

Evaluation of the effects of an orange-oil based soil ameliorant on soil water management

Nordely Wright

*Dissertation presented in partial fulfilment of the requirements for the degree
Master of Science in Agriculture
in the faculty AgriSciences at Stellenbosch University*



Supervisor: Dr. Josias Eduard Hoffman, Stellenbosch University

Co-supervisor: Dr. Dirk Cornelius Uys, Oro Agri (SA) (Pty) Ltd.

March 2013

Declaration

By submitting this thesis/dissertation electronically, I declare that the entirety of the work contained therein is my own, original work, that I am the sole author thereof (save to the extent explicitly otherwise stated), that reproduction and publication thereof by Stellenbosch University will not infringe any third party rights and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

Date: March 2013

Copyright © Stellenbosch University

All Rights Reserved

This thesis was made possible with the sponsorship
and technical support of Oro Agri (SA) (Pty) Ltd.

Abstract

Soil amelioration and conditioning is desirable and in many cases essential, due to increasing food demand and the deterioration and exhaustion of soils. A new soil ameliorant, consisting of orange oil as a base and a mixture of surfactants, is on the global agricultural market. Use of this soil ameliorant by farmers has made an impact on crop production and plant growth on many farms. The effects of this soil ameliorant on selected soil properties as well as plant traits were evaluated by a field trial, a pot trial and a Water Characteristic Curve experiment.

A field trial was performed in the Firgrove area near Somerset West, Western Cape (South Africa). It entailed the evaluation of the water content and lateral movement of water in a sandy soil after the application of the soil ameliorant. The field was already planted with *Capsicum annuum* crop at the initiation of the trial. The trial was performed in a drip irrigated field by taking soil water measurements using a Diviner 2000 probe over a nine week period. The trial showed significant increases in water content on the plots treated with the soil ameliorant. These increases are indicative of an increase in the lateral movement of the soil water, as the measurements were taken between two drippers. On average, the ameliorant treated soil had 17% higher water content than that of the control.

A Water Characteristic Curve (WCC) experiment was conducted, which entailed establishing the WCC for a sandy soil treated with the soil ameliorant. The Sandbox apparatus, from Eijkelkamp Agrisearch Equipment, was used to perform the experiment and provides suction values of 0.1 to 10.1 KPa. The WCC showed that the ameliorant application increased water retention over all suctions, especially for the 10 ℓ/ha ameliorant application. This substantiated the Field trial where water retention was increase in a sandy soil.

A pot trial was performed in a greenhouse to evaluate the effect of the soil ameliorant on selected soil properties and certain plant traits. This experiment consisted of an ameliorant treatment and a control with a combination of four different Plant Available Water Depletion (PAWD) regimes namely, 10% depletion, 50% depletion, 80% depletion and 50% C depletion, where "C" refers to *covered*. The trial layout, with five single pot replicates per treatment combination, was according to a randomized block design. The surface covering

of one of the 50% PAWDs was a plastic sheet which to prevent evaporation from the soil surface. The ameliorant treatment resulted in significant improvements in overall plant growth, total biomass production, especially dry root biomass. Leaf Area Index and plant height were also improved. The Biomass Water Use Efficiency was improved with the ameliorant application, especially for the 50%C PAWD illustrating the beneficial use of a mulch. Bulk density was decreased with application of the ameliorant but this difference was not statistically significant. Aggregate stability for the moist soils (10% and 50%C PAWD) was significantly improved with the ameliorant application.

The application of this soil ameliorant made significant improvements in various facets of plant growth and certain soil physical properties. Especially water holding capacity in sandy soils and the overall improvement in plant growth. There is still much opportunity for research in this field and many questions remain, especially those pertaining to the mechanisms involved in the workings of a soil ameliorant containing a mixture of ingredients.

Opsomming

Die bestuur van besproeiingswater en die optimisasie van gewasproduksie is 'n studieveld wat baie aandag verg, aangesien varswater bronne bedreig word. As gevolg van die stygende vraag na voedsel en die agteruitgang en uitputting van die grond, is grondverbetering en-kondisionering aanbeveelbaar en in sommige gevalle noodsaaklik. 'n Nuwe grond verbeteraar, bestaande uit lemoen olie as 'n basis en 'n mengsel van benattingsmiddels, is beskikbaar op die wêreld landbou mark. Die gebruik van die grondverbeteraar deur boere het 'n impak gemaak op gewasproduksie en plantegroei op baie plase. Die effek van die grondverbeteraar op geselekteerde grond-eienskappe sowel as plantkenmerke is geëvalueer deur 'n veld proef, 'n pot proef en 'n Water Karakteristieke Kurwe eksperiment.

'n Veldproef is uitgevoer in die Firgrove omgewing naby Somerset Wes in die Wes-Kaap Provinsie, Suid Afrika. Die veldproef het die evaluasie van die grondwater inhoud en die laterale beweging van water in 'n sanderige grond behels. Die gewas *Capsicum annum* was alreeds in die veld aangeplant voor die begin van die proef. Die proef was uitgevoer in 'n drup besproeide veld deur grondwater metings wat geneem is met 'n Diviner 2000 peilstif oor 'n periode van nege weke. Die proewe het 'n beduidende verhoging in die grondwater-inhoud getoon waar die grond met die grondverbeteraar behandel is. Die verhogings was 'n aanduiding van 'n toename in die laterale vloei van grond water, aangesien die lesings tussen twee druppers geneem is. Die grond, wat met die grondverbeteraar behandel is, het gemiddeld 17% hoër grondwater-inhoud gehad as die kontrole.

'n Water Karakteristieke Kurwe (WKK) eksperiment is uitgevoer, wat bestaan het uit die opstel van die WKK vir 'n sanderige grond behandel met die grondverbeteraar. Die "Sandbox" apparaat van Eijkelkamp, Agrisearch Equipment is gebruik wat negatiewe druk waardes van 0.1 tot 10.1 KPa toon. Die WKK het getoon dat die toediening van die grondverbeteraar die water retensie verhoog het oor al die drukke, veral in die 10 ℓ /ha toediening. Dit staaf die resultate van die Veld eksperiment waar water retensie verhoog is in die sanderige grond.

Die pot-eksperiment is uitgevoer in 'n tunnel om die effek van die grondverbeteraar op geselekteerde grond eienskappe en verskeie plant eienskappe te evalueer. Die eksperiment het bestaan uit 'n grondverbeteraar behandeling en 'n kontrole met 'n kombinasie van vier verskillende plantbeskikbare wateronttrekkings naamlik, 10%, 50%, 80% onttrekking, en 'n 50%C onttrekking, waar "C" verwys na "covered". Die proef uiteensetting, met vyf enkel pot herhalings per behandeling kombinasie was volgens 'n ewekansig blok uitleg. Die oppervlakte dekking van 50%C plantbeskikbare wateronttrekking was 'n 60 μm plastiek-vel wat verdamping vanaf die grondoppervlak verhoed het. Die grondverbeteraar behandeling het 'n beduidende verbetering in algehele plantgroei, totale biomassa produksie en spesifiek droë wortel biomassa getoon. Die blaararea indeks en planthoogte het ook 'n verbetering getoon. Die biomassa-watergebruiksdoeltreffendheid het verbeter met die toediening van die grondverbeteraar, spesifiek vir die 50%C plantbeskikbarewateronttrekking wat die voordele van die gebruik van oppervlakdekking illustreer.

Die brutodigtheid is verminder deur die toediening van die grondverbeteraar, maar die verskil was statisties nie wesenlik nie. Agregaat-stabiliteit vir die grond met 'n hoër vogregime (10% en 50%C plantbeskikbare wateronttrekking) is wesenlik verbeter met die toediening van die grondverbeteraar.

Die toediening van die grondverbeteraar het wesenlike verbeteringe in verskeie plantegroei- en grondfisiese-eienskappe getoon. Spesifiek laterale beweging in sanderige grond en die verbetering van algehele plantegroei. Daar is nog baie geleenthede vir navorsing in die veld en baie vrae bly onbeantwoord, veral in verband met die meganismes met betrekking tot die werking van die grondverbeteraar wat uit 'n mengsel van bestandele bestaan.

Table of Contents

Declaration	i
Abstract	iii
Opsomming.....	v
Table of Contents	vii
List of Figures	x
List of Tables	xiii
Dedication.....	xv
Acknowledgements.....	xvi
Introduction	1
Chapter 1: Literature Review.....	4
1.....	4
1.1. Nonionic and anionic surfactants	4
1.1.1. Surfactant chemistry and sorption at soil-water interfaces	4
1.1.2. Water repellency and water infiltration	7
1.1.3. Evaporation: mechanisms and effects of surfactant application	9
1.1.4. Soil water content and hydraulic conductivity.....	10
1.1.5. Aggregate stability and soil structure	12
1.1.6. Plant response and Biodegradation.....	14
1.2. Orange oil	18
1.2.1. Properties of orange oil and its major constituent, Limonene	18
1.2.2. Transport and fate of limonene in soil.....	18
1.2.3. Biodegradation of limonene.....	19
1.2.4. Effect of limonene on plant growth.....	20

Chapter 2: Materials and methods	22
2.....	22
2.1. Firgrove Field Trial.....	22
2.1.1. Materials and Methods	22
2.1.2. Statistical analysis	25
2.2. Sandbox experiment	25
2.2.1. Materials and Methods.....	25
2.3. Pot Experiment in Greenhouse	26
2.3.1. Materials and Methods	27
2.3.2. Statistical analysis	35
Chapter 3: Results and Discussion	37
3.....	37
3.1. Firgrove Field Trial.....	37
3.1.1. Water measurements	37
3.1.2. Bulk density	41
3.2. Sandbox Experiment	42
3.3. Pot experiment in greenhouse	43
3.3.1. Water content of pots.....	43
3.3.2. Evapotranspiration.....	45
3.3.3. Bulk density	49
3.3.4. pH Measurements	50
3.3.5. Aggregate Stability	51
3.3.6. Dry Root biomass.....	53
3.3.7. Dry Shoot biomass	55
3.3.8. Total Plant Biomass.....	57
3.3.9. Leaf Area Index	59

3.3.10.	Plant height	60
3.3.11.	Chlorophyll content	62
3.3.12.	Leaf Chemical Analysis.....	63
3.3.13.	Biomass Water Use Efficiency.....	68
3.4.	The percentage increase from control to treated for selected properties	70
Conclusions		71
References		74

List of Figures

Figure 1.1: Structure of (a) D-limonene and (b) Limonene oxide (c) 8-p-menthene-1,2-diol	18
Figure 2.1: Google image of site location, where the field is outlined by the yellow block. The direction of the slope is given by the white arrow. (Image date: 2-01-2011)	23
Figure 2.2: A schematic representation of the layout for the field trial with two treatments on two soils with four replications. The individual plots will be randomised across the field according to the plant height at the beginning of the experiment. Soils are given as A and B. Orange denotes treatment (T) and the green denotes the control (C).	24
Figure 2.3: Photograph of the samples in the sandbox randomly arranged.	26
Figure 2.4: Representation of eight treatments for the Pot Experiment.	28
Figure 2.5: <i>Wet sieving Apparatus</i> for the determination of the percentage water stable aggregates.	31
Figure 2.6: Maize plants in greenhouse at week six from planting.	34
Figure 3.1: Mean water content at each depth in the profile for the treated versus the control plots over a period of nine weeks for Soil A.	37
Figure 3.2: Mean profile water content for the treated versus the control plots over a period of nine weeks for Soil A.	38
Figure 3.3: Mean profile water content for the treated plots versus the control plots over a period of seven weeks for Soil B.	39
Figure 3.4: Mean bulk density of the treated versus the control plots for both Soil A and B.	41
Figure 3.5: Water Characteristic Curve for two treatments with different ameliorant application rates and a control treatment.	42
Figure 3.6: Mean water content over nine weeks for treated versus control of the 10% plant available water depletions.	44
Figure 3.7: Mean water content over nine weeks for treated versus control of the 50% plant available water depletion.	44
Figure 3.8: Mean water content over nine weeks for treated versus control of the 50%C plant available water depletions.	44
Figure 3.9: Mean water content over nine weeks for treated versus control of the 80% plant available water depletion.	44

Figure 3.10: Cumulative mean evapotranspiration of the treated and control for each of the plant available water depletions. 45

Figure 3.11: The average weekly wind speed outside the greenhouse in meters per second over the trial period of nine weeks..... 47

Figure 3.12: Evapotranspiration losses for all the plant available water depletions over a period of nine weeks and the mean weekly maximum temperature over the same period. 48

Figure 3.13: Mean bulk density of the treated and control for each of the plant available water depletions. 49

Figure 3.14: Aggregate stability for the treated versus control for each of the PAWDs. 51

Figure 3.15: Mean dry root biomass for the treated and control for each of the plant available water depletions. 53

Figure 3.16: Linear correlation of dry root biomass and aggregate stability..... 55

