing for water movement. The amendment ratios of 10% and

20% equate to 225 and 450 tons/ha respectively. Each pot was placed on a saucer to collect leachate. Six equally spaced Swiss Chard seeds were planted, in each pot and thinned to three uniformly sized plants 14 days after sowing (DAS). The small container size was chosen based on available greenhouse space, practical feasibility and the short duration of the trial (Johnson & Johnson, 2017).

4.2.1.3 Fertiliser application and drought simulation

The fertilised treatments received fertiliser based on a leafy vegetable specific program from YARA South Africa (Pty) Ltd. 400 kg/ha SuperStart fertiliser (30.8, 30.8, 30.8, 40.0, 3.2, 27.6 mg of N, P, K, Ca, Mg, S, respectively) was mixed into the growth medium before planting after which the fertilised treatment groups received the equivalent of 150 kg/ha Unika Kali fertiliser (18.6, 0.0, 18.9, 15.8, 2.3, 4.4 mg of N, P, K, Ca, Mg, S, respectively) weekly for the duration of the trial.

Two water content levels were introduced after the plants were well established in their vegetative growth stage under water-unstressed conditions, 23 DAS. The water content (levels) are a percentage of the field capacity, which was determined with pressure plates at -10 kPa (Oosterveld & Chang, 1980). The water-unstressed treatment were watered to 90% of field capacity (FC), and the water-stressed, to 50% of FC. These water contents were maintained for 20 days. The limited water application of 50% (FC) aimed to induce chronic water-deficient conditions (Hansen *et al.*, 2016). Nether water content resulted in a loss of water-soluble nutrients through leaching since the water application never exceeded field capacity. The irrigation requirement for each pot was calculated gravimetrically after which the pot was watered from above.

The plant response after the trial was expressed as the above-ground biomass production per unit of water. The cumulative water use was gravimetrically recorded to calculate the WUE.

The experiment consisted of 20 treatment combinations; 6 amendment mixtures, 2 water levels and 2 fertiliser levels, with three replicates of each; resulting in 60 experimental units (pots) (Table 4.2). The amount of experimental units were based on the greenhouse size and the time needed to conduct measurements, based hereupon, no fertilized 10% amendment mixtures were included in the experimental setup. The 60 experimental units were arranged in a completely randomised block design. The pots were moved at random daily to prevent the effects of micro-climate variations within the greenhouse (Brien *et al.*, 2013). The average daytime temperature of the greenhouse was 20.4 ± 4.1 °C with 13.5 ± 0.5 hours of daylight (Time and Date, 2019).

Table 4.2 Experimental design of the 2 x 2 x 6 factorial layout resulting in 20 treatment combinations

Amendment mixture [a]	Water level [b]	Fertiliser level [c]
Control sand	S	0
Control sand	U	0
Control sand	S	F
Control sand	U	F
10% WTR	S	0
10% WTR	U	0
20% WTR	S	0
20% WTR	U	0
20% WTR	S	F
20% WTR	U	F
10% Compost	S	0
10% Compost	U	0
20% Compost	S	0
20% Compost	U	0
20% Compost	S	F
20% Compost	U	F
WTR-compost	S	0
WTR-compost	U	0
WTR-compost	S	F
WTR-compost	U	F

[a] Amendment mixture (Table 4.1)

[b] S - Water-stressed 50% of FC; U - Water-unstressed 90% of FC

[c] F - Fertilised; 0 – Unfertilised

4.2.1.4 Measurements during the trial

Over the duration of the greenhouse study, daily soil water measurements were taken gravimetrically, with a four decimal (kg) scale. The plant leaf length was measured weekly with a 300 mm steel ruler to the nearest mm. The leaf colour of the second oldest leaf was measured non-destructively with a SPAD 502DC Plus Chlorophyll meter. Photographs with a mm ruler for scale were taken of each pot against a white background at weekly intervals for a visual comparison of the plant response to the different treatment combinations. The plants were inspected during each irrigation, to monitor for diseases and visual nutrient deficiency signs.

4.2.1.5 Post-harvest

After 43 days, the Swiss Chard plants were harvested. The roots and shoots were separated after being cut at ground level and photographed. The roots were carefully separated by hand as well as dry sieving from the soil material; the final sand was washed from the roots and dried with a paper towel. The above and below-ground biomass was determined after drying for 24 hours at 65°C after which the weight was determined using a 0.001 g scale.

The relation between biomass production and water use (WUE) will be used as the primary indicator of the effect of the treatment combinations, fertiliser application and water deficit. $WUE = Y/ET$ Where Y is oven-dried above-ground biomass (g) and ET is the total irrigation water applied (ml) (Leskovar & Piccinni, 2005; Nyathi *et al.*, 2016).

The root: shoot ratio was calculated as the root biomass divided by the shoot biomass (Lynch *et al.*,2011). The leaves were analysed for foliar metals (Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn.) and macronutrients (N, P and K). The P and K of the unfertilised treatments for both water-stressed and water-unstressed treatments were extracted in a 1:1 plant material: solution ratio of 32% HCl by the Elsenburg laboratories. The foliar N was extracted following the Kjeldahl method. The Central Analytical Facility (CAF) at Stellenbosch University analysed the same. 1:1 plant material: solution ratio of 32% HCl for foliar metals with ICP-AES spectroscopy. method.

4.2.1.6 Soil chemical measurements

The mineral nitrogen was determined in the soils used in the pot trial by extracting 1:10 soil: solution of a 2 M KCl solution at the field moist condition (extraction weight adjusted for moisture content). For the measurement of the available nitrogen extracted from the soils, Merck spectroquant Nitrate (14773) and Ammonium (100683) test kits were used. Both kits come equipped with pre-mixed chemicals used to measure the nitrate and ammonium in 2 M KCl. The absorbance was measured in a spectrophotometer (Spectroquant Pharo300 MERCK) equipped with the included calibration standard for each test.

Available phosphate was colorimetrically determined at 660 nm from 10 ml of a 1:10 soil: solution ratio of Mehlich 3 (0.2 N acetic acid; 0.25 N NH_4NO_3; 0.015 NH_4F; 0.013 N HNO_3; 0.001 M EDTA) following the method of Myers & Pierzynski (2000). The soil pH of all the treatments was conducted in a 1:2.5 soil: solution ratio in 1 M KCl (The Non-Affiliated Soil Analysis Work Committee, 1990). The electrical conductivity was measured in a 1:2.5 soil: solution ratio in 1 M KCl after 10 minutes of shaking (Sonmez *et al.*, 2008).

4.2.2 Statistical analysis

Data were analysed using parametric statistical tests with the RStudio statistical Package. All error bars on graphs are the standard error ($s_{\bar{x}}=s^2/n$). If $p < \alpha$, the result is deemed significant, where alpha is 0.05. A 2 x 2 x 6 Factorial ANOVA tests were performed on the WUE, pH, Mehlich-3 phosphate and 2 M KCl extractable nitrogen to determine the effect of the amendment mixtures (6), water level (2) and fertiliser level (2). A 2 x 6 factorial ANOVA was performed on the germination with amendment mixtures (6) and fertiliser level (2). A single factor ANOVA on the foliar macronutrients were performed to investigate the effect of the treatment combinations. To analyse for significant differences between and within treatments

Post hoc Tukey HSD test were performed (only when there was no significant interaction between the levels). The ANOVA validity assumptions of normality and homoscedasticity were visually based on the normal Q-Q plots.

4.3 Results and Discussion

The germination success of the various treatment combinations was analysed with a 2 x 6 factorial ANOVA of fertiliser and treatment showed no interaction between levels ($p > 0.05$). Neither the amendment mixture nor fertiliser application level had a significant effect on the germination of the Swiss Chard seeds, ($p > 0.05$).

The lack of any significant difference in germination shows that all the treatment combinations can support the initial growth and germination of the Swiss Chard. Furthermore, no plants died over the course of the trial. Despite the initial equal performance of the Swiss Chard, clear differences in growth and biomass production in response to the treatments can be seen in the later vegetative growth stages (Table 4.3, Figure 4.1). The unfertilised treatments of 10% and 20% WTR, as well as the control, showed, for both water levels, severely stunted growth and low biomass production (Table 4.3, Figure 4.1). The addition of fertiliser resulted in a marked increase in biomass production of the control treatment, while the 20% WTR treatment did not show the same pronounced response, with the Swiss Chard still being severely stunted (Table 4.3, Figure 4.1).

The WTR-compost co-amendment had a higher biomass production than the 20% WTR single treatment for all fertiliser and water combinations. The unfertilised WTR-compost treatments fared better than the control sand, while it was outperformed by the unfertilised 10% and 20% compost treatments for both water levels (Table 4.3). With the addition of fertiliser to the WTR-compost co-application, the water-unstressed treatment was only outperformed by the water-unstressed 20% compost treatments (both water levels). The highest biomass production was for the water-unstressed fertilised 20% compost treatment. The reduction in biomass of Swiss Chard in response to water-deficient conditions were also reported by Nyathi *et al.* (2016). To accurately relate the growth response of the Swiss Chard grown in different treatment combinations, the total amount of water used over the duration of the trial should also be considered.

Table 4.3 Biomass and water use results of the different treatment combinations. (n=3)

Amendment mixture	**Water level [a]**	**Fertiliser [b]**	**Shoot biomass (g)**	**Leaf [c] (cm)**	**Root biomass (g)**	**Water use (ml/day)**	**Root: shoot ratio**
Control sand	S	0	0.058	3.100	0.125	86.346	2.2
Control sand	U	0	0.126	4.767	6.167	107.475	3.4
Control sand	S	F	1.820	10.100	0.503	110.017	4.0
Control sand	U	F	3.010	12.122	6.123	120.915	2.0
10% WTR	S	0	0.074	3.244	0.131	88.842	1.8
10% WTR	U	0	0.080	3.622	0.195	117.213	2.4
20% WTR	S	0	0.058	3.056	0.070	82.662	1.2
20% WTR	U	0	0.037	3.100	0.595	115.328	2.6
20% WTR	S	F	0.231	4.900	0.100	97.379	2.7
20% WTR	U	F	0.409	6.300	0.724	125.701	1.8
10% Compost	S	0	1.438	8.589	4.631	94.186	3.2
10% Compost	U	0	2.509	10.633	6.441	128.891	2.6
20% Compost	S	0	2.472	9.356	0.070	100.852	1.2
20% Compost	U	0	4.733	12.356	4.320	133.911	1.4
20% Compost	S	F	3.042	9.989	8.916	102.426	1.9
20% Compost	U	F	6.306	14.522	6.994	133.279	1.1
WTR-compost	S	0	0.974	7.000	1.456	88.764	1.5
WTR-compost	U	0	2.215	10.256	2.861	118.497	2.5
WTR-compost	S	F	1.162	7.678	7.332	91.393	3.3
WTR-compost	U	F	4.402	13.289	8.826	134.101	2.0

[a] S-Stressed 50% of FC; U-Unstressed 90% of FC

[b] F- Fertilized; 0 – Unfertilised

[c] Longest leaf measured from the soil surface to the leaf tip.

[d] The % change in WUE between water levels for a specific treatment and fertiliser application

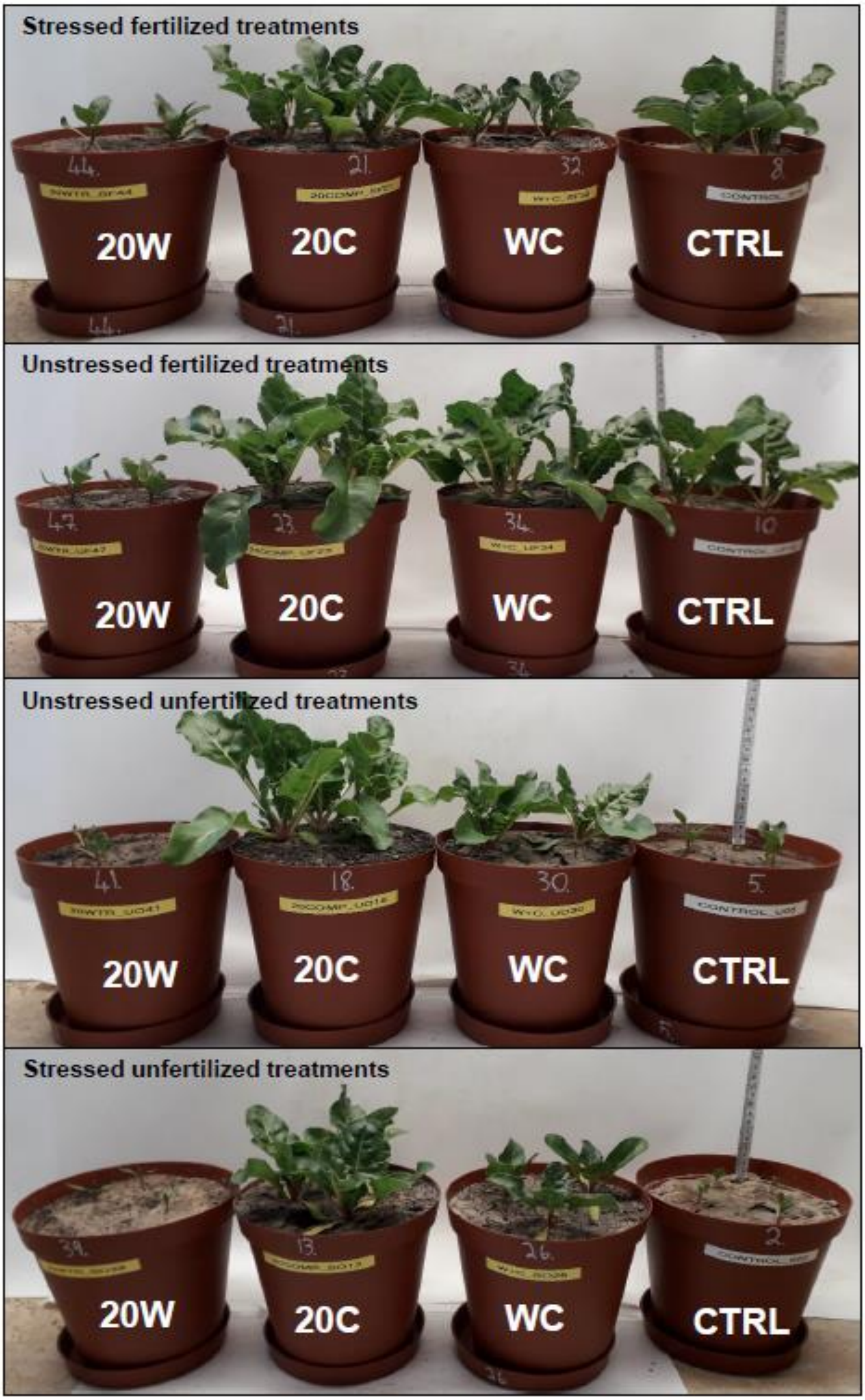

Figure 4.1 The final size of the plants 43 DAS. 20W- 20% WTR treatment; 20C- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand. cm-scale in control pot.

4.3.1 Water use efficiency

The water use efficiency, was calculated for all treatments (Figure 4.2). The 2 x 2 x 6 factorial ANOVA of fertiliser, water and treatment showed a significant interaction between levels ($p > 0.05$). Subsequently, no further statistical analysis of the factorial ANOVA was performed. The interaction indicates that these factors superimposed on each other had vastly different effects on plant performance and WUE than each of the factors in isolation. The 20 treatments were analysed as a single factor ANOVA ($p < 0.05$), and all further discussion with regards to WUE is based thereupon. A Post-Hoc Tukey HSD test was performed on the 20 treatment options; significant differences are displayed in Figure 4.2. The addition of WTR and compost to the control sand had significant effects on the WUE. Furthermore, Figure 4.2 shows that both water and fertiliser application resulted in differences within each treatment.