Figure 3.17: Mean dry shoot biomass for the treated and control for each of the plant available water depletions. 56

Figure 3.18: Mean total biomass for the treated and control for each of the plant available water depletions as components of shoot and root biomass..... 57

Figure 3.19: The Leaf Area Index for the treated and control for each of the plant available water depletions. 59

Figure 3.20: Plant height for the treated versus control plants for each of the plant available water depletions. 61

Figure 3.21: Chlorophyll content of the treated versus the control for each of the plant available water depletions as a Chlorophyll Content Index (CCI) 62

Figure 3.22: Ca content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. 66

Figure 3.23: Mg content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. 66

Figure 3.24: Na content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. 66

Figure 3.25: K content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. 66

Figure 3.26: Fe content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. Figure 3.27: Cu content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions..... 67

Figure 3.28: Zn content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. 67

Figure 3.29: Mn content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions. 67

Figure 3.30: The mean Biomass Water Use Efficiency of the treated versus the control for each of the PAWDs..... 68

List of Tables

Table 1.1: Summary of the soil properties and how they may be altered with the use of different types of surfactants.....	17
Table 1.2: Biodegradation rates for Limonene and Limonene oxide using various chemical fragment methods.	20
Table 2.1: Five fraction textural analysis expressed as a percentage of the Firgrove soil.....	22
Table 2.2: Seven fraction textural analysis for the soil used in the Sandbox experiment	26
Table 2.3: Five fraction textural analysis of the soil used for the Pot experiment	27
Table 2.4: Elemental composition of the multi-element fertilizer, Chemicult, used in the Pot Experiment for fertigation.....	29
Table 3.1: Means of profile water content of Soil A and B for the comparison of the treated and control and the comparison between different depths of the treated and control combined.....	40
Table 3.2: Means of bulk density for the comparison of the treated and control.....	42
Table 3.3: Means of the cumulative evapotranspiration over the nine-week period for the comparison of the treated and control within each of the PAWD.....	46
Table 3.4: Means of bulk density for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.....	50
Table 3.5: pH of the soil samples in H ₂ O and KCl for treatment and control for all plant available water depletions.	50
Table 3.6: Means of the aggregate stability for the comparison of the treated and control within each of the PAWD.	52
Table 3.7: Mean of the Dry Root Biomass for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.....	54
Table 3.8: Means of the Dry Shoot Biomass for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.....	56

Table 3.9: Means of the Total Biomass for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined..... 58

Table 3.10: Means of the Leaf Area Index for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined..... 60

Table 3.11: Means of the plant height for the comparison of the treated and control within each of the PAWD. 62

Table 3.12: Means of Chlorophyll Content Index for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined..... 63

Table 3.13: The Macro- and Micro-nutrients for the soil ameliorant treated and control pots for each PAWD in milligrams nutrient per plant. 65

Table 3.14: Means of the BWUE for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined..... 69

Table 3.15: The percentage increase from the control to the treated for some selected soil properties and plant traits..... 70

Dedication

I dedicate this thesis to the Lord God Almighty,
Who is and was and always will be!
By His grace we may learn, love and live forevermore!

“Now to Him who is able to keep you from stumbling,
And present you faultless
Before the presence of His glory with exceeding joy,
To God our Saviour,
Who alone is wise,
Be glory and Majesty,
Dominion and power,
Both now and forever.
Amen.”

Jude verses 24 and 25
New King James Version

Acknowledgements

Dr Uys, thank you for your guidance and support throughout my thesis. I appreciated all your many emails and calls to answer all my questions and for keeping me up to date with the latest developments.

Dr Hoffman, thank you for teaching me to work hard. You are an outstanding lecturer.

Thank you to all my Frolleagues; Makhosazana Sika, Pieter Botha, Nico Wasserfal, Nina Swiegelaar, Jacques Smith, Naudé Smith and Cou Pienaar. Each of you are special to me as I got to know you during the many hours spent in the Postgrad offices.

Special thanks to my Soil-Chemistry pal, Daniel Viljoen. I really appreciate our long meaningful discussions to try and make sense of our theses.

Thank you to Dr Hardie, Dr Rozanov, Dr Ellis, Prof Lambrechts, Dr de Clercq and Dr Clarke of the Soil Science Department for the invaluable contribution to create a vibrant environment of learning.

Many thanks to the staff of the Soil Science Department. Tannie Annatjie and Aunt Delphine who, with their feminine touch, brought life to the department. Nigel Robertson for his endless jokes and positive approach to life. The CAF team who quietly work their magic in the lab including of Cynthia Sanchez-Garrido, Matt Gordon and Herschel Achillies; Charlo Scheepers for keeping the lab in order with a song in the air.

Angelique Zeelie, thank you for your encouragement and all the help with my thesis, also your friendship.

Yusaf Ras, thank you for always being willing to help me find my way through the myriad of books and articles in the library. Your friendliness and helpfulness will not be forgotten.

Thank you to Oro Agri for their financial support, in the form of a bursary and research funding. Thank you for the wonderful opportunity to be part of such exciting new research. Special thanks to Erroll Pullen for his enthusiasm and vision.

My new parents in-law; Mommy Irene for your love, many prayers and hugs. Pops for those priceless chemistry conversations, where only we knew what we were talking about.

My sister Marely! Thank you for all our laughs and tears together. Those endless hours in the flat in Stellenbosch, priceless memories! You are so special to me.

My Mommy and Daddy, thank you for your endless love and encouragement throughout my life. You are God fearing parents and who could ask for more. I am so proud of you both!

My husband David, you are my safe place, my place of joy, my place of love. You fully supported my long study hours, even in our dating years and made sacrifices for me that I am so grateful for. I love you so much!

Thanks and praise be to my heavenly Father who gives life now and the hope of a future. Thank you Father for providing for all my needs from the smallest to the greatest.

Introduction

Soil water management is of great importance for future crop production as the “Challenges of growing water scarcity for agriculture are heightened...” (Rosegrant et al., 2009) . It is well recognised that due to the growing global population and food demand, water saving is an essential part of future agricultural enterprise, especially for irrigated crops (Wang et al., 2002, Wallace, 2000). The lack of freshwater supplies requires optimisation of soil water management and the water use efficiency of crop production.

The soil ameliorant evaluated in this study contains cold-pressed orange oil as a base and a blend of anionic and nonionic surfactants, hereafter referred to as “the ameliorant”. The application rates for the ameliorant, as recommended by the manufacturer, was initially 30 L per hectare. During the course of the study this recommendation was adjusted to 10 L per hectare as the manufacturer found that lower doses perform as well, if not better. The ameliorant can be applied to the soil via the irrigation lines of any irrigation system.

The ameliorant is highly effective in the alleviation of soil water repellency and the improvement of infiltration into water repellent soils. The application of the ameliorant, in commercial field trials, has shown that Water Use Efficiency and water holding capacity may be improved. Farmers observed a lowering of the crop’s water requirements, or more efficient use of water, with the increase in crop yields with the application of the ameliorant (Uys, 2011).

According to the manufacturer, the ameliorant also functions as an irrigation line cleaner, but this attribute has not been evaluated in this study. One comment which can be made regarding the cleaning of the irrigation lines is that there is ample research demonstrating that orange oil is an effective bactericide, fungicide and pesticide (Subba et al., 1967; Isman, 2000; Sharma and Tripathi, 2006 and Friedly et al., 2009).

Although the ameliorant is a relatively new product on the agricultural market, it is already being widely used in the agricultural sector. It is not the only product of its kind currently available, yet the notable results of its use would suggest that it is unique. Comparison of products is often difficult because different products each contain mixtures of a variety of compounds. Research regarding the expected effects of the ameliorant on crop and soil

needs to be evaluated and quantified to establish concrete scientific data that can further be used in the agricultural industry. Qualification of the benefits of the use of the ameliorant is necessary to determine whether its application is worthwhile for the improvement of crop production and soil quality.

The aim of this study was to qualify, and where possible quantify, the ameliorant as a viable product for the improvement of soil water management, to increase crop production as well as enhance or maintain soil physical properties. In order to make effective use of the ameliorant it is necessary to identify the possible effect(s) that the product may have on the soil system.

The key objective was to evaluate certain soil properties and plant responses as affected by the application of the ameliorant. The evaluation was carried out by assessing the following soil physical properties; water-holding capacity, aggregate stability, bulk density and water retention at various suctions. The effect on the crop can be monitored by assessing the vertical growth (plant height), the leaf size (Leaf Area Index) and biomass production (shoot and root). If the ameliorant does have an effect the water-holding capacity of the soil and does improve crop production, it will improve the Water Use Efficiency of the crop.

The hypotheses that were tested in this study are as follows;

1. The water holding capacity of the soil increases when the soil has been treated with the ameliorant.
2. The aggregate stability of the soil improves when the soil has been treated with the ameliorant.
3. The bulk density decreases with a concomitant increase in the porosity of the soil treated with the ameliorant.
4. The root system is improved with the application of the ameliorant.
5. The overall plant growth (shoots, LAI, plant height) is improved with the application of the ameliorant.
6. The chlorophyll content increased in the plants grown in the soil which received the ameliorant application.
7. The Biomass Water Use Efficiency is improved with the application of the ameliorant.

Research is necessary to determine the effects of this ameliorant as an amendment for use on soils. Once the effects that the ameliorant has on the soil and crop have been assessed,

predictions can be made to improve its use and application on different soil types, as the results of application may differ with differences in soil type. The application of surfactants to the soil system alters the surface tension of bulk soil solutions and may have an effect on matric potential, flow rates, infiltration, evaporation, aggregate stability solute solubilities, and diffusion rates in the soil solution and at the water-air interface.

Chapter 1: Literature Review

1.1. Nonionic and anionic surfactants

The scope of this literature review is very broad in the sense that it covers the background and dominant attributes of anionic and nonionic surfactants even though these attributes may not be directly related to this study. However, it is important to have an understanding of these attributes as they may have ancillary effects with regard to the particular observations made in this study.

1.1.1. Surfactant chemistry and sorption at soil-water interfaces

Surfactant molecules consist of both a hydrophilic and a hydrophobic component. This amphiphilic nature affords surfactants their unique chemical properties that grant them an important role in surface and interfacial chemistry of soils. Surfactants have been researched extensively for remediation of soils containing hydrophobic organic contaminants. For remediation purposes, surfactants are recognised primarily by their ability to form micelles in solution at a concentration known as the Critical Micelle Concentration (CMC). In the case of surfactant application as a soil ameliorant to alter water tension, infiltration and alleviating water repellency, the concentration of surfactant applied is often lower than the CMC.

For the purpose of this study, there are two surfactant types of interest namely, anionic and nonionic surfactants. Anionic surfactants dissociate in water yielding the corresponding surfactant ion and its counter-ion. Nonionic surfactants are uncharged and include a highly polar moiety, which affords the characteristic hydrophilic head and a non-polar or hydrophobic tail.

Surfactants may sorb to soil components by three main mechanisms; ion exchange, adsorption and surfactant partitioning to organic matter. Anionic surfactants do not sorb readily to soils and sediments (Brownawell et al., 1997) and when sorption does occur it is not in substantial quantities (Law and Kunze, 1966). The nature of the adsorption of anionic surfactants may be electrostatic or hydrophobic (Allred and Brown, 1996). The presence of

Ca^{2+} and Mg^{2+} cations in the soil solution facilitates co-adsorption of anionic surfactant molecules. Co-adsorption, or cation-bridging, requires relatively high levels of Ca^{2+} or Mg^{2+} . Hydrophobic partitioning occurs because of the amphiphilic nature of surfactant molecules. The molecules try to orientate themselves in such a way as to afford maximum stability in an aqueous (polar) environment. The molecules tend to accumulate at phase boundaries and this allows them to play a role in interface chemistry.

Nonionic surfactants adsorb to surfaces that are hydrophobic or hydrophilic in character. Their orientation depends on the nature of the surface in terms of polarity. If the soil surface has hydroxyl or oxygen groups (polar groups) which are able to form hydrogen bonds (Law and Kunze, 1966) with the nonionic surfactant, it will result in the surface being more hydrophobic. If polar groups are not present, the molecules will orientate with their hydrophobic group towards the surface making the consequent surface more hydrophilic (Rosen, 2004).

The study by Abu-Zreig (2003) conjectures that nonionic surfactants may attach to the soil surfaces by their hydrophobic component and hence reduce the contact angle, as the hydrophilic part is orientated toward the pore space. These observations clarify the impression that when the soil is moist (a hydrophilic environment), the hydrophobic component of the nonionic surfactant will favour sorption to the soil surface, thus allowing the hydrophilic component to associate with the water surrounding the soil particle. The result is that the surfaces of the soil particles are now hydrophilic. However, would this relationship be reversed upon drying?

The comparative study by Rodríguez-Cruz et al. (2005) found similar results. They found that the adsorption of anionic versus nonionic surfactants is dependent on the physiochemical and mineralogical properties of the soil and that there are differences in the mechanisms of adsorption of anionic and nonionic surfactants. They concluded that the anionic surfactant, sodium dodecyl sulphate, adsorbed to soil particles by hydrophobic interactions with organic matter, by ligand exchange and/or electrostatic attraction with kaolinite. The nonionic surfactant, octylphenoxypolyethoxyethanol (Triton X-100), showed hydrogen bonding of the oxygen atoms of the ethoxyl groups with the 2:1 type clay minerals. Swelling type, 2:1, clays are known to intercalate alcohol ethoxylates, a nonionic surfactant.

Concentration plays an important role in the effect of surfactants on the soil environment. The surfactant properties and the soil type influence the relation between concentration and the efficacy of the application. The sorption of the surfactant molecules to the soil particles may form a surfactant bilayer on the soil surface, hence the surfactants hydrophilic moieties would be orientated outwards (Karagunduz et al., 2001). Surfactants at high concentrations form micelles. Whether there is a reduction in the partitioning of nonionic surfactant molecules to the soil when the concentration exceeds the CMC is not certain. However, the study by Ussawarujikulchai et al. (2008) showed that the effective CMC was increased with increasing organic matter content. This suggests that sorption to organic matter is more favourable than the formation of micelles.

The total adsorption of surfactants to the soil water interface may be significantly increased in surfactant mixtures as compared with the individual surfactants, due to the formation of mixed hemi-micelles (Scamehorn et al., 1982). Studies on anionic-nonionic mixtures, at concentrations below the CMC, show that adsorption of each of the surfactants on kaolinite is enhanced by the presence of the other. Further, synergistic interaction between surfactants was observed, the adsorption of ionic surfactants may be enhanced by the presence of nonionic surfactants and vice versa, by means of chain-chain interactions of adjacent molecules on the soil particles (Xu et al., 1991).

The dominant role that organic matter plays in the sorption of surfactants is one that has been encountered frequently (Liu et al., 1992; Rodríguez-Cruz et al., 2005; Ussawarujikulchai et al., 2008). Studies found that increasing amounts of organic matter in the soil resulted in increased sorption of anionic surfactants. The effective critical micelle concentration (CMC) also showed an increase with increasing organic matter content (Ussawarujikulchai et al., 2008). However, the study by Brownawell et al. (1997) indicated that the affinity of nonionic surfactants for sediment soils did not follow the order of increasing organic carbon content.

1.1.2. Water repellency and water infiltration

Water repellency affects the way that water infiltrates and penetrates the soil and causes preferential flow paths and increased spatial variability in terms of water content. Water repellency in soils arises from hydrophobic coatings on soil particles. The hydrophobic compounds that form these coatings vary in origin. The main sources include plant root exudates, decomposing organic matter, fungi and waxes from plant leaves. The causes of hydrophobicity in sands include the following; the coating of sand particles with organic matter (DeBano, 1981) and also amorphous substances (Bisdorn et al., 1993), presence of interstitial soil materials such as micro-aggregates, clay and fine plant remains. Research conducted in the Netherlands on water repellent sands by Bisdorn et al. (1993) showed that few of the sand fractions had any type of coatings thus it was proposed that the cause of hydrophobicity was interstitial soil materials between sand grains. This study also showed that different sand fractions have varied degrees of water repellency. In some cases the finest sand fraction was extremely hydrophobic but this did not have an effect on the hydrophobicity of the soil at large.

The extent of water repellency in a soil is related to the number of soil particles coated with hydrophobic compounds (Doerr et al., 2006). As this relates to the surface area of the bulk soil, texture also plays a role in the degree of water repellency. That is to say, clay soils with a large surface area will have fewer hydrophobic particles than that of sandy soils with a smaller overall surface area. For this reason it is more common for sandy soils to exhibit water repellent properties. All soils are affected by water repellency to a greater or lesser degree.

The occurrence of soil water repellency is the rule rather than the exception (Bachmann et al., 2007), as most soils exhibit water repellent properties to some extent. The concept of a sub-critical water repellent soil was introduced by Tillman et al. (1989) and has since been used (Hallett et al., 2001) to describe soils that appear wettable yet possess hydrophobic properties that impede infiltration and often cause preferential flow, resulting in uneven wetting of the soil (Jarvis et al., 2008; Ritsema and Dekker, 1996).

Hydrophobicity is increasing in agricultural soils where large applications of pesticides and herbicides are applied seasonally. Greater drying out of soils has also led to soils with

increased hydrophobicity (Doerr et al., 2006). Hydrophobicity is also a major problem in the management of turf where applications of hydrophobic sand for the levelling of the turf are used. Hydrophobic soils are prevalent in areas where there are predominantly sandy soils where additions of organic acids from the vegetation impart a hydrophobic nature to especially the topsoil. Studies show that the rhizosphere has greater water repellency than the bulk soil (Hallett et al., 2003). The origin of hydrophobicity in the rhizosphere is chiefly that of root exudates.

Fernández-Gálvez and Mingorance (2010) looked at the vapour and liquid hydrophobic characteristics affected by surfactant application. They stated, “Water repellency affects the way in which water penetrates the soil, thereby inducing preferential flow paths and increasing the spatial variability of soil moisture.” Thus water repellency in a soil causes uneven wetting of the soil surface and consequently the subsoil. Surfactant application in their study showed up to a 40% increase in adsorption of vapour molecules, thus enhancing soil wetness. Surfactant efficacy in the alleviation of water repellency is also greatly influenced by water quality, as marked differences were found between rain-fed and irrigated locales (Lehrsch and Sojka, 2011).

Regarding the effect of surfactant on infiltration, Equation 1.1 illustrates the effect that a shift in the surface tension has on infiltration.

$$\psi = \frac{-2\gamma \cos(\theta)}{g\rho r} \quad \text{Equation 1.1}$$

where ψ is the soil water potential, γ is the surface tension, θ is the contact angle, ρ is the solution density, g is the gravitational acceleration and r is the radius of an equivalent circular tube. Thus, a decrease in the surface tension will result in an equivalent decrease in the capillary pressure or the negative water potential. According to Feng et al. (2001), altering the value of the surface tension, γ , with the addition of a surfactant, also affects the contact angle, θ , thereby increasing infiltration of water into hydrophobic soil. In the case of non-hydrophobic soil the addition of a surfactant may cause the soil to become water-repellent depending on the concentration and type of the surfactant applied. The effect of contact angle on infiltration at the wetting front becomes less pronounced as the wetting

front extends deeper into the soil and gravity starts to have a greater influence than capillarity (Letey et al., 1962).

Substantial reductions in the surface tension with the addition of a powerful surfactant was shown in a study by Read and Gregory (2008) where root mucilage surfactants reduced the surface tension of pure water by 40%. Such a drastic change in the Ψ may have an important effect on the water relations of the rhizosphere.

1.1.3. Evaporation: mechanisms and effects of surfactant application

Evaporation from the soil occurs from the soil surface layer. Water is drawn to the surface by capillary action and heating of the soil surface by the sun converts the water to vapour and hence it is lost to the atmosphere. If the surface soil layer is dry, it is a hindrance to evaporation. Penman (1941) has shown that “self-mulching” of a soil, by the rapid drying out of the surface soil, will reduce evaporation. This is due to the formation of a diffusional barrier hence capillary action is decreased.

A study by Kolasew (1941; as cited by Lemon, 1956) showed that the surfactant treated chernozem lost water more rapidly at first compared with the control, but reached the critical water content (permanent wilting point) at a higher moisture level. The rate of water loss was slower in the treated soil after reaching the critical point up to the air dry range.

In terms of the effect of a surfactant application, the research of Tschapek and Boggio (1981) shows that the movement of water is dependent on where the concentration of surfactant is highest. In the absence of gravitational forces, water will move to where the concentration of surfactant is lower. According to these findings, the application of a surfactant on the soil surface would cause decreased evaporation, as water movement will tend to be downward. This may be related to the change in matric potential but it was not referred to in their study.

Greater soil water content as referred to in Section 1.1.4 may be due to a reduction in the evaporation rather than an increase in the water-holding capacity of the soil.

1.1.4. Soil water content and hydraulic conductivity

Effective soil water management requires a consistent monitoring of the soil and climatic conditions in order to predict and model the water dynamics of the soil. The use of a surfactant would thus not exclude the use of efficient monitoring systems but would alter the conditions in the soil towards more favourable soil water environment for plant growth.

Increased water content has been observed with the use of surfactants. Increases in soil water content have been attributed to a change in the particle arrangement due to an increase in the relative macro-porosity following the application of a anionic soil conditioner (Brandsma et al., 1999), which suggests a change in the bulk density of the soil.

A study by Leinauer et al. (2001) on the effects of surfactants on water retention in turf-grass, has shown that the extent to which there is a change in soil moisture retention at different depth is influenced by the soil type, the type of surfactant applied and its application rate. The study showed increased water retention in the root zones for both nonionic surfactants evaluated. The study further concluded that the data obtained from the particle size distribution, bulk density and total porosity were not able to verify the findings of increased water content in the root zone. It is suggested that a hydrophilic coating may be responsible for the increase in soil moisture but more research is required to establish this. If the surfactant provided a hydrophilic coating where before the soil was hydrophobic, greater soil water retention could be attributable to more pore space available for water storage and less water lost due to preferential flow.

In a rhizosphere study by Dunbabin et al. (2006) water and nutrient uptake were evaluated. It was found that there was a decrease in the soil water content and hydraulic conductivity at any given soil water potential with the application of lecithin which is used as an analogue to the phospholipid surfactants found in root mucilage. The addition of a surfactant may cause marked differences in the vadose zone which may not be as apparent when evaluating the bulk soil. In a study by Henry and Smith (2003) surfactant effects on flow phenomenon in the vadose zone was evaluated. It was observed that there is a shift in the water characteristic curve of the treated versus the untreated areas. Thus, at the same matric potential the surfactant treated soil showed a decrease in the water content. A

reduction in the surface tension of the water caused a proportional shift on the pressure axis of the water retention characteristics.

Henry and Smith (2003) also noted that there are concentration gradients between areas which received surfactant treatment and those which did not, thus resulting in varied hydraulic properties. General observations were then drawn regarding the behaviour of unsaturated flow in these systems. In short these points are: the capillary fringe height in a surfactant treated soil will be smaller; soil water pressure is greater in the surfactant treated porous medium; the water content is lower for the surfactant treated soil at all pressures below air-entry potential.

Soil water drainage may also be enhanced with the use of a surfactant. A study by Zartman and Bartsch (1990) evaluated 17 surfactants representing three surfactant classes; anionic, cationic and nonionic, each of these at six different concentrations. The study showed that there was an increase in the drainage of dewatered columns with a concomitant increase in the concentration of the surfactant applied. It was further shown that there was no significant difference between the different surfactant classes. After chemical assessment of the surfactant it was concluded that maximum drainage occurred for surfactants in which the number of ethylene-oxy units (EO units) had values of 14 to 16.

Most research conducted around the use of surfactants for the improvement of soil water retention was conducted on turf studies, particularly for golf courses. A study by Soldat et al. (2010) reported that during periods of drought there was increased uniformity of the soil water content in soils that were treated with a nonionic surfactant for all three the nonionic surfactants tested. The treated soils also displayed lower water repellency than the untreated soils, which is expected.

A study conducted by Karagunduz et al. (2001) found that the addition of a nonionic surfactant incrementally decreased the soil water content in an unsaturated soil, as the concentration of the applied surfactant increased. This high variability in water content is often due to hydrophobicity causing preferential flow paths (Ritsema and Dekker, 1996). Application of surfactants on soils has a significant effect on the water retention and hydraulic conductivity of the rhizosphere.

According to Lui and Roy (1995) the type of surfactant and the concentration applied has a strong influence on the results obtained for hydraulic conductivity evaluation. A study by Cid-Ballarín et al. (1998) explained that the decrease in hydraulic conductivity of a peat growing medium is due to an increase in the number of small pores available to water and thereby enhancing the lateral flow of water. They also observed an increase in the water retention ability of the peat with the application of the nonionic surfactant.

1.1.5. Aggregate stability and soil structure

It is widely accepted that poor soil structure, particularly poor aggregation and porosity, is a key restriction to water infiltration, redistribution, water storage in the soil profile and the water balance as a whole, thus impeding sustainable crop production (Connolly, 1998). Aggregation is an important soil property in terms of soil water management. This is because the stability of soil aggregates, and the soil texture, determines the intrinsic properties of the soil and the pore geometry. It affects the movement of water, the storage of water and soil aeration. These factors in turn have an influence on the biological activity of the soil and ultimately affect crop growth. In the event that the soil structure is disrupted, a subsequent disruption of the pore geometry and hence changes in the infiltration, hydraulic conductivity and water management of the soil system would occur.