The stunted nature of some of the treatments, most notably the WTR single amendments, resulted in low biomass production and ultimately a low WUE. This, coupled with the single factor ANOVA not distinguishing between treatments, fertiliser application, and water level, makes statistical differentiation between results difficult. As a result, there were no significant differences in WUE within certain treatments with respect to water and fertiliser applications. However, there are trends, in that the biomass of certain combinations are higher than others with the same treatment with respect to different water and fertiliser application levels. These trends, although not significant, will still be discussed.

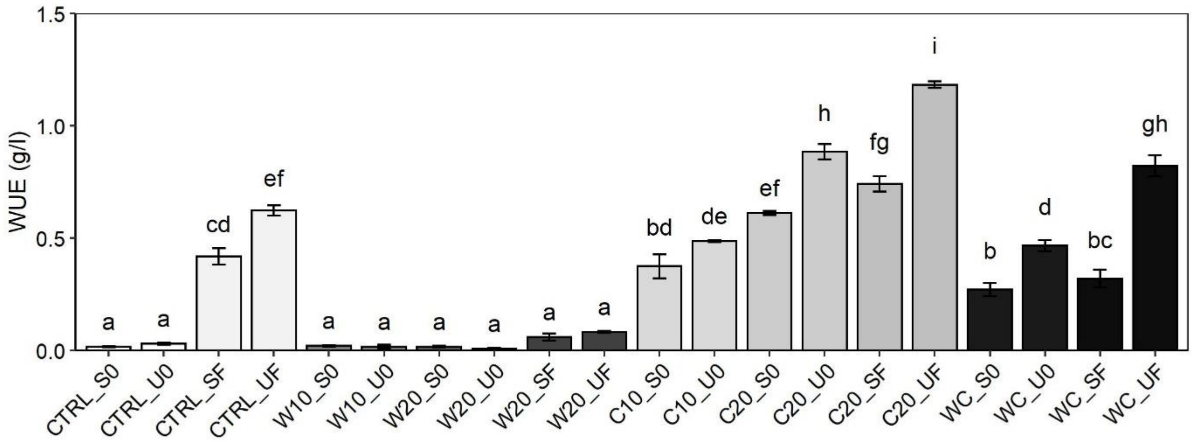

Figure 4.2 The WUE (g/l) of all treatments.Treatment combinations that are not significantly different from each other shares the same letter. All significance levels are set at $p<0.05$. 10W- 10% WTR treatment; 20W- 20% WTR treatment; 10C- 10% compost treatment; 20C- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand.

4.3.1.1 Control sand

The unfertilised control sand samples showed an insignificant increase in WUE between the water application levels (Table 4.3, Figure 4.2), with the WUE of the water-unstressed control 1.7 times higher than the water-stressed unfertilised control. The WUE of the water-unstressed fertilised control sand increased 21-fold with relation to the water-unstressed unfertilised control samples (Figure 4.1). The effect of fertiliser addition was evident with the unfertilised water-stressed control having a significantly lower WUE than the fertilised equivalent (Figure 4.2), with the effect on biomass production shown in Figure 4.1. Furthermore, the fertilised control sand samples showed a significant increase in WUE between the water application levels (Table 4.3, Figure 4.1). The ability of Swiss Chard to tolerate drought conditions (water stress) was significantly increased by the addition of fertiliser.

4.3.1.2 WTR single amendment

The Swiss Chard grown in the WTR treatments showed poor, stunted growth (Figure 4.1). The stunted growth resulted in insignificant changes within the WTR treatment; however, there are still observable trends. Although not significant, the application of WTR (samples 10W and 20W) affected the WUE. Increasing the WTR loading from 10% to 20% without fertiliser decreased the WUE, despite the increase in water use (Table 4.3). Furthermore, relative to the unfertilised control, the water-unstressed 20% WTR treatment resulted in a 3.6-fold decrease in WUE and, the water-stressed 20% WTR treatment showed no difference to the control. Fertiliser addition to the water-unstressed 20% WTR treatment resulted in a 10-fold increase in WUE.

Fertiliser application to the 20% WTR treatment did increase the drought tolerance of the Swiss Chard. The effect of the fertiliser application to the 20% WTR treatment was not as pronounced as the control sand (Figure 4.1).

4.3.1.3 Compost single amendment

The compost amended sand had the highest biomass production and WUE. The water-unstressed fertilised 20% compost treatment had the highest WUE, followed by the unfertilised water-unstressed 20% compost treatment. In relation to the unfertilised control, the unfertilised 20% compost treatment resulted in a 30-fold increase in WUE for the water-unstressed application and a 36-fold increase under water-stressed conditions.

For the unfertilised 10% compost treatment, increasing the water application did not result in a significant increase in WUE. Fertiliser addition to the water-stressed 20% compost treatment did not increase the WUE significantly, while an increase in water application for both fertilised and unfertilised compost treatments increased the WUE significantly. The unfertilised water-unstressed 20% compost treatment had a significantly higher WUE than the fertilised water-stressed 20% compost treatment. In relation to the 20% compost treatments, the change in WUE is more pronounced between water application levels than fertiliser levels. With the addition of compost, the effect of drought (water-deficient conditions) on Swiss Chard growth is more pronounced than the effect of nutrients.

4.3.1.4 WTR-compost co-application

For both fertiliser levels of the WTR-compost co-application treatment, increasing the water application increased the WUE significantly (Figure 4.2). In relation to the unfertilised water-unstressed control the unfertilised water-unstressed WTR-compost co-application treatment resulted in a 16-fold increase in WUE. While the unfertilised water-stressed WTR-compost co-application treatment also resulted in a 16-fold increase in WUE relative to the unfertilised water-stressed control.

For the water-stressed WTR-compost co-application treatment, fertiliser addition did not increase the WUE significantly; in contrast, the water-unstressed WTR-compost co-application showed a significant WUE increase with fertiliser addition. This relationship between water-stress and fertiliser was also observed in the 20% compost treatments. The change in WUE of the WTR-compost co-application is more pronounced between water application levels than fertiliser levels. With the addition of the WTR-compost co-application, the effect of water stress on Swiss Chard growth is more pronounced than the effect of nutrients.

Within a treatment, water deficit conditions reduced the WUE of the Swiss Chard, which echoes the results of Ekinci *et al.* (2015), Gavili *et al.* (2018) and Zhang *et al.* (2015). Furthermore, the nutrient status also influences the WUE for a specific treatment (Ekinci *et al.*, 2015; Hatfield *et al.*, 2001; Zhang *et al.*, 2015). The results from this study concur, the type of treatment, water stress level and available nutrients will affect the Swiss Chard growth response, as reflected in the WUE and visual differences (Figure 4.1).

If the treatment contains sufficient nutrients, and the nutrient requirements of the Swiss Chard are satisfied, only then will the Swiss Chard be able to utilise the increase in the water application. Within a treatment, the nutrients are the primary limiting factor; water is only a limiting factor if the nutrient requirement of the Swiss Chard is satisfied. The drought resistance of Swiss Chard grown in different treatment combinations is therefore affected by both factors, which is dependent on the treatment combination. With the unfertilised control and 20% WTR single amendments, the nutrients were limiting, limiting the Swiss Chards ability to benefit from the increase in water application. The Swiss Chard in these treatments will not be robust to drought conditions.

In contrast, the WTR-compost co-application and 20% compost treatment yielded more robust Swiss Chard plants due to their higher nutrient status, increasing their drought tolerance. With respect to the control sand and WTR single amendment, WTR-compost co-application does increase the drought tolerance of Swiss Chard.

These results suggest that for optimum utilisation of WTR, it should be applied as a co-application with compost. WTR, as a single amendment is detrimental to plant growth. Similarly, Lucas *et al.* (1994) reported a decrease in biomass production of fescue grass with the application of 2% AlWTR; and the reduced plant response was attributed to phosphate deficiencies related to WTR application. Oladeji *et al.* (2009) found that 2.5% AlWTR reduced the dry matter production of Bahia grass (*Paspalum notatum* F.) cultivated in sand. The reduction of biomass production by WTR application is in contrast to Hsu & Hseu (2011), who found an increase in biomass production by a single amendment of 2.5% AlWTR, despite the decrease in plant-available phosphate.

Hsu & Hseu (2011) also found that co-applied AlWTR and compost yielded a significant increase in biomass production of Bahia grass. Johnson & Johnson (2017) and Walpole & Johnson (2012) found that the co-application of compost and FeWTR outperformed the control and single amendment of FeWTR with regards to biomass production of wheat (*Triticum aestivum* L.). Results from this greenhouse experiment show that the co-application of FeWTR and compost resulted in a significant increase in WUE of Swiss Chard with respect to the control and WTR single treatments but was outperformed by the compost alone at all water and fertiliser levels. This result is in contrast to the findings of Clarke *et al.* (2019) who showed with a 3-month wheat greenhouse study, that co-application of WTR and compost was more favourable than compost or FeWTR alone. The contrasting results may be related to the longer duration of the aforementioned study, or crop choice.

4.3.2 Soil pH

A single factor ANOVA on the pre-trial treatment combinations showed a significant difference in pH measured in KCl ($p < 0.05$) (Figure 4.3). The addition of any material to the control sand increased the pH. The pH of the control sand is 4.3 in KCl. Adding WTR increased the pH to 5.7 and 5.9 for 10 and 20% of WTR, respectively, whilst compost addition had the most significant change in pH with 6.4 and 6.9 for 10 % and 20% compost treatments, respectively. Adding WTR and compost as a co-application resulted in a 6.8 pH in KCl (Figure 4.3).

The post-trial pH (KCl) was subjected to an unbalanced factorial ANOVA. The 2 x 2 x 6 factorial ANOVA of fertiliser, water and treatment showed no significant interaction between levels ($p > 0.05$). Neither fertiliser application nor water application level had significant effects on the pH ($p > 0.05$). Henceforth the pH will refer to the treatment combination with no further distinction within each treatment due to fertiliser or water application level (Figure 4.3). The treatment combination had a significant effect on the pH (KCl) ($p < 0.05$) (Figure 4.3).

All treatment combinations are different from the control (Figure 4.3). With respect to the pre-trial pH, the pH for all treatments increased. Over the duration of the trial, the 20% WTR treatment increased to 6.9, and the WTR-compost co-application resulted in a pH of 7.07, while the control sand pH only increased to 4.5. The highest measured pH was for the 20% compost treatment at 7.2.

The post-trial EC values for all treatment combinations, of amendment mixture, fertiliser and water levels were not significantly different, as shown by the unbalanced factorial ANOVA. The 2 x 2 x 6 factorial ANOVA of fertiliser, water and treatment showed no significant interaction between levels ($p > 0.05$), and neither level had any significant effect.

The increase in pH after the addition of WTR is in contrast to a study by Mahdy *et al.* (2020), who found that WTR and biosolids addition decreased the pH of the soil; which is attributed to their pH being lower than that of the soil. However, the control sand of this study had a much lower pH than that of the WTR and compost.

The capacity of WTR to act as a liming agent is noted by various studies (Heil & Barbarick, 1989; Kim *et al.*, 2002; Van Rensburg & Morgenthal, 2003; Wai *et al.*, 2012). The ability of WTR to act as a pH buffer is due to small amounts of the carbonates present within the WTR as a by-product of the lime added during the water treatment process.

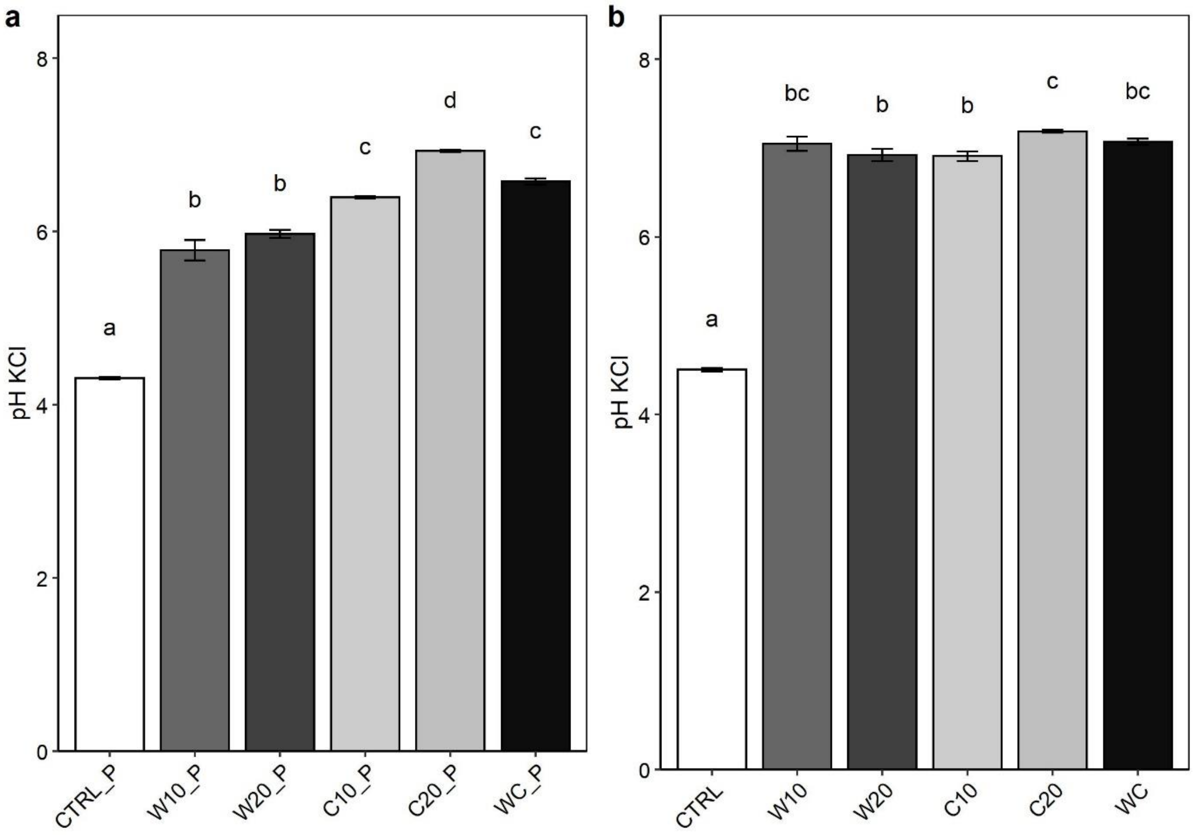

Figure 4.3 The pH in KCl of the treatment combinations, pre- and post- pot trial. a) the pre-trial KCl pH and b) the post-trial KCl pH. Treatment combinations that are not significantly different from each other share the same letter. All significance levels are set at $p<0.05$. W10- 10% WTR treatment; W20- 20% WTR treatment; C10- 10% compost treatment; C20- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand.

4.3.3 Plant available phosphate

The unfertilised treatments were used to investigate the effect of the treatment combination and water application level on the post-trial plant-available P. The 2 x 6 unbalanced factorial ANOVA of water application and amendment mixturesshowed no significant interaction ($p > 0.05$). The factorial ANOVA results can be used on each unfertilised treatment and water application level to investigate their effect on plant-available P. The water application level did not result in a significant effect on the plant-available P within a given treatment ($p > 0.05$). The treatment did result in a significant change in plant-available P ($p < 0.05$). A Post-Hoc Tukey HSD test was performed on the six treatment combinations; significant differences are displayed in Figure 4.4.