Effects on soil factors, such as water content and aggregate stability, may be opposite when comparing the effect of a nonionic surfactant to an anionic surfactant (Lui and Roy, 1995). In a study by Mbagwu et al. (1993) the aggregate stability, measured as percentage water stable aggregates, is increased with the addition of nonionic surfactants, while application of anionic surfactants decreases the aggregate stability. The texture of the soil should be taken into consideration when selecting a surfactant for soil application as sandy soils would respond differently to clay soils, and different types of clay also have an effect (see Section 1.1.1.)

The chemical mechanism involved in the reduction or enhancement of aggregate stability is the orientation of the anionic or nonionic surfactant molecules respectively, as they sorb to soil particles. These mechanisms are discussed in Section 1.1.1. In a study by Brandsma et al.

(1999) regarding the evaluation of soil conditioners on erosion and soil structure, it was found that aggregate stability was increased significantly with the addition of an anionic surfactant, contrary to Mbagwu et al. (1993)

The following speculation was made in a study by Lehrs et al. (2012) with regard to aggregate strength of soils treated with a nonionic surfactant: the applied nonionic surfactant decreased the solid-liquid contact angle, thereby allowing water to enter pores more readily and thickening of water films surrounding soil particles within aggregates. Cementing agents (Ca^{2+} , iron and aluminium oxides) diffuse more easily from soil particle surfaces to the water films. As the soil dried, cementing agents were concentrated at the inter-particle contact points and clay particles and domains were drawn and reoriented at those points, thereby strengthening the nonionic surfactant-treated aggregates more than the control.

Mingorance et al. (2007) evaluated laboratory methodology approaches for evaluating the effects of three surfactant types on soil structure. The surfactant concentrations applied were above the CMC. The study shows that the use of anionic surfactants may cause precipitation of Ca^{2+} and Mg^{2+} , if these cations are present in sufficient concentrations. The precipitate formed is a salt of Ca or Mg, thus clogging pores, which in turn may reduce porosity. The added effect of the surfactant counter-ion, Na^+ , can cause clay dispersion and flocculation of clays and colloidal organic matter (Mingorance et al., 2007). The risk of clay dispersion is increased with increased concentration of anionic surfactant applied to the soil. However, large quantities of anionic surfactants need to be applied to soil before clay dispersion can occur.

In a study by Brandsma et al. (1999) when comparing four different soil ameliorants and their effects on soil physical properties all the ameliorants showed a decrease in the bulk density of the treated soil. Remediation of hard setting soils with high bulk density may be achieved with the use of an anionic surfactant as shown in the study by Chan and Sivapragasam (1996). It was found that there was a significant reduction in the tensile strength and the bulk density. The success of the amelioration on the hard setting soil was attributed to the stabilisation of micro-aggregates by the increased development of water stable bonding of the fine material ($< 50\mu\text{m}$).

The literature review in the study by Sutherland and Ziegler (1998) pointed out that the aggregate stability in the presence of anionic surfactants varies greatly and is a challenging field of study. They stated that there is a “need to rigorously test products containing anionic surfactants on different soil types before widespread application.” They suggested that factors, which influence the relation between aggregate stability and anionic surfactants, include pH, anion and cation exchange, clay mineral types present, sesquioxides present and the concentration of the anionic surfactant applied.

For anionic surfactants; weak van der Waal’s forces and hydrophobic bonding occur between the surfactant and the apolar soil components. The anionic surfactant thus has its hydrophilic part orientated outwards forming a coating and reducing the surface tension and hence increased water infiltration into the aggregates by reduction in the contact angle. Conversely, non-ionic surfactants, which form hydrogen bonds with the hydroxyl or oxygen groups of clay minerals (Law and Kunze, 1966), have their apolar or hydrophobic tail orientated toward the pore space creating a hydrophobic coating around the aggregates, hence an increase in the contact angle.

1.1.6. Plant response and Biodegradation

Water use efficiency of a crop is of great importance especially in a water scarce country such as South Africa (Visser and Verhoog, 2007). The potential advantages of the use of soil ameliorants, especially on problematic soils, chiefly ensues a lowering of crop water requirements and an increase in production. Reports on the effect of surfactant application, as described by Parr and Norman (1964), suggest that surfactants do not only affect the surface tension of the hydrologic system but that they have an effect on plant physiology affecting chemical adsorption (Read et al., 2003) and microbial processes (Hamme et al., 2006).

Lowering the surface tension of the soil solution, also the contact angle, will cause a proportional decrease in the matric potential (see Section 1.1.2). Therefore, the limits of plant available water is extended and plants can take-up more water as the matric potential is lower. This was substantiated in a study by Lehrs et al. (2011), which showed that soils

treated with a nonionic surfactant have increased water retention at high water potentials, possibly due to increased water film thickness around particles. While surfactants enable more water to be extracted by the root from the rhizosphere, the decrease in hydraulic conductivity of the rhizosphere may slow water extraction from the bulk soil (Ritsema and Dekker, 1996).

The use of surfactants has shown improvements in seedling emergence and therefore improvement in crop yield (Crabtree and Henderson, 1999). Application of a nonionic surfactant on golf tees and greens showed improvement in visual wetting uniformity and moisture in treated soils compared to a control soil (Kostka, 2000).

The application of a nonionic surfactant to New Guinea impatiens at increasing concentrations, 0 to 100 mg.L⁻¹, caused a decrease in the transpiration rate and stomatal conductance by 43% to 47%, respectively, while the water use efficiency increased by 47% (Yang, 2008). The fresh and dry mass of peace lily increased from 17% to 33% when comparing the control to the nonionic surfactant application.

Research relating the effects of surfactants on nutrient availability in the soil is somewhat limited. Considering the affinity that surfactants have for soil interfaces (Refer to Section 1.1.1), there may be more to the displacement of sorbed nutrients than is currently available.

There are many organic substances produced by plants and microbial organisms which can behave like surfactants, including humic and fulvic acids, proteins and also fatty acids (Read and Gregory, 2008). Sorption of surfactant molecules to the soil components results in competition for sorption sites on the soil particles and possible desorption of nutrients from soil. Thus a reduction in nutrient sorption could cause an increase in the nutrient uptake by plant roots. This was shown by Dunbabin et al. (2006) where application of lecithin, simulating phospholipid exudation by roots, to growing root sections showed a 13% increase in P acquisition in nutrient rich-soil and up to 49% in soils with a poor nutrient status.

In a study on the effect of a nonionic surfactant application on Nitrogen (N) utilization by potato (*Solanum tuberosum*), it was observed that there was a significant increase in the N

concentration of the tubers with a dual surfactant-N application, versus merely a N application, although there was no significant yield increase (Arriaga and Lowery, 2009). Thus there was an increased N uptake by plants in the surfactant-treated areas. The study also noted that there was a decrease in the leaching of NO_3 with the application of a surfactant.

A study examining the effects of phospholipid surfactants on the physical and chemical properties of soil showed effects on soil matrix potential, phosphate adsorption and nitrogen dynamics (Read et al., 2003). For these experiments lecithin was used to simulate the effects of the phospholipid surfactants in root mucilage. Phosphate adsorption to soil was decreased with the application of lecithin in the rhizosphere, therefore P was present in solution at higher concentrations and more easily available to the plant. Read et al. (2003) points out that if plants can maintain sufficient levels of surfactant in the rhizosphere, they would be able to take up water and nutrients from smaller pores, which would otherwise not be accessible.

Many authors are concerned with the degradation of surfactants and the effects of their degradation products remaining in the soil. Biodegradation is a principle mechanism for the breakdown of surfactants in the soil environment. Microorganisms may utilise surfactants as a source of energy and nutrients or they may co-metabolise the surfactants (Federle and Schwab, 1989). Anionic surfactants are readily degraded by microorganisms, while the degradation of nonionic surfactants occurs at a much slower rate. A study by Ang and Abdul (1992) shows that biodegradation of nonionic surfactants occurs readily by native soil microbes. They also showed that addition of oxygen increased the biodegradation rate of the non-ionic surfactant by 30% while the addition of nutrients effected a 50% increase in the rate of biodegradation.

Table 1.1: Summary of the soil properties and how they may be altered with the use of different types of surfactants

Soil Property	Surfactant Effect	Surfactant type	Soil Texture/Type	References
Water content	Decrease	Anionic	Sandy loam	Dunbabin et al., 2006
	Increase	Nonionic	Loamy sand and Sand	Leinauer et al., 2001 and Karagunduz et al., 2001
Hydraulic conductivity	Decrease	Anionic, Nonionic	Sandy loam, loam	Abu-Zreig, 2003
	Decrease	Anionic	Silty clay loam	Lui & Roy, 1999
Cumulative Infiltration	Increase	Nonionic	Clay and Clay loam	Mingorance et al., 2007
Bulk density	Decrease	Anionic	Alfisol	Chan and Sivapragasam, 1996
Hydrophobicity	Decrease	Non-ionic	Sand	Park et al., 2004
Aggregate stability	Decrease	Anionic	Entisol, Ultisol	Mbagwu et al., 1993
	Increase	Nonionic	Entisol, Ultisol	Mbagwu et al., 1993
	Increase	Anionic	Loamy sand	Brandsma et al., 1999
	Increase	Nonionic	Five different textures	Lehrsch et al., 2012
Nitrogen uptake	Increased	Nonionic	Loam	Arriaga and Lowery, 2009
Sorptivity	Increase	Nonionic, Anionic	Sandy loam and Silt loam	Abu-Zreig, 2003
	Decrease	Anionic	Sandy loam	

1.2. Orange oil

1.2.1. Properties of orange oil and its major constituent, Limonene

The orange oil contained in the soil ameliorant is cold-pressed from the peels of sweet orange varieties. It has the characteristic aroma of oranges, attributable to its major constituent, limonene, which makes up approximately 95% (Shaw and Coleman, 1974) of the composition (Figure 1.1a). Limonene forms part of the monoterpenes which is the simplest class of terpenes. They are synthesised from isoprene units through stereoregulated processes.

Orange oil exhibits surfactant-like properties as it has a low interfacial tension with water. This is attributed to the presence of 8-p-menthene-1,2-diol in orange oil which is a product of the oxidation of limonene (Arneodo et al., 1988). These molecules are able to form an organised layer at the liquid-vapour interface thereby lowering the interfacial tension thus increasing solvency of oil and water.

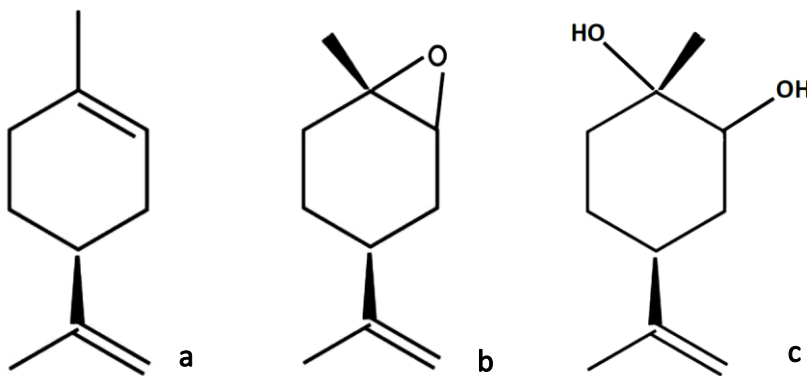


Figure 1.1: Structure of (a) D-limonene and (b) Limonene oxide (c) 8-p-menthene-1,2-diol

1.2.2. Transport and fate of limonene in soil

A theoretical study, in two parts, by van Roon et al. (2005a) and van Roon et al. (2005b) evaluated the fate and transport of monoterpenes through soils. The following is a summary of their findings regarding diffusion and partitioning in the soil as it relates to limonene.

They found that the mobility of monoterpenes is lower at higher soil water content. Although monoterpenes partition predominantly to the soil-water interface, the diffusion coefficient in atmospheric air ($\text{m}^2.\text{day}^{-1}$) is considerably higher than that of bulk water. The gas-water interface is also not an important retention zone for monoterpenes, however at low water contents it shows greater capacity for retention (Van Roon et al., 2005a).

Limonene has the greatest cumulative percentage volatilization (VOT%), at all temperatures for both the 0% and 1% organic matter content, of the four monoterpenes evaluated in the study by van Roon et al. (2005a). Though limonene's VOT% was high, it also had the largest retardation factor, which describes retention of the limonene due to partitioning to the soil matrix. This relationship is apparent when looking at the reduction in VOT% due to an increase in organic matter. VOT% were half or even less when organic matter was increased from 0% to 1%. Thus an increase in organic matter causes an increase in the retardation factor, so the limonene is retained in the soil.

Organic matter greatly influences the partitioning of monoterpenes. The organic matter-water partitioning coefficient ($\text{m}^3.\text{kg}^{-1}$) remains the dominant influence, when compared with the air-water or soil matrix-water partitioning coefficient, even when considering the high statistical uncertainty coupled with the calculation of the organic matter-water partitioning coefficient. This is so because the organic matter-water partitioning coefficient depends not only on the properties of the monoterpene but largely on the type of organic matter, which is highly variable throughout soil types. In the field, mineral soil can act as a sink for monoterpenes as they are transported. They move via gas exchange or via water in the soil (White, 1991).

1.2.3. Biodegradation of limonene

The aerobic biodegradation of monoterpenes, including limonene, was examined by Misra et al. (1996). They found that the monoterpenes were readily degraded under aerobic conditions at 23°C through biodegradation due to the increase in microbial growth and mineralisation. They also observed that a significant fraction of D-limonene-derived carbon that was non-extractable, dissolved organic carbon, which was not utilised by microbial

organisms. Therefore the biodegradation of D-limonene increases the stable organic carbon content in the soil.

An evaluation of the rates of biodegradation of various monoterpenes by Van Roon et al. (2005b) using the BIOWIN program which includes various chemical fragment methods is presented in Table 1.2.

Table 1.2: Biodegradation rates for Limonene and Limonene oxide using various chemical fragment methods.

Compound	MITI BPM ^a	BPM ^b	Primary BM ^c	Ultimate BM ^d
Limonene	Not-readily	Fast	Days-weeks	Weeks
Limonene oxide	Not-readily	Slow	Days-weeks	Weeks-months

^a Ministry of International Trade and Industry Biodegradation Probability Model

^b Biodegradation Probability Model

^c Primary Biodegradation Model

^d Ultimate Biodegradation Model

A study by (Bowen, 1975) showed that *Penicillium italicum* and *P. Digitatum* transform d-limonene into the following major transformation products: p-mentha-2,8-dien-1-ol, p-mentha-1,8-dien-4-ol, carvone, cis- and trans-carveol, perillyl alcohol, and p-menth-8-ene-1,2-diol. These products of biodegradation would most likely be present in the soil after the application of limonene.

1.2.4. Effect of limonene on plant growth

Limonene is widely used as a repellent or deterrent for insects and some plant diseases by foliar application. This however is a very different application than in this study. Very little research has been done on the effects of limonene in the soil. The research that has been performed is related to cases where limonene is produced naturally by plants and not an external application. Therefore, the concentrations of limonene are much lower than that applied to the foliage of plants for pest and disease management. It is necessary to determine critical threshold values for phytotoxicity of limonene to plants for foliar application. A study by Ibrahim et al. (2004) showed that concentrations of 90 to 120 ml. L⁻¹

were significantly phytotoxic to both cabbage and carrot plant, but that the response was cultivar specific.

As research is limited, assessment of the effects of limonene on plant growth as it is applied to the roots or in the soil is very brief. A study by Abraham et al. (2000) examined the effect of monoterpenes on germination and primary root growth. Of the four monoterpenes examined, camphor, eucaliptol, limonene and α -pinene, limonene did not have a largely negative effect on germination at concentrations ranging between 0.1 and 10.0 nM. The primary root growth was also not negatively affected by limonene, unlike the other monoterpenes.

Much research has been done on the effect of monoterpenes on inhibition of nitrogen cycling in the soil (White, 1994, Paavolainen et al., 1998 and Smolander et al., 2006) and these processes would affect plant growth. A study by White (1991) on the role of monoterpenes in soil nitrogen cycling processes, found that immobilisation of nitrogen did not occur even with the highest additions of limonene. This study looked at the limonene content in a natural forest soil and found that the concentration of monoterpenes in the soil decreased with increasing depth, with the exception of limonene, which increased with increasing soil depth. The study also showed that limonene was most effective at increasing NH_4^+ -N relative to NO_3^- -N at all levels of addition. Nitrate-N decreased with increased amounts of limonene addition in the assays that had an initially high NH_4^+ -N content. Research shows inhibition of both mineralisation and nitrification.

There has been extensive research on the effects of monoterpenes on lipid oxidation (Zunino and Zygodlo, 2004, Zunino and Zygodlo, 2005 and Cristani et al., 2007). As monoterpenes have interfacial chemistry, they are able to affect bio-membranes and have been reported to alter membrane composition and functionality.

Chapter 2: Materials and methods

2.1. Firgrove Field Trial

The Field Trial focused on the possible effects that the soil ameliorant application may have on the water content of the soil as well as the movement of water in the soil.

2.1.1. Materials and Methods

The site was located on a farm in the Firgrove area, Cape Town Metropolis, Western Cape, South Africa, with co-ordinates 34°02'52.00" S and 18°46'40.64" E.

The soil was classified according to *Soil Classification: A Taxonomic System for South Africa*. The soil of the upper part of the field, which will be referred to as Soil A, was classified as a Kroonstad 2000 (Orthic A, yellow E Horizon, G horizon). The lower part of the field, referred to as Soil B, was classified as a Kroonstad 1000 (Orthic A, grey E Horizon, G horizon). The G-horizon and clay layer of Soil A is below 1.5 m deep and for Soil B the clay layer starts at a depth of 0.7 m. The texture of the top soil was Sand and the textural analysis is presented in Table 2.1. The field had a 5% slope on a South-South West bearing.

The field trial involved the application of two treatments on two soil types with four replicates in each combination, which totalled 16 plots. The plots were chosen according to the uniformity of the young *Capsicum annum* plants already planted in the field. A schematic representation of the plots is presented in Figure 2.2. The treatments were applied in a completely randomized design, although the plot selection was done according to the uniformity of the pepper plants already present.

Table 2.1: Five fraction textural analysis expressed as a percentage of the Firgrove soil

Fraction	Coarse Sand	Medium Sand	Fine Sand	Silt	Clay
Particle size (mm)	2.0-0.5	0.50-0.25	0.250-0.053	0.05-0.002	<0.002
Soil A	31	24	41	2	2
Soil B	31	24	41	2	2



Figure 2.1: Google image of site location, where the field is outlined by the yellow block. The direction of the slope is given by the white arrow. (Image date: 2-01-2011)

To avoid error in the application of the treatment being replicated over the two soil types, the treatment was applied by hand under each dripper and not through the dripper-lines, as the same dripper-line provides water for both soil types. The application of the soil ameliorant was made at a rate of 30 ℓ/ha and was applied under the dripper at 0.74 mℓ ameliorant per dripper in 100 mℓ of water. After the soil ameliorant application, one litre of water was applied to distribute the product in the soil.

Differentiation is made between the different soils as follows; the deeper soil being Soil A and the shallower soil referred to as Soil B. The 5% slope caused water to accumulate in Soil B until the soil was saturated and therefore in week eight and nine no water content readings were taken for Soil B.

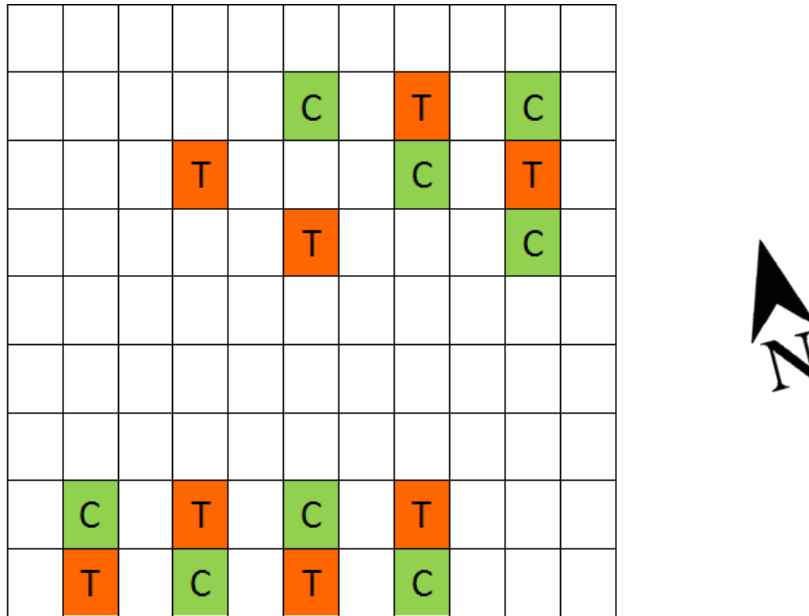


Figure 2.2: A schematic representation of the layout for the field trial with two treatments on two soils with four replications. The individual plots will be randomised across the field according to the plant height at the beginning of the experiment. Soils are given as A and B. Orange denotes treatment (T) and the green denotes the control (C).

For the measurement of water content in the soil, specialised pipes (access tubes) were installed in the plots for use with a *Diviner 2000* probe. Two access tubes were installed in each plot midway between the drippers. The dripper spacing was 0.6 m and the line spacing was 1.5 m. The *Diviner 2000* probe makes use of *Frequency Domain Reflectometry* (FDR) to measure water content in the soil and measures in depth increments of 10 cm. The water content is given in units of volumetric water content as a percentage. In order to convert the volumetric water content to millimetres water, the volumetric water content is multiplied by the depth over which the reading was taken.

Due to the differences in the depth of the two soil types shorter access tubes were installed in the lower part of the field where water readings were only taken up to a depth of 50 cm. However in the deeper soil, water measurements were taken up to a depth of 80 centimetres. Readings were taken once a week over a period of nine weeks, and each reading was taken in triplicate.

Although water content was the property measured in this field trial, the property observed is not only the water content but also the lateral movement of water. This is because the

access tubes were located between the drippers and hence an increase in the water content in that position would indicate an increase in the lateral movement of water.

The bulk density was determined by the Core Method (Blake and Hartage, 1986). Bulk density samples were taken at the end of the trial period at this time the soil was saturated. The very wet conditions were due to rainfall and excessive irrigation. Sampling of the cores was hindered by the wet conditions as compaction of samples may have taken place. The volume of the cores for the determination of bulk density was 66.4 cm^3 .

2.1.2. Statistical analysis

A completely randomised design was used as a layout for the field trial. Statistical analysis was performed with SAS Enterprise Guide 4. A linear model ANOVA was performed for the water content data. Differences between treated and control were identified with the Tukey's studentised range test. Bulk density was analysed with a One-Way ANOVA and statistically significant differences between treatments were identified using Tukey's studentised range test.

2.2.Sandbox experiment

The aim of the Sandbox experiment was to examine if application of the soil ameliorant has an effect on water retention at different suction pressures of a sandy soil also at different application rates of the ameliorant.

2.2.1. Materials and Methods

The layout of the sandbox experiment consisted of two treatments and an untreated control. The treatments were applications of soil ameliorant at two concentrations, 0.1% and 0.3% (v/v). To house the samples metal rings (dimensions: diameter of 47 mm and height of 32 mm) were prepared as filter paper was glued to one end of the metal rings and the other left open. A loamy sand soil (See Table 2.2 for soil textural analysis) was then used to fill the metal rings to a depth of 27 mm, 5 mm from the top of the metal ring. There were 5 replicates for each of the treatments and the control, totalling 15 rings.

Table 2.2: Seven fraction textural analysis for the soil used in the Sandbox experiment

Fraction	Coarse Sand	Medium Sand	Fine Sand	Very Fine Sand	Coarse Silt	Fine Silt	Clay
Particle size (mm)	2.0-0.5	0.50-0.25	0.250-0.106	0.106-0.053	0.05-0.02	0.02-0.002	<0.002
%	19	31	27	8	8	3	4

Sand was supplied by Daniel W. Viljoen who performed the Textural analysis.

The procedure for the use of the Sandbox from Ekeljkamp, Agrisearch Equipment, was performed according to the manual specifications. The suction pressures applied in pF units were 0.0, 0.5, 0.8, 1.0, 1.8, 2.0 which is equivalent to 0.1, 0.3, 1.0, 3.2, 6.4, 10.1 kilo-Pascal.



Figure 2.3: Photograph of the samples in the sandbox randomly arranged.

2.3.Pot Experiment in Greenhouse

The Pot Experiment focused on the water use efficiency of *Zea mays* with varying amounts of water applications as well as the effect of a soil ameliorant. The aim of the experiment was to evaluate the effects of a soil ameliorant application on selected soil properties and

on the response of the maize plant. The Pot Experiment had eight treatments, with five single pot replications in each. The eight treatments consisted of four different irrigation depletion regimes and for each of these there was a treatment (the application of the soil ameliorant) and a control. The treatment and control combinations with the four water depletion regimes are represented in Figure 2.4. Irrigation followed a deficit irrigation management schedule, with 10%, 50%, 50%C, and 80% depletion of plant available water (PAW). For example, the deficit irrigation for the 10% depletion irrigation depletion allows for 10% depletion of PAW before the pots were irrigated to field capacity. The “C” in 50%C refers to *covered* as the surface of the soil was covered with a plastic sheet preventing evaporative losses from the soil surface. Thus water was lost largely due to transpiration of the plant for this treatment.