The addition of WTR, compost and their co-application to the sand influenced the availability of P. The plant-available P does not differ significantly between the two water application levels indicating that its availability is independent of water application. From here on, the average P concentration (mg/kg) for each treatment will be reported, with no further distinction based on the water level. The sand is P poor, and the primary source of P in the unfertilised treatments is the compost. An increase in compost loading increased the plant-available P from 0.18 mg/kg for the control sand, to 2.39 mg/kg for 10% compost, and 4.83 mg/kg for 20% compost treatment. The plant-available P in the WTR single amended treatments is less than that of the control. Increasing the WTR loading resulted in a decrease in plant-available P, from 0.16 mg/kg to 0.13 mg/kg for 10% and 20% WTR loadings, respectively. Similar to the reduction in plant-available P of the sandy soil amended with WTR, Novak & Watts (2004) also reported a reduction in plant-available P in sandy soil. In the case of WTR and compost co-application, the plant-available P is higher than that of the control at 1.26 mg/kg. The WTR-compost co-amendment contains the same amount of compost as the 10% compost treatment; however, the plant-available P is lower indicating that the WTR reduces the plant-available P. The compost, being a source of P, can offset the effect of the WTR adsorption of P (Hsu & Hseu, 2011). The organic matter of the compost can adsorb to the WTR, reducing its specific surface area by blocking some of the micropores, which in turn reduces the capacity of the WTR to absorb and immobilise P (Kaiser & Guggenberger, 2003).

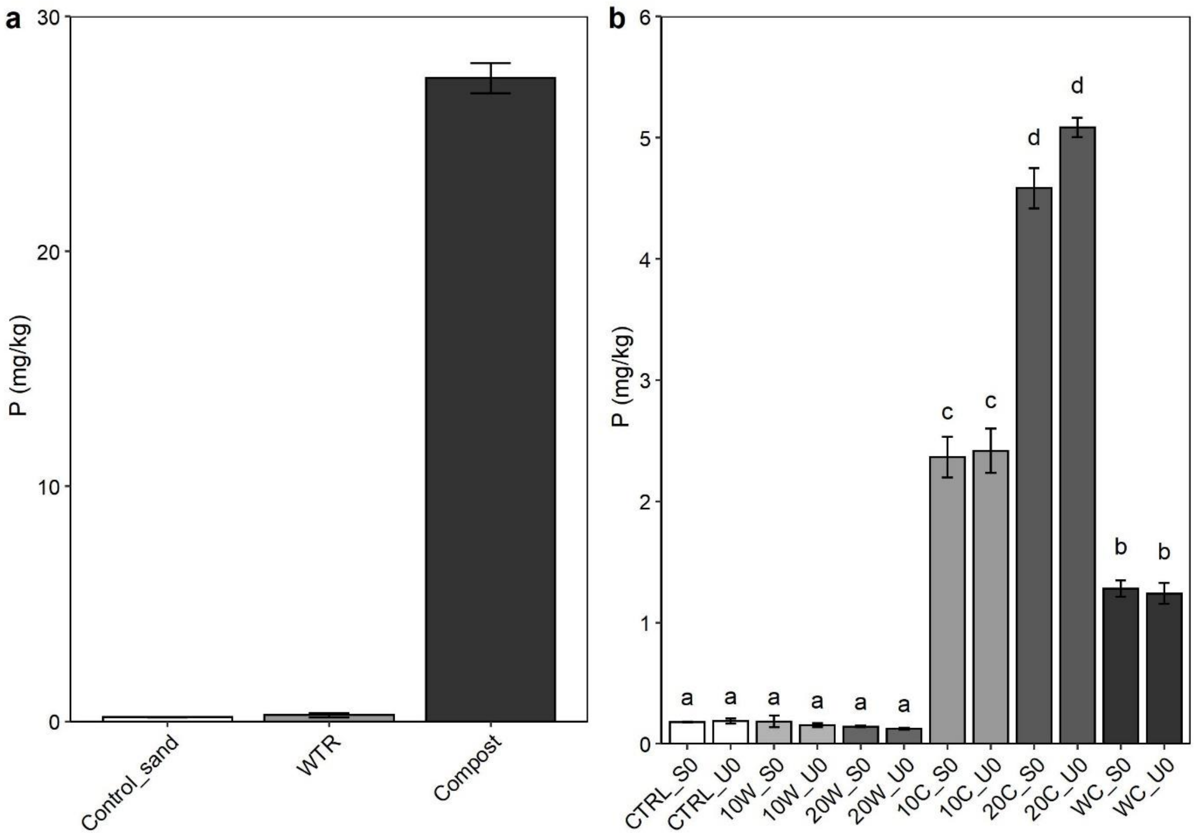

Figure 4.4 a) The plant-available phosphate of the individual materials. b) Plant available phosphate of the treatment combinations. Treatment combinations that are not significantly different from each other share the same letter. All significance levels are set at $p<0.05$. 10W- 10% WTR treatment; 20W- 20% WTR treatment; 10C- 10% compost treatment; 20C- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand.

4.3.4 Plant available nitrogen

The unfertilised treatments were used to investigate the effect of the treatment combination and water application level on plant-available N (mg/kg). A 2 x 6 unbalanced factorial ANOVA with water application and amendment mixture was conducted, with no significant interaction between the levels ($p > 0.05$). A Post-Hoc Tukey HSD test was performed on six treatment combinations to investigate the effect of treatments and water application on the total N content (Figure 4.5). The addition of material to the sand resulted in significant changes in plant-available N between treatments ($p < 0.05$). The addition of WTR single amendments increased the plant-available N from 17.78 mg/kg in the control sand to 20.94 mg/kg and 27.21 mg/kg for the 10% and 20% loadings respectively. The increase in plant-available N is in alignment with various studies that have reported that WTR addition increased the total N content of the WTR- amended soil (Heil & Barbarick, 1989; Oh *et al.*, 2010; Van Rensburg & Morgenthal, 2003; Skene *et al.*, 1995). The plant-available N for the compost amended sand was lower than the control; this may be due to the larger Swiss Chard plants of the 10% compost treatment having a higher N requirement. The 10% compost loading only contained 10.80 mg/kg, and the 20% loading 15.53 mg/kg N. The plant-available N of the WTR-compost co-application was 21.62 mg/kg. The unstressed treatments had a lower N content than the stressed treatments for all treatment combinations; the amount of irrigation water therefore influenced the plant-available N ($p < 0.05$).

The limited water can interfere with plant processes, reducing photosynthesis due to stomatal closure and related metabolic processes (Zhang *et al.*, 2015). The biomass production of the stressed WTR-compost co-application and 20% compost treatments is lower than the unstressed counterparts, which may be attributed to the metabolic slowdown that resulted from the water deficiency.

The water-unstressed Swiss Chard grew faster than that of the water-stressed treatments, depleting the limited N source faster (Liu *et al.*, 2006). The smaller plants of the water-stressed treatments did not deplete the available N as occurred with the water unstressed plants. If this experiment were allowed to go on longer, the treatments would likely have the same foliar N content, since the nutrients are the limiting factor, rather than the water, over an extended growth period. Water is an acute limiting factor, while nutrient availability is a chronic long-term growth-limiting factor.

Despite the high plant-available N in the 10% and 20% WTR treatments, the biomass production for both water levels is low (0.08 g and 0.037 g, respectively, for the water-unstressed, unfertilised treatments) (Table 4.3). In comparison, the biomass production for 10% and 20% compost treatments was much higher (Table 4.3) for both water levels. For this short trial duration, the limiting nutrient was not N, but rather P (Figure 4.4,Figure 4.5 and Table 4.3).

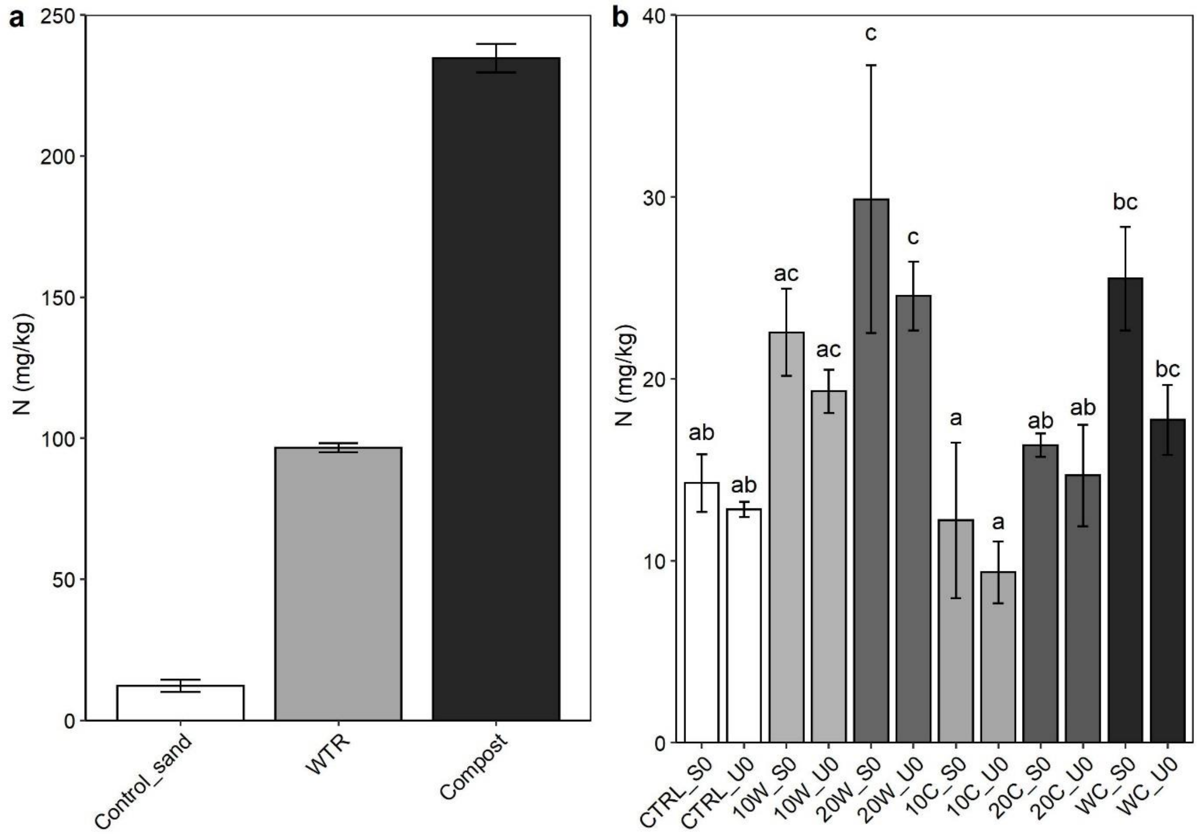

Figure 4.5 a) Total plant-available nitrogen of each component. b) Total plant-available nitrogen of each unfertilised treatment. Treatment combinations that are not significantly different from each other share the same letter. All significance levels are set at $p<0.05$. 10W- 10% WTR treatment; 20W- 20% WTR treatment; 10C- 10% compost treatment; 20C- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand.

4.3.5 Plant roots

Similar to shoot growth, root growth is also affected by limited water and nutrients (Figure 4. 6 - 4.9, and Table 4.3). Both the nutrient level and the water-stress influenced the root: shoot ratio (Table 4.3). Bonifas *et al.* (2005) showed that nitrogen supply would increase the root: shoot ratio of corn (*Zea* mays L.) and velvetleaf (*Abutilon* theophrasti). The increased root growth in the unfertilised treatments is in response to the limited nutrients, as more extensive root systems are needed to access this limited nutrient supply (Lynch *et al.*, 2011). Within all treatments where water is sufficient (water-unstressed), the root: shoot ratio decreased from the unfertilised to fertilised treatments, in accordance with the finding of Bonifas *et al.* (2005) (Table 4.3). In contrast, Swiss Chard grown in water-deficient conditions, the root: shoot ratio increases with fertiliser application, with the exception of 20% WTR treatment (Table 4.3). The increased root growth relative to the shoot growth despite the nutrient availability due to fertiliser addition is in response to the water deficit rather than the nutrients (Lynch *et al.*, 2011). Under drought (water stress) conditions, plants increase root growth to access limited water (Kramer, 1983). The root: shoot ratio changes in response to nutrients and water indicate that only when nutrients are sufficient, will the Swiss Chard be able to respond to the water deficiency (Lynch *et al.*, 2011). A soil medium with sufficient nutrients will allow the plant to utilise the limited water source, through plant responses like a more extensive root network. This interaction between nutrient and water availability is also seen in root morphological changes.

Morphological changes can be in response to water-deficiency and the nutrient content of the soil. The effect of a water deficit can be seen in the root architecture and development of the unfertilised treatments. The water-unstressed, unfertilised 20% compost treatment had a finer root system with more small, lateral growing roots, while the water-stressed, unfertilised 20% compost roots were less fine and not as developed with respect to the smaller lateral roots (Figure 4.9) The WTR-compost co-amendment showed the same morphological features (Figure 4.8).

The effect of nutrient availability is clearly exhibited in the water-stressed control sand treatments. Figure 4.6 shows the morphological difference between root growth in the control sand treatment for the same water level with different fertiliser application. The fertilised root system was bigger and better developed with more fine roots while the unfertilised root system was small, stunted and underdeveloped. In contrast to the control, the root development of the Swiss Chard in 20% WTR amendment was small and stunted, despite the addition of fertiliser (Figure 4.7).

The effect of water application on root development is clearly seen in the architecture of the unfertilised 20% compost and WTR-compost co-application treatments; the smaller root system can affect the ability of a plant to absorb nutrients, which may further limit the plant growth (Figures 4.8 and 4.9). The unfertilised control sand and 20% WTR treatments showed poor root development in both stressed and unstressed water levels. The root development of the fertilised control sand for the same water level is more pronounced than that of the unfertilised control sand. The increased availability of nutrients such as P for the fertilised control sand resulted in better root and shoot growth and WUE despite the limited water (Table 4.3). However, despite the addition of the same amount of fertiliser, the 20% WTR treatment did not exhibit the same increase in root growth as the control (Figure 4.7). Root growth is severely impacted by P availability, which in turn affects the plant's ability to utilise the limited water resource. This can be seen in the reduction of WUE between the 20% WTR unstressed unfertilised, and the 20% WTR stressed unfertilised treatments where despite the increased water availability the P deficiency reduced root growth and in turn the plant's ability to utilise the available water. The nutrient status of the soil will have a profound effect on the plant's drought tolerance (Kammann *et al.*, 2011). Plants grown in nutrient-deficient medium will be less tolerant of potential water stress due to poor root development (Steynberg *et al.*, 1989; Zhang *et al.*, 2015). This interaction between nutrient availability and water stress explains the significant interaction of the three-way factorial ANOVA.

Figure 4.6 Comparison of the roots of the water-stressed control under two fertiliser levels. a) water stressed unfertilised, b) water stressed fertilised. cm-scale reference.

Figure 4.7 Comparison of the roots of the water-stressed 20% WTR-treatment under two fertiliser levels. a) water stressed unfertilised, b) water stressed fertilised. cm-scale reference.

Figure 4.8 Comparison of the roots of the unfertilised 20% compost treatment under two water stress regimes. a) water stressed unfertilised, b) water stressed unfertilised. cm-scale reference.

Figure 4.9 Comparison of the roots of the unfertilised WTR-compost co-application under two water stress regimes. a) water stressed unfertilised, b) water unstressed unfertilised cm-scale reference.