2.3.1. Materials and Methods

The soil used for the Pot Experiment was taken from Welgevallen Experimental Farm, Stellenbosch University, Stellenbosch, Western Cape, South Africa; co-ordinates 33° 57' 03.68" S and 18° 52' 16.21" E. The soil was from uncultivated land and was collected from the top soil up to a depth of 20 centimetres. The soil was passed through a two millimetre sieve before use. The textural analysis is given in Table 2.3.

Table 2.3: Five fraction textural analysis of the soil used for the Pot experiment

Fraction	Coarse Sand	Medium Sand	Fine Sand	Silt	Clay
Particle size (mm)	2.0-0.5	0.50-0.25	0.250-0.053	0.05-0.002	<0.002
%	8	14	38	20	20

Black plastic pots, with a volume of seven litres, were filled with 5.6 kg of the sieved, air dried soil. The pots were packed to a bulk density of 1400 kg.m⁻³. The soil was “packed” into the pot by adding small amounts at a time and thumping the pot on a hard surface to settle the soil so that a resulting in a bulk density of 1400 kg.m⁻³ was attained. The bulk density value was arbitrarily chosen; the primary aim was to keep all the pots uniform. This bulk density, however, is comparable to soils in the field.

10% depletion	50% depletion	50%C depletion	80% depletion
10% depletion + ameliorant	50% depletion + ameliorant	50%C depletion + ameliorant	80% depletion + ameliorant

Figure 2.4: Representation of eight treatments for the Pot Experiment.

Thereafter the field capacity was determined as follows: The pots of soil were saturated with water and then allowed to drain freely for 48 hours. After the 48 hour period the pots were weighed. The average mass of the water in the pots was taken as the water to fill the soil to Field Capacity (FC), also referred to Plant Available Water _{Upper limit} (PAW _{Upper Limit}). The seeds used were Zea mays L., STAR 7714 hybrid. The seeds were sprouted before planting. After FC had been determined the sprouted seeds were planted.

The application of the ameliorant was made at a rate of 30 L/ha full surface application after planting, at a concentration of 0.2 % (v/v), which is 0.1 ml in 50 ml of water. After the application of the ameliorant, the soil was slowly irrigated to FC in order to reduce drainage to the minimum so that no product was leached from the pots.

Deficit irrigation management was applied. During the first week an average irrigation amount was determined for each of the treatments but this resulted in deviations between replicates over time due to unequal evapotranspiration rates for pots in the same treatment. Hence each treatment was irrigated individually according to its specific requirement. Pots were rotated weekly in the greenhouse to prevent effects due to differences in sun exposure and air movement in the greenhouse.

The gravimetric water content was determined by weighing the pots, and then the mass of the plastic pot and soil were subtracted to yield the water content. The pots were weighed between 8:00 and 11:00. The amount of water required for irrigation was calculated for each treatment individually. At the end of the experiment the gravimetric water content was converted to volumetric water content using the bulk density as a conversion factor. The volumetric water content was then converted to millimetres per treatment according to the depth of the pot, which was 130 mm.

The meticulous measuring was necessary due to the limited number of replicates and the possibility for high variation within treatments. Initially, while the plants were small, the

pots were weighed every two to three days. Later, as the plants were larger and had higher water usage, it was necessary to weigh the pots once a day and apply the required irrigation. No adjustments were made to compensate for the biomass increase of the plants as this mass is negligibly small compared to the mass of soil and water. As the plant usage increased, irrigation was applied more regularly.

All of the treatments received a fertigation application once a week with a broad spectrum fertilizer (Chemiculte); 100 mℓ at a concentration of 1 g/ℓ as part of the irrigation water. See Table 2.4 for composition of Chemicult. The maize plants reached the V8 growth stage before they were harvested.

Table 2.4: Elemental composition of the multi-element fertilizer, Chemicult, used in the Pot Experiment for fertigation.

Macro-elements	%	Micro-elements	%
N	6.50	Fe	0.150
K	13.0	Mn	0.024
P	2.70	B	0.024
Ca	7.00	Zn	0.005
Mg	2.20	Cu	0.002
S	7.50	Mo	0.001

Including 0.077 % of the non-essential element Na.

Following is a summary list of the properties of the soil and the maize plants that was evaluated or analysed at the end of the pot experiment and next is the materials and methods for each of the analyses.

- Soil properties
 - Bulk density
 - Soil pH
 - Aggregate stability
 - Evapotranspiration
- Plant Traits
 - Root and shoot biomass
 - Leaf Area Index (LAI)
 - Plant height
 - Leaf Chemical analysis
 - Chlorophyll content
 - Biomass Water Use Efficiency (BWUE)

a. Bulk density

The bulk density was determined for each treatment using the Core Method (Blake and Hartage, 1986). Two replicates were taken from each pot for bulk density determination. The soil cores were oven-dried at 105 degrees Celsius for two days. The soil cores were then weighed once dry. The volume of the soil core and the mass of soil were used to calculate the bulk density.

b. Soil pH

The soil pH was determined for each of the treatments. The pH in distilled water and 0.05 M KCl was determined using an *827 pH lab*, Metrohm pH-meter. A 1:2.5 soil to solution ratio was used.

c. Aggregate stability

The aggregate stability was determined for all the treatments. Aggregates were sampled from the core samples taken for bulk density determination and not from the entire pot, as remainder of soil was lost when roots were removed by rinsing with water. The method that was used, as described by Kemper and Rosenau (1986), determines the percentage water

stable aggregates versus the aggregates which are unstable in water using the *Wet Sieving Apparatus* from Eijkelkamp, Agrisearch Equipment. As the percentage of water stable aggregates is a measure of the aggregate stability of the soil, it will be referred to as just “aggregate stability” hereafter. The average soil-pH measured in distilled water was between five and six, therefore 0.05 M NaOH was used as a dispersion agent.



Figure 2.5: *Wet sieving Apparatus* for the determination of the percentage water stable aggregates.

d. Evapotranspiration

Evapotranspiration is the sum of water evaporated from the soil surface and the transpiration of the plant per unit time. In this experiment, the evapotranspiration was calculated from the change in water content of the pots as determined by weighing throughout the duration of the trial. The Evapotranspiration, in this case, is the mass of water lost from the pot between successive measurements with the addition of the water applied at the time of irrigation. The root zone water balance (Hillel, 1998) was used to make this calculation.

$$(\Delta S + \Delta V) = (P + I + U) - (R + D + E + T) \quad \text{Equation 2.1}$$

Where, ΔS is the change in root-zone moisture, ΔV increment of water incorporated into vegetative biomass, P precipitation, I irrigation, U upward capillary flow into the root zone, R runoff, D drainage, E direct evaporation from the soil surface and T is transpiration by the plants. A rearrangement of the equation to determine the evapotranspiration would be

$$E + T = P + I + U - R - D - \Delta S - \Delta V \quad \text{Equation 2.2}$$

E and T can be combined as ET . As no precipitation occurred, P is zero. U is zero as no capillary rise occurred, because there was no source of water below the root zone from which this could take place. R and D are also zero as no run-off or drainage occurred from the pots. Although the pots were allowed to drain freely, the irrigation applied never exceeded Field Capacity and hence negligible drainage occurred. ΔS and ΔV in terms of the Pot Experiment denote the water content in the pots. Hence the equation becomes;

$$ET = I - (\Delta S + \Delta V) \quad \text{Equation 2.3}$$

e. Dry Root Biomass

The dry root biomass was determined at the end of the Pot Experiment. After the shoot biomass had been harvested, the roots and the soil were removed from the pot and the soil was carefully washed out from between the roots. The roots were then dried at 50 degrees Celsius in a convection oven for approximately four days. The dry root biomass was then determined by weighing. The data was converted to kilograms of biomass per hectare. See Section 2.2.14 for the conversion factor used.

f. Dry Shoot biomass

The dry shoot biomass was determined at the end of the Pot Experiment. The entire plant was harvested one centimetre above the soil surface. The shoots were then dried at 50 degrees Celsius in a convection oven for approximately four days. The dry shoot biomass was then determined by weighing. The data was converted to kilograms of biomass per hectare. See Section 2.2.14 for the conversion factor used.

g. Total Biomass

The total biomass was determined as the sum of the dry root and dry shoot biomasses.

h. Leaf Area Index

Four mature leaves were selected and cut from the maize plant 0.5 cm from the stem. The leaves were placed in plastic bags and then in an insulated bag to prevent dehydration. The leaves were immediately taken to the laboratory where they were fed through a LI-3100 Area Meter to determine the area of the leaves.

The Leaf Area Index (LAI) was determined using the measurements of the leaves taken during the duration of the experiment. The leaf length and width were measured and the leaf area was determined by multiplying the length by the width and using the conversion factor of 0.75 in accordance with the research of Francis et al. (1969). See Equations 2.4 to 2.6. The leaf areas measured with a Leaf Area Meter were compared with the length-width measurements for accuracy adjustments. The area of all the fully expanded leaves was summated to determine the plant area.

$$\text{Leaf Area (m}^2\text{)} = 0.75 \times l \times w \quad \text{Equation 2.4}$$

$$\text{Plant area (m}^2\text{)} = \Sigma \text{Leaf area \{leaf 1 to 9\}} \quad \text{Equation 2.5}$$

$$LAI = \frac{\text{Plant area (m}^2\text{)}}{\text{Surface area of soil in pot (m}^2\text{)}} \quad \text{Equation 2.6}$$

i. Plant Height

The plant height was determined according to Cornelissen et al. (2003), which states that the plant height is the shortest distance between the upper limit of the principal photosynthetic tissues on a plant and the soil surface. The plant height was measured every two weeks throughout the experiment period.

j. Chlorophyll content

Chlorophyll content was determined just before the maize plants were harvested with a handheld chlorophyll meter; Chlorophyll Content Meter CCM-200 from Opti-Sciences. The reading is given as a Chlorophyll Content Index (CCI). Readings were taken on four mature leaves and the average of these was used as a measure of the chlorophyll content of the plant.



Figure 2.6: Maize plants in greenhouse at week six from planting.

k. Leaf chemical analysis

Composite samples from six leaves per plant for each of the eight treatment combinations were selected, oven-dried at 50 degrees Celsius and then ground to a powder. To minimise costs, replicates were ground together as a single sample. Leaf powder samples were prepared for analysis by microwave digestion. Atomic Absorption with a Varian FS240 AAS was used for the elemental analysis performed by the Environmental Laboratory, CAF at Stellenbosch University.

I. Biomass Water Use Efficiency

The Biomass Water Use Efficiency (BWUE) is a measure of the mean total shoot biomass produced per unit of water used to produce that biomass. The BWUE was calculated using the mean dry shoot biomass and the evapotranspiration as indicated in Equation 2.7. The evapotranspiration used is in units of millimetres water and the dry shoot biomass in units of kilograms per hectare.

$$BWUE = \frac{\text{Mean dry shoot biomass}(kg.ha^{-1})}{\text{Evapotranspiration}(mm)} \quad \text{Equation 2.7}$$

m. Conversion to hectares

For the biomass measurements and the BWUE it was necessary to convert the plant biomass data to hectares. The surface area of the pot was calculated and extrapolation to hectares was made. The calculation for this conversion is as follows;

$$\text{Pot area} = \pi \left(\frac{d}{2}\right)^2 = \pi \left(\frac{207 \text{ mm}}{2}\right)^2 = 33653.52 \text{ mm}^2 = 0.033654 \text{ m}^2 \quad \text{Equation 2.8}$$

$$\text{Pot areas per hectare} = \frac{10000 \text{ m}^2}{0.033654 \text{ m}^2} = 297145.91 \text{ m}^2 \cdot \text{m}^{-2} \quad \text{Equation 2.9}$$

Therefore the conversion from the area of a pot to an area per hectare the conversion factor of 297145.91 was used. This means that the planting density is relatively high at approximately 30 000 plants per hectare.

2.3.2. Statistical analysis

The Pot experiment was a completely randomised block design. Statistical analysis was performed with SAS Enterprise Guide 4. Two linear-model Analysis of Variance (ANOVA) were performed depending on whether there was interaction or not between treatment and the PAWD. In the first linear model ANOVA, interaction between PAWD and the treatment was evaluated. If interaction was not present, differences between means of the treated and control for all PAWDs combined were tested, as well as the differences between means of each of the PAWDs individually.

Evaluating the PAWDs individually does not have any bearing on the effect of the soil ameliorant but solely on of the irrigation applied. The second linear model ANOVA was

applied when the data showed interaction between treatment and PAWD. In this case, the data was analysed after grouping the data according to the PAWD. The differences between the ameliorant treated and control within each of the PAWD's were tested. For both linear model ANOVAs statistical differences between the means in question were identified with Tukey's studentised range test at the 5% significance level.

Chapter 3: Results and Discussion

3.1. Firgrove Field Trial

3.1.1. Water measurements

The water content results for Soil A are presented in Figure 3.1 and Figure 3.2. . Results for Soil B are presented up to week seven of the trial period as saturated soil conditions in Soil B during the last two weeks of the trial caused measurements to be of no use. In Figure 3.1 is presented the mean water content over the period of nine weeks for the various profiles. The water content of the treated plots is higher than that of the control plots up to a depth of 700 mm. From 700 to 800 mm depth the water content is comparatively similar, and these values are approaching saturated conditions. As the access-tubes for taking the water measurements were installed between drippers, the higher water content is consequently an indication of improved lateral flow of water in the soil or improved water distribution throughout the soil profile.

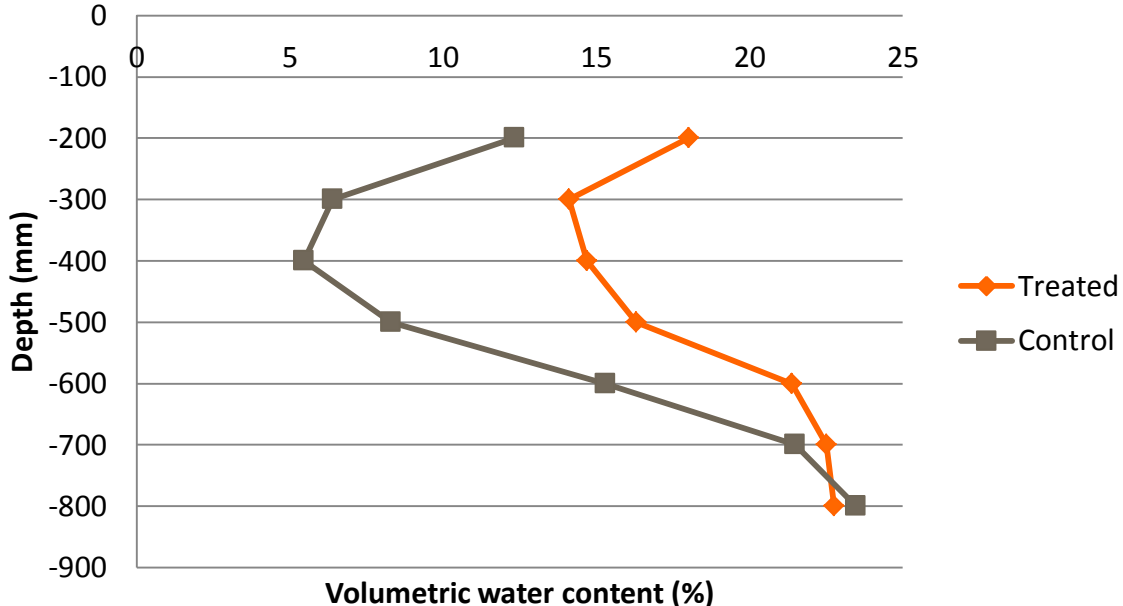


Figure 3.1: Mean water content at each depth in the profile for the treated versus the control plots over a period of nine weeks for Soil A.

In Figure 3.2 a similar trend is observed as in Figure 3.1; increased lateral flow of water due to higher water content in between drippers for the plots which received the ameliorant application. From Figure 3.2 it is also evident that there is more uniformity of the water content for the ameliorant treated soil over the nine-week period. There is less fluctuation in the water content of the ameliorant treated soil. The soils of the untreated control had greater variable water content, more fluctuations. Sandy soils have poor water retention properties and present a risk of preferential flow and non-uniform wetting of the soil profile (Jarvis et al., 2008). This is especially true for soils with hydrophobic properties (Dekker and Ritsema, 1996).

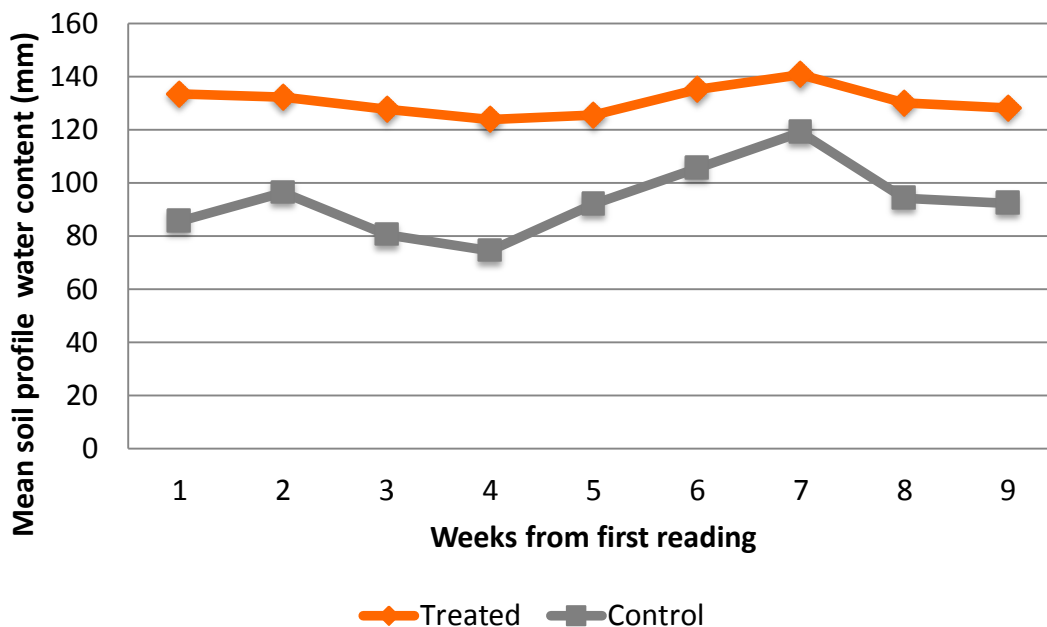


Figure 3.2: Mean profile water content for the treated versus the control plots over a period of nine weeks for Soil A.

In Figure 3.3 are the results of the data for Soil B. It is evident that the peaks and troughs of treated and control over the seven week period correlate with one another. The treated plots had substantially higher mean profile water content than those of the control plots for each week. The results for Soil B does not display the trend described for Soil A, i.e. more uniformity of the mean water content for the treated plots, this may be due to the limited depth of Soil B.

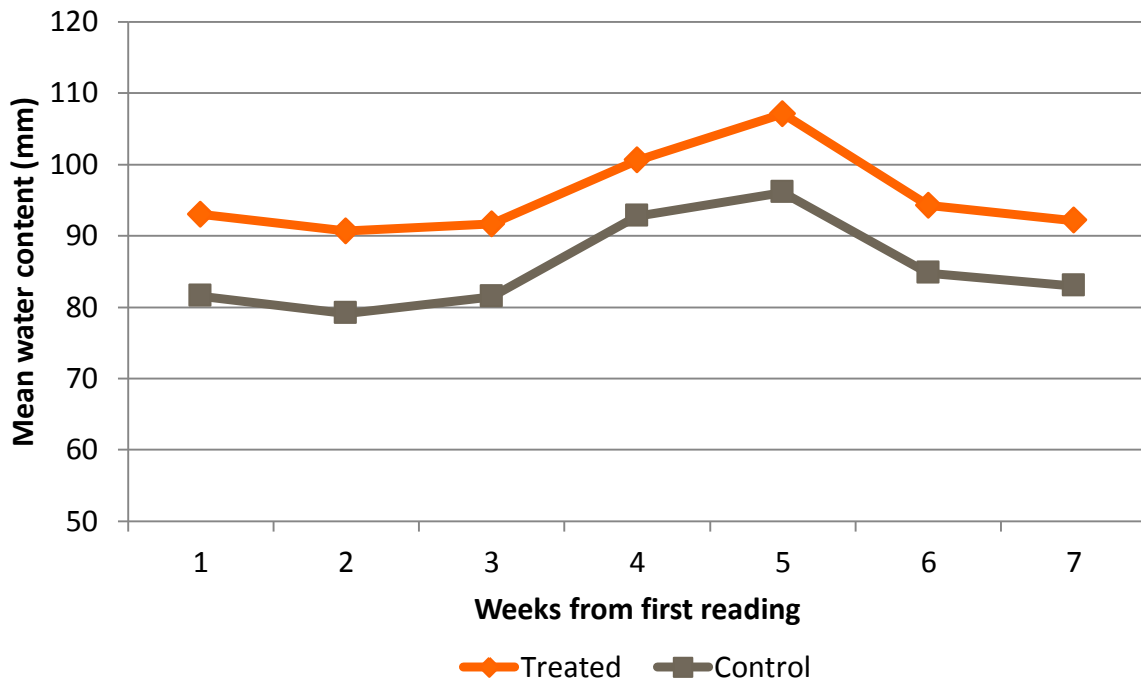


Figure 3.3: Mean profile water content for the treated plots versus the control plots over a period of seven weeks for Soil B.

The water content for Soil B was mostly near saturation due to the clay layer at 700 mm restricting drainage, while Soil A was able to drain effectively as the clay layer was below 1500 mm. Therefore, Soil A is better representation of the effect of the soil ameliorant on the uniformity of the soil water content. For Soil A the mean water content in millimetres water was calculated over a soil depth of 800 mm while that of Soil B was over a depth of 500 mm. Therefore, the mean water contents of Figure 3.2 and Figure 3.3 should not be compared directly. The differences in the observed effect of the ameliorant treatment for Soil A and Soil B is due to the higher water table in Soil B, a much shallower effective soil depth, while Soil A is a well-drained soil. Therefore the water dynamics are expected to differ and the effect on the ameliorant application is more pronounced for Soil A.

Statistical analysis shows that there is a significant difference ($p < 0.0001$) between plots which received the ameliorant treatment for Soil A and Soil B combined (Table 3.1). They had significantly higher mean profile water content than that of the control plots. This shows that the ameliorant application increased the water retention of the soil, or rather increased the lateral distribution of water throughout the soil profile and thereby improving the overall wetting of the soil. The effect of the ameliorant application is a combination of increased water retention and lateral water movement.

Table 3.1: Means of profile water content of Soil A and B for the comparison of the treated and control and the comparison between different depths of the treated and control combined.

Mean Water Content for Soil A and B (mm)	
Treatment	Mean
Treated	0.1513 a
Control	0.1205 b
<i>MSD</i>	<i>0.0109</i>
<i>p-value</i>	<i><0.0001</i>
Depth	Mean
0-10 cm	0.0132 c
10-20 cm	0.1788 a
20-30 cm	0.1567 b
30-40 cm	0.1581 b
40-50 cm	0.1727 a
<i>MSD</i>	<i>0.0241</i>
<i>p-value</i>	<i><0.0001</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

The water content results for the Firgrove field trial correlate with the research by Leinauer et al. (2001) and Lehrsich et al. (2011) which also show increased water retention with the application of non-ionic surfactants. However, the study by Karagunduz et al. (2001) found that the application of surfactants decreases the water retention of the soil. The ability of surfactants to improve the uniformity of water content by increased lateral flow is shown in a study by Soldat et al. (2010).

Due to the ability of surfactants to reduce the surface tension of water their application allows water to enter smaller pores than would otherwise be possible (Lehrsich et al., 2011).

This action may enhance the overall wetting of the soil. A reduction in the hydraulic conductivity may also occur due to the flow of water into smaller pores, thereby increasing lateral flow and resulting in an even wetting of the soil (Cid-Ballarín et al., 1998). However, the study by Leinauer et al. (2001) shows that the capillary porosity was unaffected by the application of a surfactant and they attributed the increase in water retention to an increase in water bound to a hydrophilic layer on the soil particles.

The statistical analysis between the depths shows that the water content was greatest in the 10 to 20 cm depth, which did not differ from the water content of the 40 to 50 cm depth. The surface layer, as expected, had the lowest water content.

3.1.2. Bulk density

The results for the bulk density measurements are presented in Figure 3.4. Sampling of the undisturbed cores was challenging due to wet conditions, therefore the bulk density values are higher than expected as provided by Skopp (2002) for a sandy soil. These higher than expected values may have been due to compaction of samples. The textural analysis shows a large percentage of coarse sand, 31%, which adds to the elevated bulk density values. The statistical analysis, presented in Table 3.2, shows that the results for the bulk density of the treated versus control plots are not significantly different ($p = 0.3907$).

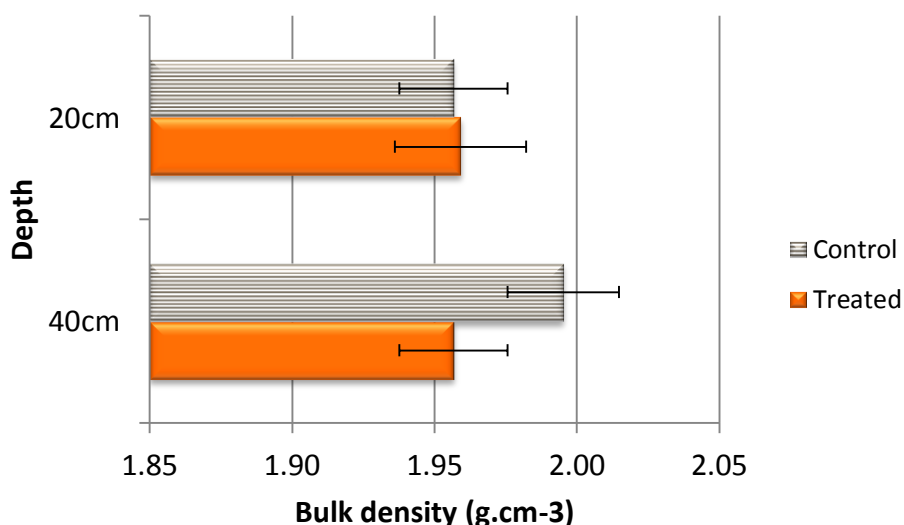


Figure 3.4: Mean bulk density of the treated versus the control plots for both Soil A and B.