4.3.6 Foliar macronutrients

A single-factor ANOVA was performed on the unfertilised treatments for both water application levels. Similar to the plant-available soil nutrients within the various treatments, the addition of material to sand affected foliar nutrient percentages of the Swiss Chard (Figure 4.10). The foliar macronutrients correspond well with the plant-available P and N (Figure 4.4, Figure 4.5). The addition of WTR and compost increases the foliar N relative to the control sand ($p < 0.05$). The 20% WTR treatment resulted in the highest foliar N, which corresponds to the mineral N results (Figure 4.5). Both 20% WTR treatments and the water-stressed 20% compost treatments have sufficient N, while the control sand, WTR-compost co-application and water-unstressed 20% compost are below the sufficiency threshold (Figure 4.10a). The addition of 20% WTR to the sand decreased the foliar P, while the 20% compost treatment showed a marked increase ($p < 0.05$) in the foliar P (Figure 4.10b), which correlates well with the plant-available soil P and N results. The foliar N and the plant-available N in the unfertilised samples show an inverse correlation, where the plant-available N is lower in the water-stressed treatments while the foliar N shows that the unstressed treatments are higher in N. The treatment combinations resulted in significant differences in foliar potassium (Figure 4.10c). The control sand and 20% WTR treatment fall below the sufficiency threshold, while the 20% compost treatment and the WTR-compost co-application are sufficient. The compost containing treatments are enriched in potassium, indicating that the compost is the source of this nutrient (Table 2.4). Except for the 20% WTR treatment, the foliar potassium does not differ statistically within a treatment combination with respect to water application levels.

Although the nutrient levels of P and N in the WTR-compost co-application are barely sufficient in relation to the sufficiency thresholds, the WTR-compost co-application is still significantly higher than that of the nutrient-poor sand (Figure 4.10) (Campbell, 2000; Wong & Selvam, 2009). Therefore, the WTR and compost are still a nutrient provider with respect to the sand, with compost being the source of P and N, the WTR can also act as a mineral N source (Figure 4.4 and 4.5). Co-application of WTR and compost will be the most beneficial with regards to nutrient supply over the single amendment of WTR. The nutrient effect of WTR and compost is reflected in the foliar macronutrient content as well as the plant-available N and P. For the co-application of WTR and compost to have a positive effect on plant response, a nutrient-poor soil should be considered, which is in accordance to the findings of multiple studies (Mahdy *et al.*, 2020; Oh *et al.*, 2010; Park*et al.*, 2010; Titshall & Hughes, 2005). The WTR application rate should be low enough to limit the negative impact of P deficiencies (Cox *et al.*, 1997; Geertsema *et al.*, 1994; Heil & Barbarick, 1989; Mahdy *et al.*, 2009; Rengasamy *et al.*, 1980; Skene *et al.*, 1995)

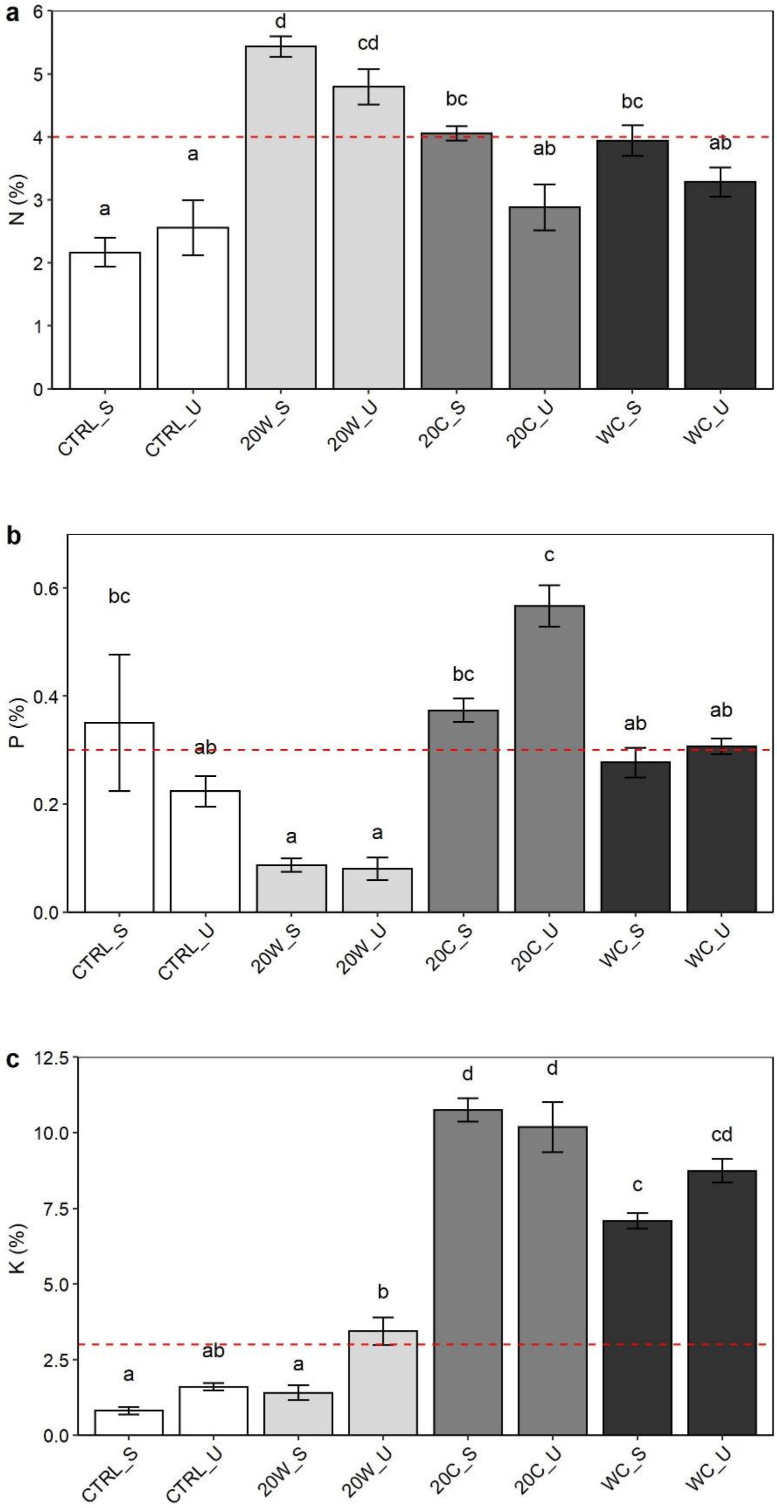

Figure 4.10 The foliar macronutrient content for control sand, 20% WTR, 20% compost and WTR compost co-application treatments. The red dashed line indicates the sufficiency threshold for each nutrient (Campbell, 2000). a) The nitrogen of the treatments; b) The phosphate of the treatments c) The potassium of the treatments. Treatment combinations that are not significantly different from each other share the same letter. All significance levels are set at $p<0.05$. 20W- 20% WTR treatment; 20C- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand.

4.4 Conclusions

WTR-compost co-application to sandy soil will result in more drought-resistant Swiss Chard than WTR as a single amendment. The capacity of the treatment to buffer potential water deficiencies is only possible if the nutrient needs of the Swiss Chard are satisfied. Under nutrient-deficient conditions, the Swiss Chard is not able to adapt to water deficiency through enlarging its root system for effective water uptake.

With the P poor sandy soil used in this study, which is already critically low in P, any loading of WTR in isolation will increase the risk of P deficiencies. Co-application of WTR and compost, however, resulted in enhanced plant response in comparison to the control sand and can offset the capacity of the WTR to absorb P. Although WTR-compost co-application limits plant response in comparison to compost as an individual amendment, the co-application still promotes plant growth in sandy soil, increasing the WUE 16-fold in relation to the unfertilised water-unstressed control, whilst the 20% WTR single amendment resulted in a 3.6-fold decrease in WUE for the same fertiliser and water levels.

This has two benefits. WTR is cheap, offsetting the cost of the compost. In addition, if WTR is land applied with a co-application of compost, it presents the possibility to turn land application of the waste product into a potential amendment to the sandy soil. This is an incentive to rethink the use of WTR for economic and environmental benefits, reducing the pressure on landfill sites.

CHAPTER 5. THE EFFECT OF WTR AND COMPOST AS CO-AMENDMENT TO A SANDY SOIL ON THE TRACE ELEMENT DYNAMICS AND UPTAKE BY SWISS CHARD (*BETA VULGARIS* CICLA.)

5.1 Introduction

Land application of water treatment residual (WTR) is one proposed alternative to diverting waste from landfill sites (Dassanayake *et al.*, 2015). In-depth knowledge of the interaction between waste and the soil-plant system it is added to is critical; especially in relation to trace elements that might be detrimental to the environment (Basta *et al.*, 2005). Amending soil with WTR can introduce trace elements into the soil environment. This chapter reviews the trace element dynamics of the WTR, compost and the receiving sandy soil. And aims to determine whether the trace metal loading introduced to a sandy soil can result in increased trace element plant availability and phytotoxicity.

The origin of trace elements will govern the type and diversity of trace elements as well as their mobility, plant availability and speciation (Kabata-Pendias, 1993, 2004). Trace elements in soils can be subdivided into three main groups based on their origin: lithogenic, pedogenic and anthropogenic (Kabata-Pendias, 1993). If the topsoil contains trace elements that do not correlate with that of the parent material or are in significantly higher concentrations, anthropogenic pollution as a possible trace element source should be considered (Tay *et al.*, 2017; Zhang *et al.*, 2002). Furthermore, the addition of trace metals due to compost and WTR application to the soil will be viewed as an anthropogenic source. In this study, the term 'trace element' will be used to refer to heavy metals, micronutrients and potentially hazardous elements (Albright, 2004).

Apart from the possible reduction in plant-available P brought on by WTR application (Chapter 4), trace elements can also be introduced into the soil environment. Although WTR is classified as inherently non-hazardous by USEPA (2011), it may contain metals such as Al, As, Cd, Cr, Cu, Fe, Pb, Mn, Ni, and Zn (Dassanayake *et al.*, 2015; Lucas *et al.*, 1994; Sidhu *et al.*, 2020; Trollip *et al.*, 2013). On the other hand, numerous studies showed through sorption experiments that WTR can reduce the mobility and plant availability of certain trace elements such as; As, B, Co, Cr, Cu, Ga, Hg, Mo, Ni, Se, V and Zn (Caporale *et al.*, 2013; Castaldi *et al.*, 2015; Finlay *et al.*, 2021; Ippolito *et al.*, 2011; Nagar *et al.*, 2010; Ren *et al.*, 2020; Shen *et al.*, 2019; Soleimanifar *et al.*, 2016; Tay *et al.*, 2017; Wai *et al.*, 2012; Zhao *et al.*, 2020).

WTR, depending on the land application scenario, can either act as a trace metal source or sink. The capacity to remove heavy metals can be especially beneficial in a co-application scenario if the compost added contains high concentrations, or on previously contaminated land (Clarke *et al.*, 2019; Shen *et al.*, 2019).

In nutrient-poor soil, such as the Cape Flats sandy soil, the amount of a trace element is governed primarily by the loading of compost or WTR. By adding a small volume of material to a soil, the trace element loading of each component will be diluted (Ippolito *et al.*, 2002). The sorption of trace elements by WTR is dependent on the initial concentration of the elements within the WTR, compost and sand and pH of the environment (Finlay *et al.*, 2021). The characteristics of the WTR itself will influence its effectiveness as a trace metal sink. The higher the BET-SSA, CEC and smaller the particle size, the more effective WTR will be for trace element adsorption (Castaldi *et al.*, 2015; Shen *et al.*, 2019). Fe-oxides can act as a sink of trace elements such as As (Basta *et al.*, 2005; Yudovich & Ketris, 2005). The addition of FeWTR to a sand increases the Fe-oxide component of the soil, which increases the capacity of the WTR amended soil to act as an oxyanion sink.

Apart from the source of the elements, other factors that influence the fate of trace elements in the soil are pH and redox potential, as well as factors such as clay minerals and clay content, soil moisture, anion exchange capacity (AEC) and CEC, oxide type and content, and amount of organic matter (Albright, 2004; Finlay *et al.*, 2021; Kabata-Pendias, 1993, 2004; Shen *et al.*, 2019; Uzoho *et al.*, 2016). The pH changes can have an especially large impact on the effectiveness of a WTR amended soil to sorb metals; which can be attributed to the amphoteric nature of the oxides. As the pH of the soil environment rises above the point of zero charge of the WTR, the capacity to absorb anions decreased significantly (Bugbee & Frink, 1985; Ociński *et al.*, 2016). batch sorption experiments have shown that trace metals can be chemisorbed, and bound as inner-sphere complexes, these complexes are stable and unlikely to be released into soil solution under normal soil conditions (Finlay *et al.*, 2021; Shen *et al.*, 2019). More than one sorption mechanism can co-exist, as inner-sphere or surface complexes (Arai & Sparks, 2001; Makris *et al.*, 2004, 2006). Competition for sorption sites can also play a significant role in the effectiveness of the WTR to remove trace elements from the soil solution. The addition of P to the soil can limit the sorption of elements such as As since they both compete for the same sorption sites (Gibbons & Gagnon, 2011; Nagar *et al.*, 2010; Shen *et al.*, 2019).

Although WTR has been shown to play a role in trace element sequestration, the addition of WTR to a soil system can introduce various elements that can be detrimental to the environment in high concentrations, and which may pose a considerable environmental risk, especially if the element makes up a large portion of the WTR, as in the case of Al and Mn (Table 2.5). Both these elements can have profound effects on plant growth, not only due to phytotoxicity but also due to antagonistic interactions with other essential nutrients.

Aluminium is not regarded as an essential nutrient (Rout *et al.*, 2001). Al toxicity hinders root development, especially in the root tips resulting in thickened, browned lateral roots (Rout *et al.*, 2001). The interference of Al toxicity with the root development and structure results in poor uptake and transport of essential plant nutrients such as Ca, Mg and P (Rout *et al.*, 2001). The risk of Al toxicity significantly increases in soils with a pH below 5.0 (Rout *et al.*, 2001).

The concern of Al toxicity is especially crucial concerning land application of AlWTR since this will increase the risk of Al toxicity to plants and aquatic ecosystems (Dassanayake *et al.*, 2015). Oladeji *et al.* (2009) reported an increase in soil Al due to AlWTR enrichment, but the Bahia grass accumulated Al was within the normal range for rangeland grass. This result is similar to a study by Mahdy *et al.* (2008) which concluded that under alkaline soil conditions pH of 8.8, AlWTR does not pose a risk for Al toxicity, despite the increase in Al. Under normal soil environmental conditions, aluminium toxicity is unlikely to result from AlWTR application to a soil system (Ippolito *et al.*, 2011).

Another possible concern of applying WTR to soils is the potential of increasing the Mn content to toxic levels. In some South African WTP, Mn toxicity is especially a concern since the lime used may contain elevated levels of Mn (Titshall & Hughes, 2005; Trollip *et al.*, 2013). Manganese is an essential micronutrient for plant growth; it can, however, be detrimental to plant growth if it is in excess within the growth medium (El-jaoual & Cox, 1998; Fertilizer Association of Southern Africa, 2016). Mn toxicity does not always have a clear, identifiable symptom, but Mn toxicity can occur well before any decrease in vegetative growth, with its effects more pronounced in the roots than in the shoots (El-jaoual & Cox, 1998). High levels of Mn can interfere with the plant uptake and utilisation of other essential plant nutrients such as Ca, Mg, Fe and P (El-jaoual & Cox, 1998).

The tolerance of plants to Mn varies considerably, and it is dependent on complex nutritional and environmental interactions (El-jaoual & Cox, 1998). The reduced, divalent form of Mn is usually a small fraction of the total pool of Mn but is of primary concern because it is plant available. Under environmental conditions such as poor soil drainage and a pH below 5.5, the divalent pool of Mn is increased, resulting in a greater risk of Mn toxicity (El-jaoual & Cox, 1998). Furthermore, the interaction between Fe and Mn can also lead to enhanced Mn toxicity in plants. Mn toxicity may develop under Fe deficient conditions; the addition of Fe too can alleviate the Mn toxicity caused by the Fe deficiency. Mn toxicity can develop despite sufficient Fe if the Mn concentration within the soil is high (El-jaoual & Cox, 1998). The narrow, pH-dependent range between a Mn deficiency and toxicity requires careful consideration of WTR application to soil (El-jaoual & Cox, 1998; Monterroso *et al.*,1999; Novak *et al.*, 2007).

Increasing the WTR loading increased the Mn that is accumulated in the plant tissue (Lucas *et al.*, 1994). Lime application with the WTRs decreased the Mn toxicity; which indicates that not only does the loading of WTR influence the Mn accumulation in the plants but also the soil environmental conditions within the WTR- amended system (Lucas *et al.*, 1994). Novak *et al.* (2007) found that a 6% WTR application increased the plant-available Mn, to levels that exceed the toxicity threshold for some crops. Similarly, Titshall & Hughes (2009) found that beans grown in a 10% WTR amended soil had an elevated Mn concentration in the seed. Clarke *et al.* (2019) reported that a 25% WTR-compost co-application to sand increased the Mn content of wheat, from critically deficient to sufficient, without resulting in any toxicity issues, which suggests if applied correctly a WTR can act as a useful Mn nutrient source.

WTR's capacity to absorb various trace elements opens the possibility of using WTR to control the leaching of metals into the groundwater, or it can be used in conjunction with compost, which may be high in trace elements. Excessive amounts of trace elements may also affect food quality (Gezahegn *et al.*, 2017). The ability to decrease metal mobility and toxicity can be especially beneficial in soil with limited sorption capacity like a sandy soil (Fan *et al.*, 2014).

5.2 <u>Materials and Methods</u>

5.2.1 Greenhouse study

The details of the greenhouse study are given in Chapter 4.

The leaves of Swiss Chard are consumed, and there is no other biological structure apart from the roots that trace elements can accumulate within. Trace element analysis of the leaves is, therefore, an accurate approximation of potential for plant toxicity and nutrient deficiencies. For the effect of the amendment mixtures on the plant availability of trace elements and foliar uptake thereof, the water-unstressed and unfertilised treatments were used.

5.2.2 Foliar metal content of the Swiss Chard

The above-ground biomass, consisting of the stem and the leaves, was dried for 24 hours at 65°C, after which it was sent to Elsenburg laboratories. The biomass of the three Swiss Chard plants grown in the same pot was combined. Each treatment consisted of 3 pots each with 3 Swiss Chard plants (Table 4.2).

The macronutrient analysis (N, P and K), of the unfertilised treatments for both water-stressed and water-unstressed treatments were extracted by the Elsenburg laboratories in a 1:1 plant material: solution ratio of 32% HCl, after which it was analyzed by the Central Analytical

Facility (CAF) at Stellenbosch University by ICP-AES spectroscopy to determine the foliar Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn.

The coefficient of variation (CV) was used to determine whether the water-stressed or water-unstressed treatment results were compared to the soil trace metal results. The CV of the water-unstressed treatments was lower than that of the water-stressed treatments. Thus, the foliar metal content of the Swiss Chard grown in the water-unstressed treatments was related to the plant available trace metals from the same water-unstressed treatments The lower CV may be related to bigger samples resulting in more accurate extractions or the fact that plant uptake and transport mechanisms are influenced by the plant health and an uncompromised metabolic structure (Mclaughlin *et al.*, 2008; Zhang *et al.*, 2015).

5.2.3 Soil metal concentration of the amendment mixtures

The plant available trace elements of the raw materials, the pre-trial amendment mixtures and the water-unstressed, unfertilised treatment combinations after harvest were analysed. The plant-available trace elements were extracted in a 1:10 soil: solution ratio of Mehlich-3 (0.2 N acetic acid; 0.25 N NH_4NO_3; 0.015 NH_4F; 0.013 N HNO_3; 0.001 M EDTA) following the method of Myers and Pierzynski (2000). The extracts were analyzed at the Central Analytical Facility (CAF) at Stellenbosch University by ICP-AES spectroscopy to determine the Al, As, B, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb and Zn concentrations.

5.2.4 Statistical analysis

Data were analysed using parametric statistical tests with the RStudio statistical Package. All error bars on graphs are the standard error ($s_{\bar{x}}=s^2/n$). If $p < \alpha$, the result is deemed significant, where alpha is 0.05. A single factor ANOVA for each trace element was performed to investigate the effect of the treatment combinations and components (sand, compost and WTR) on the trace metal concentration. To analyse for significant differences between and within treatments Post hoc Tukey HSD test was performed. The ANOVA validity assumptions of normality and homoscedasticity were based on the normal Q-Q plots. An ANOVA was performed on the foliar trace elements; however, the assumption of homoscedasticity was violated.

5.3 <u>Results and Discussion</u>

5.3.1 Plant available trace elements

The components WTR, compost and control sand were analysed with a single factor ANOVA (Table 5.1). The components (Table 5.1) were also used to calculate the weighted average based on the loading ratios and compared to the post-trial plant-available trace elements within the water-unstressed unfertilised treatments (Figure 5.1). A single Factor ANOVA on for each trace element was performed on the pre- and post-trial treatments for the water-unstressed unfertilised treatments results shown in Table 5.2.

The primary component of the control sand is quartz, which has limited capacity to absorb trace elements, resulting in a soil that is low in nutrients and trace elements; however, the organic matter associated with the control sand may provide nutrients and trace elements (Fertilizer Association of Southern Africa, 2016; Herselman, 2007; Koster, 2009; Schloemann, 1994). Any addition will change the trace element dynamics. If there were no interactions between the WTR, compost and sand, the mixing of the material would result in a trace element concentration similar to that of the weighted average of the treatment combinations (Figure 5.1) (Ippolito *et al.*, 2002). Soil chemical processes like sorption, redox and pH driven changes can take place within the waste amended soil, which may decrease or increase the plant availability of the trace elements. Despite the limited fraction that compost and WTR makes up of the amended soil, it may contribute disproportionally to the trace element signature of the soil. The WTR and compost will contribute more to the trace element signature than the control sand, and are likely to be the primary driver of trace element reactions (Figure 5.1) (Basta *et al.*, 2005). The WTR contains more Al, Cr, Mn, Fe, Co and Ni in comparison to compost that is dominant in B, Cu, Zn, As, Mo, and Pb over WTR (Table 5.1). The Mehlich-3 extractable elements can be used as a guide for toxicity; however, the toxicity levels are strongly dependant on the pH (Table 5.3) (Monterroso *et al.*, 1999). The Mehlich-3 extractable Pb and Mo exceeds the aqua regia determined results for compost (Table 2.5 and 5.1). The lower than expected aqua regia results is likely due to incorrect analysis.

The low concentrations of trace metals associated with the sand mean that the added WTR and compost will be the primary trace metal source (Table 5.1) (Basta *et al.*, 2005).

Table 5.1 WTR, compost and sand trace element loading (mg/kg) extracted with a Mehlich-3 solution. (n=3)

Element	Sand	WTR	Compost
Al	71.1 a	248.533 b	50.923 a
As	0.661 b	0.066 a	0.967 c
B	7.965 b	6.778 a	10.65 c
Co	0.015 a	0.462 c	0.275 b
Cr	0.04 a	0.168 c	0.124 b
Cu	0.258 a	0.431 a	2.829 b
Fe	56.95 a	664.967 c	415.667 b
Mn	2.497 a	167.5 c	17.803 b
Mo	0.006 b	0.002 a	0.003 a
Ni	0.042 a	1.055 c	0.195 b
Pb	0.761 b	0.002 a	3.887 c
Zn	1.833 a	2.499 a	23.14 b

Components that are not significantly different from each other share the same letter. All significance levels are set at $p < 0.05$

Table 5.2 Plant-available metals (mg/kg) extracted with a Mehlich-3 solution. (n=3)

Element	Control		20% WTR		20% Compost		WTR-compost	
	Before	After*	Before	After	Before	After	Before	After
Al	71.1 a	58.81 a	145.933 c	203.567 e	126.633 b	137.37 bc	164.1 d	169.6 d
As	0.661 d	0.656 d	0.45 c	0.182 a	0.819 e	0.782 e	0.222 a	0.388 b
B	7.965 bc	7.825 ab	8.227 c	7.492 a	8.983 d	8.705 d	7.626 ab	7.807 ab
Co	0.015 a	0.013 a	0.162 c	0.348 f	0.107 b	0.098 b	0.187 d	0.211 e
Cr	0.04 a	0.029 a	0.133 c	0.256 e	0.104 b	0.08 b	0.202 d	0.178 d
Cu	0.258 ab	0.559 c	0.815 d	0.454 bc	1.177 e	1.459 f	0.211 a	0.995 de
Fe	56.95 a	45.047 a	414.233 c	820.3 f	148.533 b	137.6 b	736.7 e	579.0 d
Mn	2.497 ab	2.111 a	25.53 d	84.16 f	7.507 bc	8.024 c	43.247 e	45.343 e
Mo	0.006 bc	0.007 c	0.007 c	0.003 a	0.006 bc	0.006 ac	0.004 ab	0.005 ac
Ni	0.042 a	0.04 a	0.306 c	0.817 f	0.101 b	0.09 b	0.486 e	0.442 d
Pb	0.761 bc	0.642 b	1.166 c	0.019 a	1.951 d	1.884 d	0.028 a	0.669 b
Zn	1.833 a	1.62 a	5.348 b	2.307 a	8.393 c	8.764 c	2.297 a	4.672 b

* The post-trial samples are all from the unfertilised water unstressed treatments. Treatment combinations that are not significantly different from each other shares the same letter. All significance levels are set at $p < 0.05$

Table 5.3 Toxicity threshold for Mehlich-3 measured trace elements (mg/kg)

Element	pH		
	4	5	6
Cu	48	49	50
Mn	90	100	115
Ni	2	3.5	4.8
Pb	9.8	10.2	11.0
Zn	91	91.5	92

Modified after Monterroso et al. (1999)

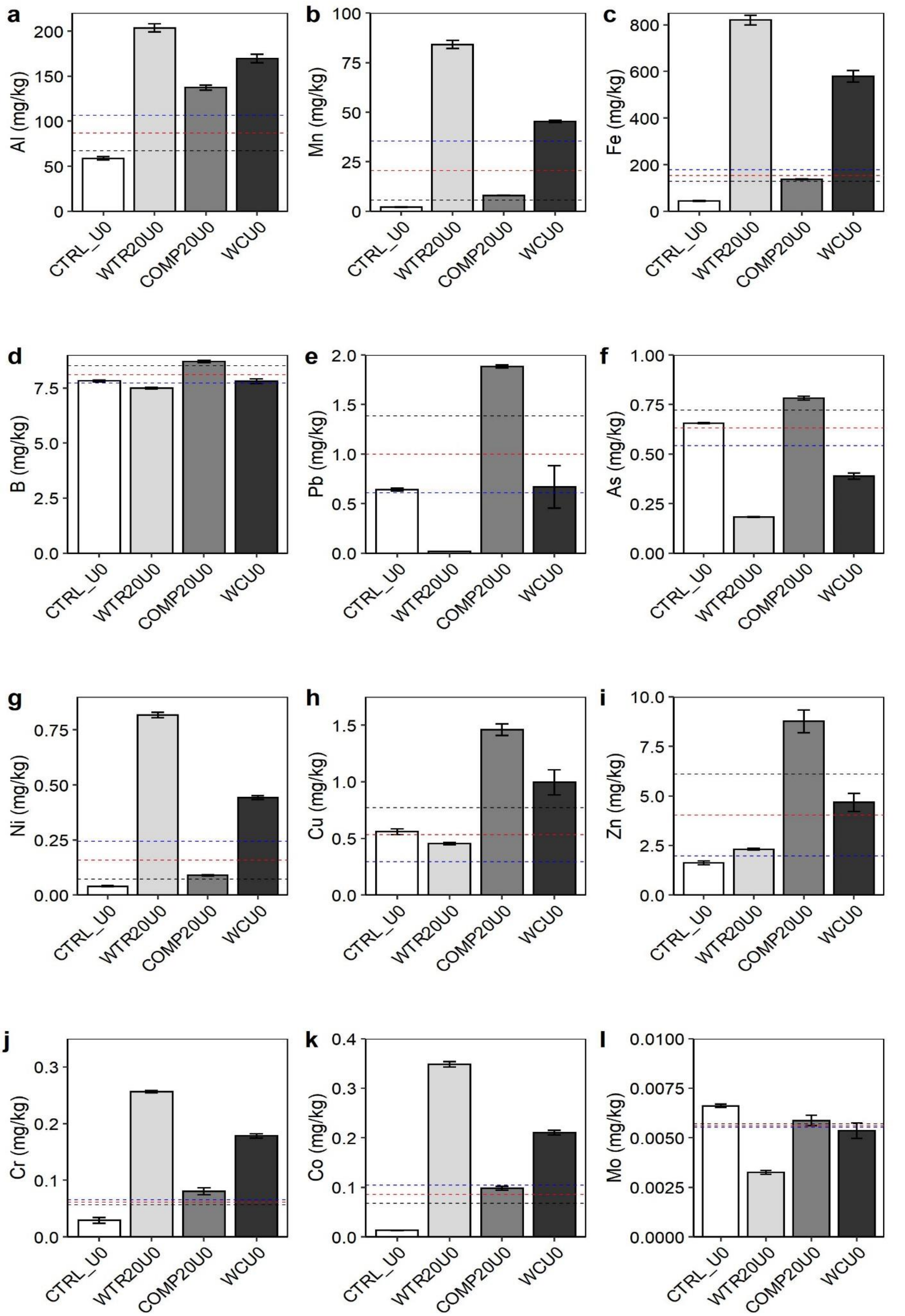

Figure 5.1 The water-unstressed unfertilised post-trial treatments compared to the weighted average. The weighted average trace element loading of each treatment combination, calculated from the plant available trace elements within each of the components (Table 5.1) Blue: 20% WTR treatment; Red: WTR-compost co-amendment Black: 20% compost. 20W- 20% WTR treatment; 20C- 20% compost treatment; WC- WTR-compost co-application; CTRL- control sand.

5.3.2 Trace elements within the treatments

5.3.2.1 Aluminium (Al)

Even though the main flocculant used by Faure WTP is an iron-sulfate, the resulting WTR still contains high concentrations of Mehlich-3 extractable Al (Table 5.1). The WTR amended treatments (20% WTR single amendment and WTR-compost co-application) showed elevated levels of Al with respect to the control (Table 5.2, Figure 5.1a).

Inspection of the roots did not show any visible Al toxicity related morphological changes, such as browned lateral roots, that can be distinguished from other root limiting factors like a water deficit or P deficiency (Figure 4.7) (Rout *et al.*, 2001). Addition of compost and WTR did have a significant effect on the soil pH. With the addition of WTR and compost, the pH of the sand increased from 4.3 to 5.9 with 20% WTR addition and to 6.8 for the WTR-compost co-application (Figure 4.3). These are well above pH 5.0, below which the risk of Al toxicity increases.

The foliar content of Al for the 20% WTR and 20% compost amended sand is lower than the control despite the higher plant-available Al due to the addition of WTR (Table 5.4). The decrease in foliar Al could be due to the increase in pH from the addition of WTR and compost. This suggests the addition of up to 20% WTR will not result in Al toxicity in Swiss Chard; if the soil pH is above 5.0.

The results from this study confirm those of previous work such as Mahdy *et al.* (2008) and Oladeji *et al.* (2009) that despite the increase in plant-available Al, the effect on the plants grown in the WTR amended soil is negligible due to the soil environmental conditions (Ippolito *et al.*, 2011).

Table 5.4 Foliar metal content of the unstressed unfertilised treatments, plant sufficiency and toxicity ranges and WHO maximum permissible heavy metal content (mg/kg) for vegetable crops (n=3)

Element	Control	20% WTR	20% Compost	WTR-compost	Sufficiency [a]	Toxic [b]	WHO[c]
Al	69.212	57.529	40.450	28.010	-	-	-
As	0.145	0.114	0.060	0.085	-	5-20	0.03
B	73.199	75.951	64.057	45.337	25-60	50-200	-
Co	0.678	0.178	0.130	0.124	-	15-50	50
Cr	31.099	3.996	1.341	6.048	-	5-30	2.3
Cu	13.741	12.970	10.727	13.909	5-15	20-100	73.3
Fe	396.350	229.854	120.056	186.211	50-200	-	425.5
Mn	322.063	396.434	221.781	256.008	25-200	400-1000	500.0
Mo	0.686	0.799	0.755	1.113	0.2-1	10-50	-
Ni	3.745	1.258	0.751	1.420	-	10-100	66.9
Pb	1.233	0.801	0.545	0.245	-	30-300	0.30
Zn	174.892	179.176	167.583	100.205	20-75	100-400	99.4

[a] Sufficiency ranges for spinach (Campbell, 2000)
[b] Generalised for various plant species (Kabata-Pendias, 2011)
[c] After Gezahegn et al. (2017)

5.3.2.2 Manganese (Mn)

The WTR used in this study is enriched in Mn with respect to the compost and control sand (Table 5.1). Adding 20% WTR as a single amendment or as co-amendment with compost increased the Mehlich-3 extractable Mn significantly, exceeding the weighted average Mn concentration (Table 5.2, Figure 5.1b). The foliar concentration of Mn in the Swiss Chard exceeds the sufficiency range of Mn for leafy crops; however, it is still lower than the plant toxicity threshold (Table 5.4).

The soil environment was not vulnerable to Mn toxicity. The treatments were kept at a soil moisture level below field capacity and were able to drain freely; waterlogging did not occur. The pH of the WTR amended treatments was above 5.5, below which the Mn mobility and toxicity increases. However, the control sand had a pH of 4.5, which significantly increases the risk of Mn toxicity, and it may have attributed to the Swiss Chard grown in the control treatment having a high foliar content of Mn (Table 5.4), despite having a small pool of plant-available Mn(Table 5.2). The foliar concentration of Mn was highest for the 20% WTR single amendment, although it falls well below the maximum permissible content of Mn in vegetable crops (Table 5.4). Adding WTR as co-application lowered the foliar Mn, which may be related to the increased pH or due to sorption by the compost.

Adding WTR to a sandy soil increased plant-available Mn, and the foliar content of the Swiss Chard. This finding is aligned with Clarke *et al.* (2019), Lucas *et al.* (1994) and Titshall & Hughes (2009). Environmental factors like pH also contribute to the toxicity of Mn, and even if the pool of plant-available Mn is small, a pH below 5.5 can increase its plant uptake substantially, as in the case of the control sand. For a soil pH of 6, Mn will be critically deficient below 40 mg/kg in a Mehlich-3 extract (Monterroso *et al.*, 1999). The WTR-compost and WTR single amendment are above this threshold, while the single compost amendment and control sand are critically deficient (Monterroso *et al.*, 1999).

5.3.2.3 Iron (Fe)

The easy change of valence state of Fe within the soil environment in response to pH and redox conditions govern plant availability (Kabata-Pendias, 2011). Iron, which is an essential plant micronutrient, plays a vital role in energy transformations (Kabata-Pendias, 2011). WTR application increased the plant-available Fe within the soil system (Table 5.1, Table 5.2, Figure 5.1c). The 20% compost treatment Fe content was only slightly higher than the calculated weighted average, while the WTR containing treatments, 20% WTR and WTR-compost co-application far exceed the weighted average (Figure 5.1c). The foliar Fe content of the Swiss Chard grown in the WTR amended sand are also higher, relative to the WTR-compost co-application and 20% compost treatment. However, the Swiss Chard grown in the control sand had the highest foliar Fe concentration, exceeding the sufficiency range for leafy vegetables (Table 5.4).

The uptake of Fe by plants is governed by the plant availability of Fe, rather than the amount within the soil (Govindaraj *et al.*, 2011; Kabata-Pendias, 2011). Therefore, if the soil environment reduces the mobility and plant availability of an element, despite its relative abundance, plant uptake can be limited. The foliar Fe concentration of the control sand is much higher than that of the 20 % WTR single amendment, despite the significantly smaller pool of plant-available Fe in the control sand (Table 5.2). The WTR amended treatments, as 20 % WTR, and WTR-compost co-application had a soil pH of 6.9 and 7.1, respectively, in comparison, the pH of the control sand was 4.5. The low pH of the control sand may have increased the plant uptake of Fe, despite the small plant-available Fe in the sand.

5.3.2.4 Lead (Pb)

The lead concentration in the sand is higher than expected from a quartz dominated parent material. The Pb may be of anthropogenic origin, from vehicle exhaust emissions, due to the proximity of the Jacobsdal farm to urban areas (Environmental Affairs, 2010; Kabata-Pendias, 2011). The compost also contains Pb, while the WTR Pb concentration is extremely low (Table 5.1). The addition of WTR to the control sand significantly reduced the Mehlich-3 extractable Pb concentration, reducing the concentration below the weighted average (Figure 5.1e), this finding concurs with batch experiments conducted by Castaldi *et al.* (2015). The reduction of Pb to levels lower than the weighted average indicate that the WTR chemisorbed some of the plant available Pb associated with the sand (Figure 5.1e) (Finlay *et al.*, 2021; Shen *et al.*, 2019). The amount of Pb in the enriched soil falls well below the foliar and plant available toxicity thresholds (Table 5.4 and 5.4).

The different treatment combinations also influenced the foliar concentration of Pb; all treatments fell below the toxicity threshold (Table 5.4). The highest foliar Pb was observed in the control sand followed by the WTR single amendment, single compost amendment and WTR-compost co-application. The addition of WTR reduced the foliar concentration in the plant tissue (Table 5.4). Similarly, Mahdy *et al.* (2008) and Clarke *et al.* (2019) found that WTR addition reduced the Pb in their WTR amended soil and plant tissue in comparison to the control.

5.3.2.5 Arsenic (As)

The arsenic concentration of the aeolian sand is higher than expected from a sample consisting largely of mineral quartz. The As can be distributed as an airborne pollutant from the bringing of coal containing As (Wagner & Hlatshwayo, 2005). The now decommissioned coal-fired power plant in Athlone could have acted as a possible airborne source of anthropogenic As (Kading *et al.*, 2009; Yudovich & Ketris, 2005; Zyl & Heath, 2007). The Athlone power plant has been linked to elevated concentrations of trace elements within sediments, and with the close proximity of the power plant to the Jacobsdal farm, it may have been a contributing factor to the elevated topsoil concentration of As (Kading *et al.*, 2009; Zyl & Heath, 2007).

The WTR contains low concentrations of As while the compost and sand contain significantly more (Table 5.1). The addition of 20 % WTR single amendment to the sand reduced the Mehlich-3 extractable As significantly to below the weighted average (Table 5.2, Figure 5.1f). Similarly, the WTR-compost co-application reduced the As below the weighted average. The significant As reduction in WTR amended treatments indicate that WTR chemisorbed some of the plant available As associated with the compost and sand The reduction in As associated with compost in a WTR-compost co-application to sand was also reported by Clarke *et al.* (2019). These findings are in accordance with sorption experiments of As to WTR (Finlay *et al.*, 2021; Ippolito *et al.*, 2011; Ren *et al.*, 2020; Shen *et al.*, 2019). The foliar content of As was also reduced by the application of WTR and compost. Despite containing the highest loading of plant-available As, the single compost amendment had the lowest foliar As, followed by the WTR-compost co-application and the WTR single amendment. All the treatment combinations fall below the plant toxicity threshold; however, all of the treatments exceeds the WHO foliar guidelines for vegetable crops (Table 5.4).

5.3.2.6 Nickel (Ni)

Nickel is a toxic element with no essential role in plant metabolism and, when present in soluble form, is readily absorbed by plant roots (Herselman, 2007; Kabata-Pendias, 2004, 2011). The WTR is enriched in Ni compared to the compost and sand (Table 5.1, Figure 5.1g). The post-trial 20% compost treatment Ni content was only slightly higher than the calculated weighted average, while the WTR containing treatments, 20% WTR and WTR-compost co-application far exceed the weighted average (Figure 5.1g). Despite this increase in plant-available Ni, the WTR reduced the foliar Ni of the Swiss Chard grown in the 20% WTR amendment. In a greenhouse trial by Mahdy *et al.* (2008), WTR addition to the soil reduced the plant-available Ni as well as the foliar content. For all treatment combinations, the Ni concentration falls well below the soil and foliar toxicity range (Table 5.3 and 5.4).

5.3.2.7 Copper (Cu)

Copper, essential for various plant enzymes, can be actively and passively absorbed by the plant, the latter of which is of key concern with respect to crops grown in soils with high plant available Cu (Kabata-Pendias, 2011). All the treatments have foliar Cu concentrations within the sufficiency range (Table 5.4).

The compost is the primary source of Cu; as a result, the single compost amendment contains the highest amount of plant-available Cu, exceeding the calculated weighted average for the 20% compost treatment (Table 5.1, Figure 5.1h). Although the 20% WTR treatment does reduce the Cu concentration relative to the control sand, the concentration still exceeds the weighted average (Figure 5.1g). The variation in concentration of Cu is high for all treatment combinations (Table 5.2); these changes may have been because of changes in pH (Herselman, 2007). Despite the differences in plant availability, the WTR-compost co-application reduced the plant-available Cu relative to the compost treatment. None of the treatment combinations exceeds the foliar or plant-available toxicity thresholds (Table 5.4). The foliar concentration of the 20% compost treatment was the lowest, followed by the 20% WTR treatment, control and the WTR-compost co-application with the highest foliar Cu concentration. This is in contrast to Mahdy *et al.* (2008) who found that the WTR addition decreased the foliar Cu. Despite the high plant-available loading of Cu in the compost treatment, the foliar content was lower; in contrast, the WTR-compost co-application increased the foliar Cu. A field study by Fan *et al.* (2014) reduced the plant availability of Cu in a sand by adding CaWTR, the reduction in plant availability was, however, attributed to the increase in pH rather than the WTR`s ability to absorb Cu. However, Fe oxides and WTR can act as Cu sinks (Finlay *et al.*, 2021; Ippolito *et al.*, 2011; Kabata-Pendias, 2011; Ren *et al.*, 2020; Shen *et al.*, 2019). The capacity for WTR to act as a potential sink for Cu is related to the environmental conditions as well as the innate capacity of WTR to chemisorb Cu.

5.3.2.8 Zinc (Zn)

Zinc uptake by plants shows a linear relationship to the soil concentration (Kabata-Pendias, 2011). Zn plays an essential role in the functioning of various enzymes (Kabata-Pendias, 2011). All the treatments exceed the sufficiency range for Zn (Table 5.4). Excess Zn, especially in acidic soils, can lead to plant toxicity and antagonism to various other important plant nutrients such as N, Cu and Fe (Kabata-Pendias, 2011).

Both the compost and WTR contain more Zn than the control sand (Table 5.2). WTR, as a single amendment, increased the plant-available Zn; however, this increase is only marginally higher than the calculated weighted average for the 20% WTR treatment (Figure 5.1i). Similarly, the 20% compost treatment resulted in a significant increase in Zn, however, in relation to the weighted average for the 20% compost treatment, the post-trial Zn concentration far exceeds this calculated value (Figure 5.1i). Relative to the control and single compost amendment, the foliar content of Zn is increased by 20% WTR application. The WTR-compost co-application had the lowest foliar Zn. The foliar Zn concentrations for all treatments fall within the lower ranges of plant toxicity; however, all of the treatments exceed the WHO guideline for vegetable crops (Table 5.4).

5.3.2.9 Chromium (Cr)

Chromium can exist in a wide array of valency states, from -2 to +6. In most environments, it exists as the less toxic Cr(III) (Environmental Affairs, 2010). Cr plays no essential role in any plant metabolic processes (Kabata-Pendias, 2011). The WTR contains the highest concentration of Cr (Table 5.1); as a result, the WTR single amendment contains the highest concentration of plant-available Cr, followed by the WTR-compost co-application and single compost amendment and control (Table 5.2, Figure 5.1j). Under circumstances where WTR is not a source of Cr, WTR can sorb, and significantly reduce the Cr in the WTR amended soil (Finlay *et al.*, 2021; Ippolito *et al.*, 2011; Ren *et al.*, 2020; Shen *et al.*, 2019; Zhao *et al.*, 2020). Ayele and Regasa (2020) showed with batch experiments that alum based WTR could reduce Cr through adsorption. The capacity of WTR to act as a sorbent increases with WTR loading and contact time and decreases in efficiency as the pH increases (Ayele & Regasa, 2020).

Despite the low plant-available Cr in the control sand, the foliar concentration of the Swiss Chard grown in the control contains the highest concentration of Cr, followed by the WTR compost co-application, WTR single amendment and compost amendment. The Cr concentration of the control and WTR-compost co-application exceeds the general plant toxicity range (Table 5.4).

5.3.2.10 Cobalt (Co)

The WTR contains the highest concentration of Co (Table 5.1), as a result, the 20% WTR single amendment contains the highest concentration of Co, followed by the WTR-compost co-application and single compost amendment (Table 5.2).

Cobalt uptake by plants is a function of the concentration of the element within the soil, although plant accumulation rarely results in toxicity symptoms (Herselman, 2007; Kabata-Pendias, 2004). Despite the low plant-available Co in the control sand, the foliar concentration of the Swiss Chard is grown in the control contains the highest concentration of Co, followed by the WTR amendment, compost amendment and WTR compost co-application. The foliar Co falls well below the toxicity range (Table 5.4).

5.3.2.11 Molybdenum (Mo)

The molybdenum loading of the sand, compost and WTR is less than 0.001 mg/kg. The sand is the main source of Mo, followed by compost. Unlike most trace elements, the solubility of Mo increases with pH (Kabata-Pendias, 2011). The soil pH for all treatments increased over the duration of the trial; accordingly, the Mehlich-3 Mo increased for all treatments with the exception of the 20% WTR treatment, which showed a decrease in Mo to levels lower than the weighted average for the treatment combination (Table 5.2, Figure 5.1l). Similarly, Ippolito *et al.*, (2002) reported that WTR as a co-application to a biosolid reduced the Mo content, of which the biosolid was the source. These findings are in accordance with sorption experiments by Finlay *et al.* (2021), Ippolito *et al.* (2011), Ren *et al.* (2020) and Shen *et al.* (2019). Only the Swiss Chard grown in the WTR-compost treatment exceeds the sufficiency range, while no treatment combination exceeds the foliar toxicity threshold (Table 5.4).

5.3.2.12 Boron (B)

Boron is an essential micronutrient within plants, and play a key role in the translocation of carbohydrates and sugars (Kabata-Pendias, 2011). The compost is the constituent with the highest B loading, followed by sand and the WTR (Table 5.1). The WTR-compost co-application showed a reduction in plant available B with respect to the 20% compost, while the post-trial 20% WTR single amendment reduced the B to levels comparable to that of the WTR-compost co-application (Table 5.2). However, all changes within the Mehlich-3 extractable B are similar to the calculated weighted average (Figure 5.1d). With the exception of the WTR-compost co-application, the foliar B falls within the lower toxicity range (Table 5.4).

5.3.3 Trace element dynamics of a WTR amended sand

The aeolian derived quartz-dominant sand is impoverished with respect to most trace elements, and nutrients, and the addition of either compost or WTR will influence and change the trace element loading of the amended sand (Table 5.1 and Table 5.2 and Figure 5.1)

(Basta *et al.*, 2005; Ippolito *et al.*, 2002). The WTR will only be able to reduce trace elements of which it is not the source (Novak *et al.*, 2007). The WTR contains more Al, Cr, Mn, Fe, Co and Ni in relation to the compost that is dominant in B, Cu, Zn, As, Mo, and Pb over WTR (Table 5.1). In this application scenario, the WTR significantly reduced the As, Pb, Mo, Cu and Zn originating from the sand or compost. The capacity of WTR to reduce these trace elements is in accordance with Clarke *et al.* (2019), Finlay *et al.* (2021), Ippolito *et al.* (2011), Ren *et al.* (2020) and Shen *et al.* (2019).

Furthermore, how the trace elements inherited from their different sources interact in the amended system is governed by soil parameters like pH and redox. The effects of these interactions are visible in the pre- and post-trial variations within the plant availability of certain trace elements and changes relative to the calculated weighted averages (Table 5.2, Figure 5.1). The control sand and the 20% compost treatment only differ statistically between the pre- and post-trial for Cu; the remaining trace elements do not differ statistically (Table 5.2). Treatments containing WTR are more variable with respect to pre- and post-trial changes (Table 5.2). For the 20% WTR single amendment all the trace elements showed a significant change in plant availability between the pre- and post-trial concentrations, while the WTR-compost co-application had B, Al, Cr, Mn and Mo with insignificant changes.

WTR, with its aqueous origin, may contain trace elements that are not in equilibrium with the new soil environment, resulting in rapid changes in mobility as it changes in response to the new environmental conditions resulting in the significant changes during the trail in plant available trace metals for the WTR- amended soil (Table 5.2). The relative variability of WTR containing treatments stands in contrast to the limited changes in the pre- and post-plant availability of the sand, suggesting that the elements are in equilibrium with their geochemical environment.

The addition of WTR and compost changes the clay content, CEC, and organic matter content, all of which change the capacity of the soil to interact with trace metals. Furthermore, how the soil is managed will influence the pH, redox state and soil moisture, which in turn influences the mobility and plant availability of the trace elements.The ability of WTR to sorb and control trace elements within the soil might be altered with the addition of phosphate fertiliser to the soil, since both phosphate and trace elements compete for the same sorption sites (Gibbons & Gagnon, 2011; Nagar *et al.*, 2010; Shen *et al.*, 2019). Moreover, trace elements also compete for the same sorption sites, differences in electronegativity and atomic radii between trace elements may also alter the mobility of trace elements that are displaced (McBride, 1994).

The soil environmental conditions are especially relevant with regards to plant interaction and toxicity (Bose & Bhattacharyya, 2008). Despite the increase in plant availability of the trace elements, no trace element exceeds the toxicity threshold (Table 5.3). Minimising the potential risk of Al and Mn toxicity amongst others, the environmental conditions of the amended system should be monitored closely. If the pH is above 5.5 and the soil environment is not waterlogged WTR addition should not result in trace element toxicity, despite the increase in the plant availability (Ippolito *et al.*, 2011).

The most effective way of managing the trace elements within the treated soil is to determine the trace element loadings of the waste and the receiving soil prior to consideration for land application (Novak *et al.*, 2007). For example, monitoring the Mn content of the lime used to treat the water prior to earmarking the WTR for land application (Trollip *et al.*, 2013). Establishing the trace element loading of the material beforehand is especially critical for Cd, B, Zn, Cu and Pb, which show a linear relationship between the amount in soil solution and the foliar uptake (Kabata-Pendias, 2011). By using less than 20% w/w of WTR or WTR-compost co-application for land application, the loading of trace elements introduced by the compost and WTR will pose less of a toxicity risk. Furthermore, a 20% (w/w %) loading of WTR incorporated to a depth of 15 cm is 450 tons/ ha of material, which may be achieved through multiple 2% WTR (45 tons/ha) applications.

5.3.4 Foliar content of selected trace elements and safe consumption

Investigating the metal bioavailability through a plant assay is arguably the best method of investigating the effect of the potential phyto-availability of trace metals (Abedin, Beckett & Spiers, 2012; Basta *et al.*, 2005; Mclaughlin *et al.*, 2008). Quantifying the effect of water stress on plant uptake of trace elements will provide invaluable insight for land management of soils were there is the potential risk of foliar accumulation of potentially toxic and hazardous trace elements. Based on the lower CV, the water-unstressed treatments will be most closely related to the plant-available trace metals, and only the water-unstressed trace elements will be considered (Chapter 5.2.2). However, the uptake of trace elements may be different for Swiss Chard grown under water stress (Nyathi *et al.*, 2016).

Micronutrients such as Fe, Na, Cl, B, Mn, Zn, Cu, and Mo do not only limiting crop yields below sufficiency thresholds, but also human nutrition (Govindaraj *et al.*, 2011). Worldwide 3 billion people suffer from micronutrient malnutrition (Govindaraj *et al.*, 2011). WTR can provide some of these trace elements, which in turn can increase crop yield and ultimately alleviate micronutrient malnutrition without the use of fertilisers. Amending the soil with a WTR-compost co-application can increase the plant availability of these micronutrients. WTR provides Fe and Mn while the compost provides Zn and Cu (Table 5.1). Trace elements, albeit essential in higher life forms, in excess can be toxic.

The Swiss Chard grown in the amendments of WTR and compost were expected to have a higher foliar concentration of certain trace elements since the plant availability of these elements are higher; however, this was not the case with respect to certain metals such as Cr (Table 5.4) (Madejón *et al.*, 2006). The plant-available Cr of the control sand is only 0.04 mg/kg, while the foliar content is 31.1 mg/kg. The small samples may have resulted in selection bias in the sampling procedure. In order to confirm the foliar results, a similar study should be conducted with more replications over a more extended growth period. Accurate data is of the essence, especially with respect to trace elements like Cr, which is an essential micronutrient for humans, but in excess, it can be carcinogenic (Kabata-Pendias, 2011). The increase in the pH over the duration of the pot trial may also have led to the discrepancy between the foliar trace metal content and the plant-available trace metals (Bose & Bhattacharyya, 2008). However, based on these results, not even Swiss Chard grown in the control sand should be considered for consumption.

All food consumed should adhere to the World Health Organization (WHO) guidelines with respect to potentially toxic elements. If a vegetable exceeds these maximum permissible concentrations for any one of these elements, consumption should be avoided. The foliar concentration of selected metals of the Swiss Chard grown in the unfertilised water unstressed treatments is shown in Table 5.4. The foliar concentration of Cr, Zn, As and Pb of the control and 20% WTR treatment exceeds maximum concentrations as stipulated by the WHO. The WTR-compost co-application exceed the limits for Zn, As and Pb, while the 20% compost exceeds the limits for Cr, Zn and As. How plant-availability of trace elements will change over multiple growth seasons should also be considered, and whether repeated cultivation leads to decreased trace element loadings, which is safe for human consumption.

Growing a non-edible crop within WTR amended soils may result in broader agricultural use since it is not limited by WHO safe consumption standards. Plants can tolerate much higher trace element loadings than s stipulated by the WHO as safe for human consumption (Table 5.4). Alternatively, the use of WTR should be considered for non-agricultural land rehabilitation projects.

5.4 Conclusions

Any addition of material to the trace element poor sand will influence the trace element loading of the FeWTR (2018) and compost- amended soil. Compost acts as a source of B, Cu, Zn, As, Mo, and Pb. The FeWTR (2018) will enrich the soil in Al, Cr, Mn, Fe, Co and Ni. The FeWTR (2018) can reduce the mobility of trace elements of which it is not the source, and reduced As, Pb, Mo, Cu and Zn originating from the sand or compost. WTR, with its aqueous origin, may contain trace elements that are not in equilibrium with the soil environment, which may increase the initial mobility of these trace elements.

No trace element exceeded the Mehlich-3 soil extract toxicity threshold, however maintaining a soil environment that does not increase the trace element mobility, and toxicity is crucial. This entails a soil profile that is not waterlogged for extended periods of time, and with a soil pH above 5.5. The foliar toxicity threshold for safe consumption of Cr, Zn, As and Pb was exceeded in the control and 20% FeWTR (2018) treatment, while the WTR-compost co-application exceeded the limits for Zn, As and Pb.

WTR-compost co-application can improve the nutrient status of a nutrient-poor sandy soil; however, the risk of exceeding the guidelines of the WHO for vegetables does exist. Although FeWTR (2018) can act as a source of some of the essential micronutrients and trace elements, land application of FeWTR should not be determined on this factor alone. Furthermore, FeWTR application should not exceed a 20% w/w loading, increasing the total amount of material added will result in higher loadings of Al, Cr, Mn, Fe, Co and Ni, which at higher loadings, may pose an environmental risk.

CHAPTER 6. GENERAL CONCLUSIONS AND FUTURE RESEARCH

6.1 Conclusions

Finding alternative ways of disposing of waste material in a way that may be economically and environmentally beneficial are key factors in moving towards a more sustainable future. Water treatment residual is one such waste stream that has not only the potential to be funnelled to land application but also opens the possibility to improve the receiving soil.

This study aimed to establish the risks and benefits of applying WTRs generated in the Cape Town metropolitan area to the surrounding sandy soils. The WTR from Faure- and Blackheath WTP in the greater Cape Town metropolitan area, as well as the receiving soil, the aeolian deposited sand of the Sandveld Group, and a commercially available compost, which can be utilized as co-application with WTR were characterised. Furthermore, how WTR- amended soil will interact with water in relation to soil water repellency, saturated hydraulic conductivity and water retention. Lastly, a greenhouse study investigating the growth of Swiss Chard under nutrient and water stress to determine whether the WTR amended soil increases drought tolerance. The same greenhouse study was used to investigate the plant availability of selected trace elements as well as their phytotoxicity in the plant tissue. The following conclusions were reached from this study:

The results of this study underpinned the inherent variability in the WTR formed by two different WTPs, as well as the temporal variations due to plant operating conditions. Both the WTR from Faure and Blackheath WTP are highly amorphous with irregular surface morphology and large specific surface area. SEM-EDS and FTIR analysis showed that the major chemical components are: C, O, Ca, Al, Fe and Si. The XRD showed that the crystalline phases from the raw water are quartz, muscovite, kaolinite and microcline. In contrast the elements used in the flocculation process is mainly held in poorly crystalline phases. Calcite was also present in the FeWTR 2018 sample. Freeze-drying or air-drying did not result in a change in crystallinity, the significant amounts of carbon and other metal species make crystallisation under ambient soil conditions unlikely. The WTR from both WTPs contain Al, Fe, Cr, Mn, Co, Ni, Cu, Zn, As, and Pb. The different plant operating conditions and raw water quality are reflected in the wide ranges in EC, pH, C/N ratio, Fe_{ox} Al_{ox} and the CEC. These values fall within the ranges established by published works. The sorption of P onto WTR exhibits an L-shaped curve, indicating that sorption sites become increasingly occupied. WTR from Faure WTP rather than Blackheath WTP should be considered for initial land application strategies. The lower variation due to direct landfilling of the WTR, rather than pond maturation, makes it easier to characterise and use. The lower variability makes planning and implementing a successful WTR land application strategy feasible.

The addition of 20% and 10% WTR as a single amendment, 450 tons/ha and 225 tons/ha respectively, and as a co-application with commercial compost resulted in changes in the soil water dynamics of the amended sandy soil. Addition of 20% WTR to the sand resulted in a 24-fold reduction ($p < 0.05$) in soil water repellency, through masking of the hydrophobic organic matter associated with the sand. Furthermore, the saturated hydraulic conductivity of the WTR amended sand decreased due to an increase in packing efficiency by mixing the material with different particle sizes. The WTR addition resulted in an upward shift in the water retention curve, without alerting the retention curve shape. The increased water content at all matric potentials is related to water held in the micropores of the WTR. This may be of benefit to plants under water-limited conditions. The effect of WTR addition to the sandy soil is related to both the intrinsic physical properties of the WTR as well as its grain size distribution and the interaction with the receiving soil.

Any addition of material to the trace element poor sand will influence the trace element loading of the WTR and compost- amended soil. The WTR as a single amendment or in a WTR-compost co-amendment can reduce the mobility of trace elements As, Pb, Mo, Cu and Zn originating from the sand or compost.

No trace element exceeded the toxicity threshold at the w/w% loadings investigated. However, maintaining a soil environment that does not increase the trace element mobility and toxicity is crucial. For example, maintain a soil profile that is not waterlogged for extended periods of time, and with a soil pH above 5.5. WTR-compost co-application can improve the nutrient status of a nutrient-poor sandy soil, however the risk of exceeding the guidelines of the WHO safe vegetable consumption standards does exist.

WTR-compost co-application to sandy soil will result in more drought-resistant Swiss Chard than WTR as single treatment. The WUE of the unfertilised water-unstressed WTR-compost co-application resulted in a 16-fold increase in WUE, whilst the 20% WTR single amendment resulted in a 3.6-fold decrease in WUE for the same fertiliser and water levels relative to the control. The capacity of the treatment to buffer potential water deficiencies is only possible if the nutrient needs of the Swiss Chard are satisfied. Under nutrient-deficient conditions, the Swiss Chard is not able to adapt to the water deficiency through enlarging its root system for effective water uptake.

WTR amended soil will increase the risk of P deficiencies in crops. Co-application of WTR and compost, however, resulted in enhanced plant response and can offset the capacity of the WTR to absorb P. If WTR is land applied with a co-application of compost, it presents the possibility to turn land application of the waste product into a potential amendment to the sandy soil and incentive to rethink the use of WTR for economic and environmental benefits.

6.2 Future research recommendations

This research underpinned the importance of characterising waste streams (WTR) and receiving soils, as well as investigating the impact of WTR- amended soil on plant growth under various nutrient and drought conditions. Further research is required to determine the optimum ratio between WTR, compost and the receiving soil; to maximise the plant response whilst diverting a significant volume of WTR from the landfill, within the boundaries of practicality and economic feasibility.

The inherent variability of WTR requires that a range of values rather than a single value should be used to make land application recommendations. To obtain accurate and precise ranges repeat measurements of the WTR from a specific WTP must be collected over a period no less than one year, to account for all the plant-specific operating conditions as well as seasonal changes in raw water quality. The data can then be used within a multivariate regression model to define the inherent variability of WTR within a statistical framework.

Follow up greenhouse studies should be a two-phase study; 1) Small container (4.5 kg) high replication greenhouse study that focuses on the ideal ratio of WTR: compost with sufficient water application and leaching from the pots. It is recommended to keep the final amendment ratios of the WTRs used in this study, below 20% w/w, to limit the possible adverse effects of WTR, and to ensure it is practical for large scale land application. 2) Based on these results a large container (> 1 m^3) study investigating the long-term use of a WTR compost co-application should be conducted, spanning no less than two growth cycles of the chosen crop (Truter *et al.*, 2019). Although difficult to manage, such a study can investigate the long-term plant availability and plant uptake of trace elements, and whether repeated cultivation leads to a decreased risk of plant toxicity. A large container greenhouse study under controlled conditions will be a crucial stepping stone before scaling up to field trials spanning multiple years.

An alternative to co-application is to incorporate the WTR into the composting process, creating a single product. Presenting WTR as an economically viable, practical and user-friendly product is a crucial step in reducing the amount of WTR that reaches the landfill site (Yiping, 2016). Co-composting of WTR, along with plant refuse, is one possibility to create a usable product (Parr *et al.*, 1978; Wong & Selvam, 2009; Zhang & Sun, 2014). Utilising a co-

composting method of coal fly ash and sewage sludge proved to be successful in increasing plant growth, a similar approach to utilising WTR should be investigated (Wong & Selvam, 2009). The economic feasibility of WTR utilisation should be compared to the cost of WTR waste handling and landfilling.

The potential use of WTR as a cost-effective means to reduce soil water repellency also requires detailed further research. The effectiveness of WTR should be compared to different clay types as well as the influence of particle size should be investigated. Not only should research shed light on the characteristics and effects of waste products, but also explore practical strategies and economic incentives, necessary for the shift towards a sustainable circular economy where waste is considered as a resource.

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APPENDIX 2.3.2: SEM-EDS ANALYSIS

The following data from the SEM-EDS analysis show the exact area of ablation and the related mineral composition.

SEM-EDS of FeWTR 2018

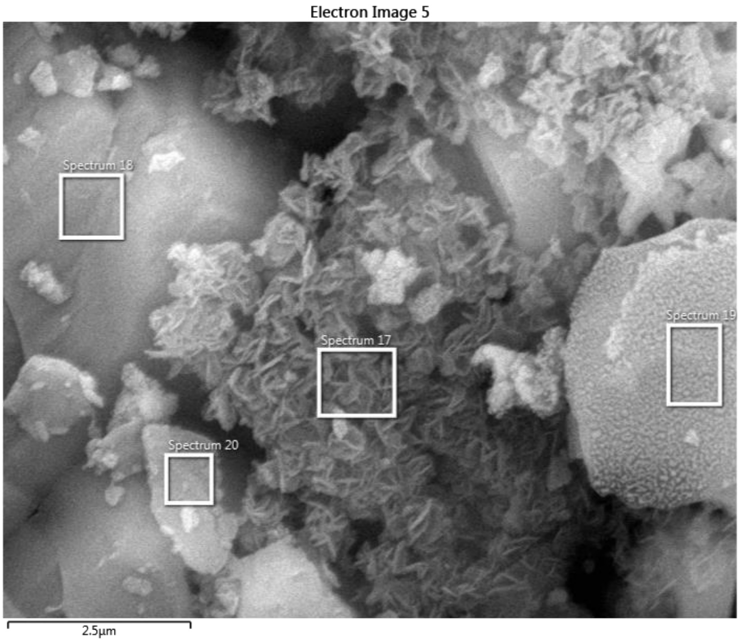

Figure A 2.3.2.1 SEM EDS ablation locations 17, 18, 19 and 20 on FeWTR 2018.

Table A 2.3.2.1 SEM-EDS of FeWTR 2018, elements as % of the total composition. Average of spectrums 17, 18, 19 and 20

Element	Max	Min	Average	Standard Deviation
C	53.59	13.58	24.53	19.39
N	0	0	0	0
O	53	32.83	45.52	8.78
Na	0	0	0	0
Mg	2.83	0.31	1.17	1.14
Al	1.75	0.33	1.09	0.66
Si	1.84	0.41	0.98	0.63
P	0	0	0	0
S	0.19	0	0.12	0.08
Cl	0.12	0	0.04	0.06
K	0.43	0	0.18	0.18
Ca	33.82	9.02	24.02	10.56
Mn	0	0	0	0
Fe	4.19	0.95	2.34	1.37

Table A 2.3.2.2 SEM-EDS of FeWTR 2018, elements as % of the total composition. Spectrums 17, 18, 19 and 20

Element	Spectrum 17	Spectrum 18	Spectrum 19	Spectrum 20
C	15.67	15.3	53.59	13.58
N	0	0	0	0
O	47.54	48.73	32.83	53
Na	0	0	0	0
Mg	2.83	0.31	1.01	0.56
Al	1.53	0.33	0.74	1.75
Si	1.04	0.41	0.61	1.84
P	0	0	0	0
S	0	0.15	0.19	0.14
Cl	0.12	0	0.06	0
K	0.2	0	0.1	0.43
Ca	26.88	33.82	9.02	26.37
Mn	0	0	0	0
Fe	4.19	0.95	1.86	2.35
Total	100	100	100	100

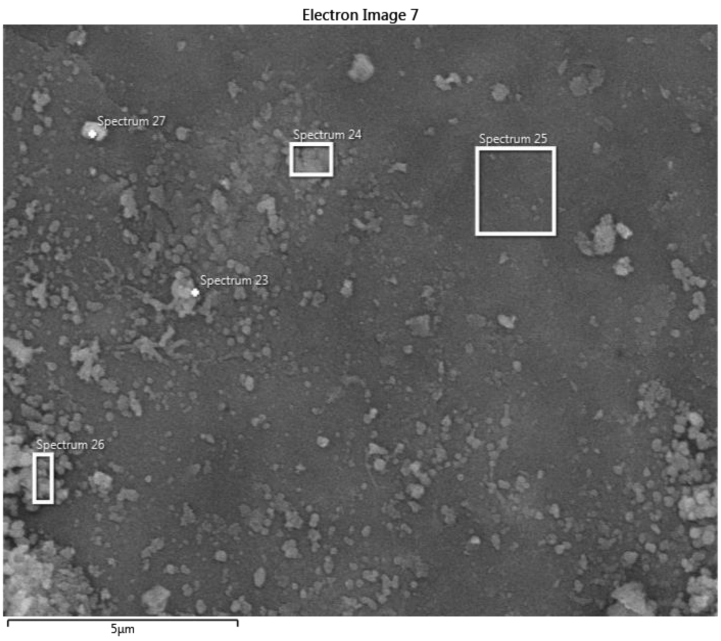

Figure A2.2 SEM EDS ablation locations 23, 24, 25, 26 and 27 on FeWTR 2018.

Table A 2.3.2.3 SEM-EDS of FeWTR 2018, elements as % of the total composition. Average of spectrums 23, 24, 25, 26 and 27

Element	Max	Min	Average	Standard Deviation
C	13.64	0	8.19	5.04
N	0	0	0	0
O	52	50.06	51.38	0.82
Na	0	0	0	0
Mg	1.56	1.18	1.34	0.17
Al	17.48	10.41	13.53	2.58
Si	21.1	12.15	16.1	3.24
P	0	0	0	0
S	0	0	0	0
Cl	0	0	0	0
K	1.74	1.1	1.37	0.23
Ca	0.42	0.15	0.27	0.1
Mn	0.12	0	0.02	0.06
Fe	10.89	5.96	7.8	1.89

Table A 2.3.2.4 SEM-EDS of FeWTR 2018, elements as % of the total composition. Spectrums 23, 24, 25, 26 and 27

Element	Spectrum 23	Spectrum 24	Spectrum 25	Spectrum 26	Spectrum 27
C	7.94	9.94	0	9.43	13.64
N	0	0	0	0	0
O	51.87	51.11	52	51.86	50.06
Na	0	0	0	0	0
Mg	1.31	1.18	1.56	1.46	1.21
Al	13.78	13.51	17.48	12.45	10.41
Si	16.42	15.81	21.1	15.03	12.15
P	0	0	0	0	0
S	0	0	0	0	0
Cl	0	0	0	0	0
K	1.35	1.28	1.74	1.37	1.1
Ca	0.21	0.25	0.15	0.32	0.42
Mn	0	0	0	0	0.12
Fe	7.12	6.92	5.96	8.08	10.89
Total	100	100	100	100	100

SEM-EDS of FeWTR 2019

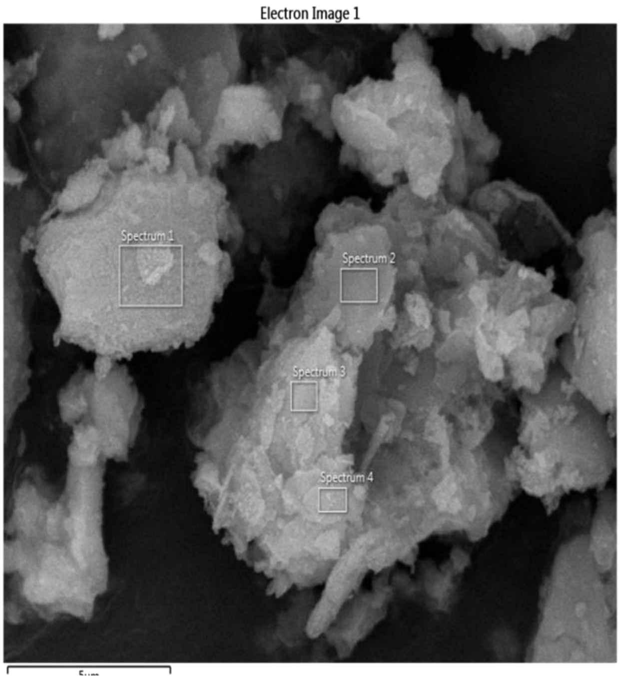

Figure A 2.3.2.3 SEM EDS ablation locations 1, 2, 3 and 4 on FeWTR 2019.

Table A 2.3.2.5 SEM-EDS of FeWTR 2019, elements as % of the total composition. Spectrums 1, 2, 3 and 4

Element	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4
C	18.2	9.26	11.28	20.09
N	0	0	0	0
O	9.18	7.22	5.32	11.32
Na	0	0	0	0
Mg	0	0	0	0
Al	1.31	1.16	1.06	1.85
Si	2.49	3.1	2.15	3.72
P	0	0	0	0
S	0	0	0	0
Cl	0	0	0	0
K	0.42	5.17	0.85	0.92
Ca	4.34	1.68	1.4	1.14
Mn	0	0	0	0
Fe	64.05	72.4	77.95	60.96
Total	100	100	100	100

Table A 2.3.2.6 SEM-EDS of FeWTR 2019, elements as % of the total composition. Average of spectrums 1, 2, 3 and 4

Element	Max	Min	Average	Standard Deviation
C	20.09	9.26	14.71	5.25
N	0	0	0	0
O	11.32	5.32	8.26	2.58
Na	0	0	0	0
Mg	0	0	0	0
Al	1.85	1.06	1.35	0.35
Si	3.72	2.15	2.87	0.7
P	0	0	0	0
S	0	0	0	0
Cl	0	0	0	0
K	5.17	0.42	1.84	2.23
Ca	4.34	1.14	2.14	1.48
Mn	0	0	0	0
Fe	77.95	60.96	68.84	7.76

SEM-EDS of AlWTR

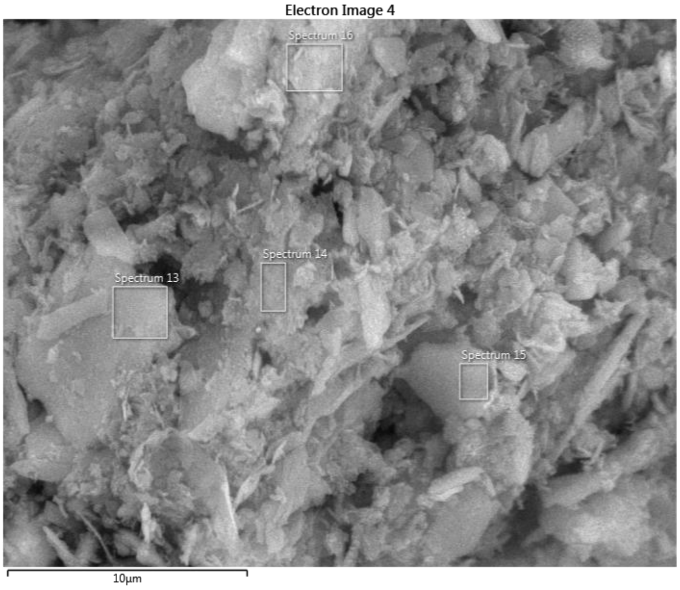

Figure A 2.3.2.4 SEM EDS ablation locations 13, 14, 15 and 16 on AlWTR.

Table A 2.3.2.7 SEM-EDS of AlWTR, elements as % of the total composition. Spectrums 13, 14, 15 and 16

Element	Spectrum 13	Spectrum 14	Spectrum 15	Spectrum 16
C	26.78	69.97	43.08	49.84
N	0	0	0	0
O	51.66	22.59	13.95	39.46
Na	0.18	0	0	0
Mg	0.23	0	0	0
Al	8.3	2.18	11.03	3
Si	8.41	1.58	14.52	5
P	0	0	0	0
S	0.94	1.99	1.07	0.82
Cl	0	0	0	0
K	2.21	0.17	3.82	0.27
Ca	0	0	0.23	0
Mn	0	0	0	0
Fe	1.31	1.52	12.29	1.61
Total	100	100	100	100

Table A 2.3.2.8 SEM-EDS of AlWTR, elements as % of the total composition. Spectrums 13, 14, 15 and 16

Element	Max	Min	Average	Standard Deviation
C	69.97	26.78	47.42	17.88
N	0	0	0	0
O	51.66	13.95	31.91	16.89
Na	0.18	0	0.04	0.09
Mg	0.23	0	0.06	0.11
Al	11.03	2.18	6.13	4.25
Si	14.52	1.58	7.38	5.52
P	0	0	0	0
S	1.99	0.82	1.21	0.53
Cl	0	0	0	0
K	3.82	0.17	1.62	1.74
Ca	0.23	0	0.06	0.12
Mn	0	0	0	0
Fe	12.29	1.31	4.18	5.41

APPENDIX 2.3.3: ADSOPRPTION ISOTHERMS OF FEWTR (2018) FEWTR (2019) AND ALWTR (2019)

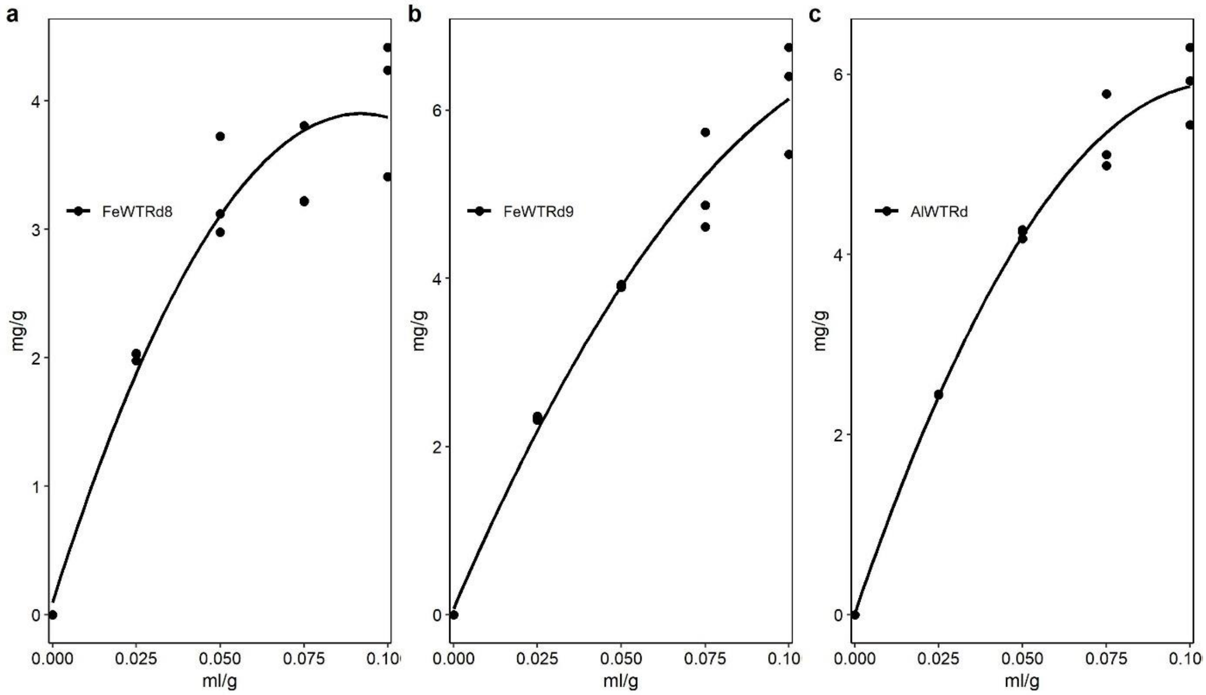

Figure A 2.3.3.1 Adsorption isotherms of FeWTR (2018) and (2019) as well as AlWTR (2019)