Table 3.2: Means of bulk density for the comparison of the treated and control.

Bulk density Soil A and B (g.cm^{-3})	
Treatment	Mean
Treated	1.96 a
Control	1.98 a
<i>MSD</i>	<i>0.044</i>
<i>p-value</i>	<i>0.3907</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

3.2. Sandbox Experiment

The results for the sandbox experiment are presented in Figure 3.5 as a Water Characteristic Curve. The suction values for the Sandbox experiment are very low and are similar to matric potential values of the saturation zone. The water retention curves for the two ameliorant treatments both lie above that of the control, showing an increase in water retention for all suctions measured. There is a large difference between the 10 ℓ /ha treatment and that of the 30 ℓ /ha treatment. There is a 10% difference between the 10 ℓ /ha treatment and the 30 ℓ /ha treatment. This shows that at high application rates the ameliorant is not necessarily more effective in improving water retention for the suction values evaluated once an optimum level has been reached.

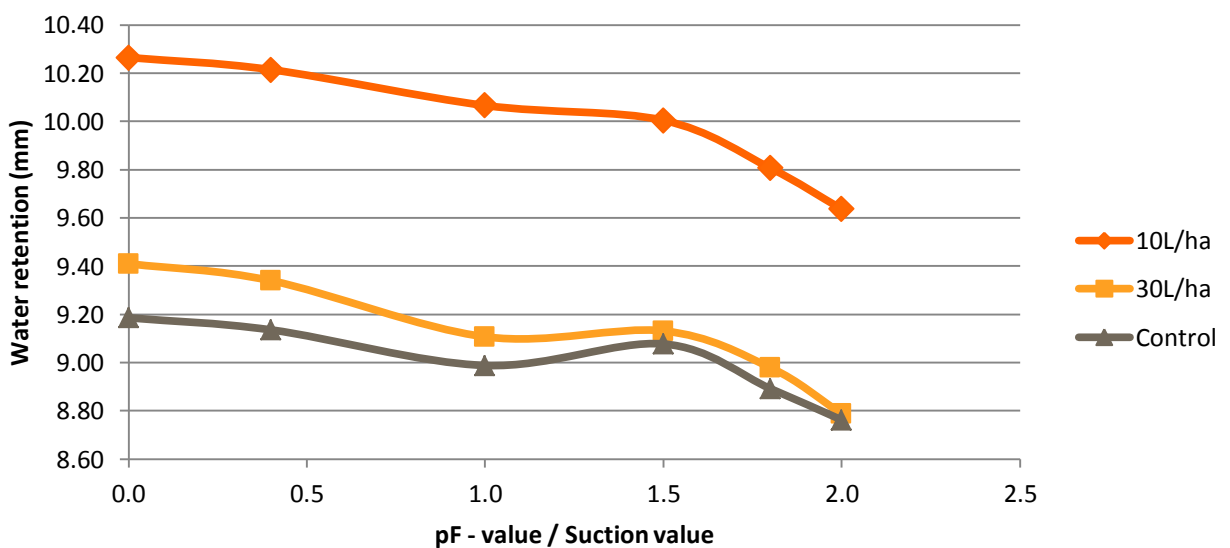


Figure 3.5: Water Characteristic Curve for two treatments with different ameliorant application rates and a control treatment.

A study by Lehrs et al. (2011) showed that the application of nonionic surfactants increased the water retention of soil even at high potentials. With the application of the ameliorant the cohesive forces are reduced at the soil-water interfaces leading to a decrease in the matric potential (Section 1.1.2). The beneficial effect of this change in matric potential is further discussed in Section 3.3.6.

The results for the Firgrove field trial and the Sandbox experiment both showed that the ameliorant has an effect on both the water retention capacity, also water distribution, and the matric potential of sandy soils. These effects are directly attributable to the effect of the surfactants and the orange-oil present in the ameliorant which lowers the surface tension of water thereby altering the water-soil contact angle. This change in the water retention capability of the soil and the effect on matric potential may have a beneficial effect on plant growth as water is more readily available for plant use.

3.3. Pot experiment in greenhouse

3.3.1. Water content of pots

The results for the mean total water content of the pots over the nine week period are presented in Figure 3.6 to Figure 3.9. The water content of the treated versus the control do not bear statistical significance, however, there are some trends.

The water content for the ameliorant treated pots versus the control for the 10% and 50% PAWD showed little variation throughout the experimental period as presented in Figure 3.6 and Figure 3.7. The water content of the 50%C PAWD, as presented in Figure 3.8, showed a marked difference in the first four weeks after which the treated pots had lower water content compared to that of the control. This may be because the surface cover prevents evaporative losses from the soil surface. However, when the plants are larger their water use is greater and the effect is no longer apparent. In the 80% PAWD there is a trend which indicates a difference in water content, where the mean water content of the treated is consistently greater than, or equal to, the water content of the control. However, these differences are small.

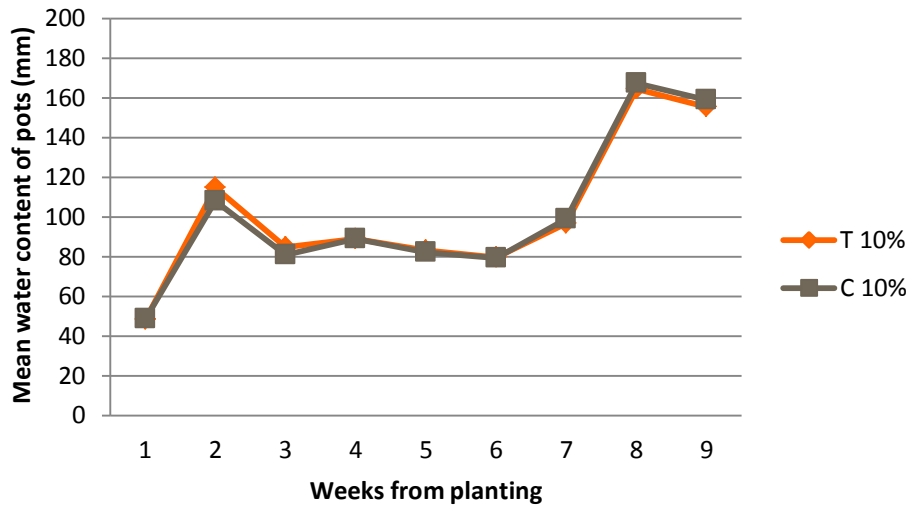


Figure 3.6: Mean water content over nine weeks for treated versus control of the 10% plant available water depletions.

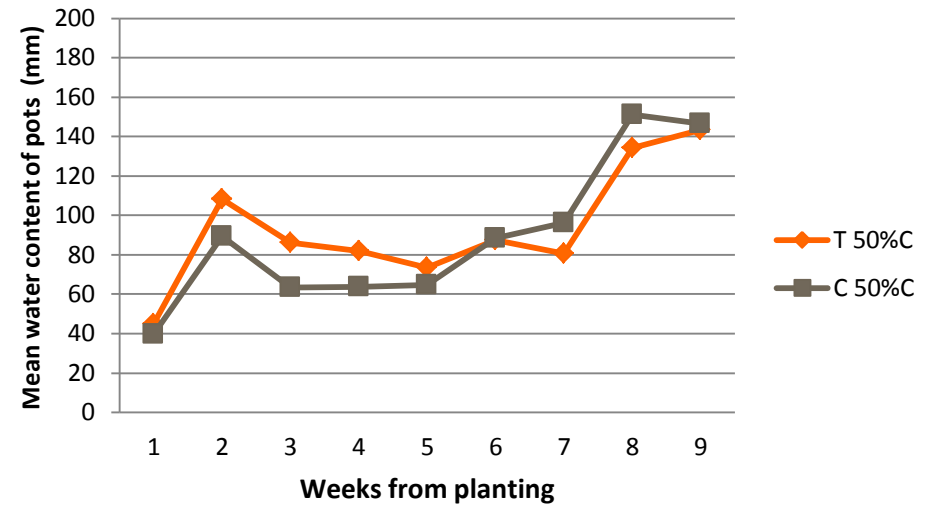


Figure 3.8: Mean water content over nine weeks for treated versus control of the 50%C plant available water depletions.

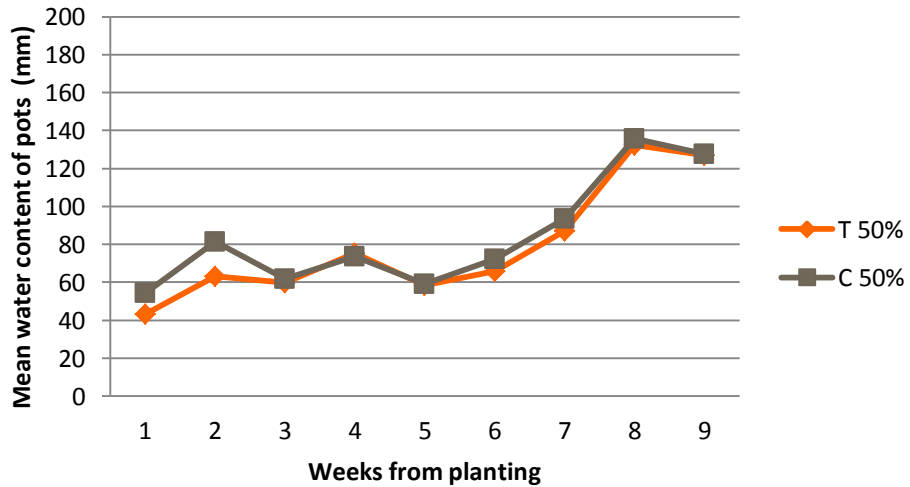


Figure 3.7: Mean water content over nine weeks for treated versus control of the 50% plant available water depletion.

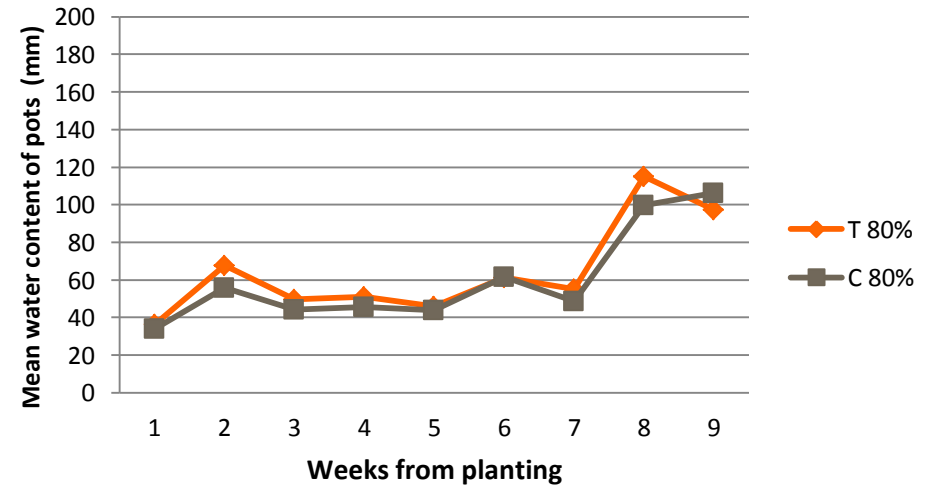


Figure 3.9: Mean water content over nine weeks for treated versus control of the 80% plant available water depletion.

3.3.2. Evapotranspiration

The cumulative mean evapotranspiration (ET) data is presented in Figure 3.10. The linear model ANOVA for evapotranspiration showed that there is interaction between the treatment and the PAWD. The main effects of the linear model, namely treatment and PAWD, cannot be evaluated on their own due to interaction. Therefore, a second model was used as described in Section 2.3.2. The means for the statistical analysis are presented in Table 3.3.

The 10% PAWD shows greater cumulative mean ET for the control compared to the treated. For the 50% PAWD the treated pots had a higher cumulative mean ET. In the case of the 50%C PAWD there is a similar trend as for the 50% PAWD, the difference is however very small. For the 80% PAWD the trend is the same as that of the 10% PAWD, where the control has a greater cumulative mean ET. In the case of the 50%C PAWD the losses were mainly due to transpiration as the surface of the soil was covered with a plastic sheet.

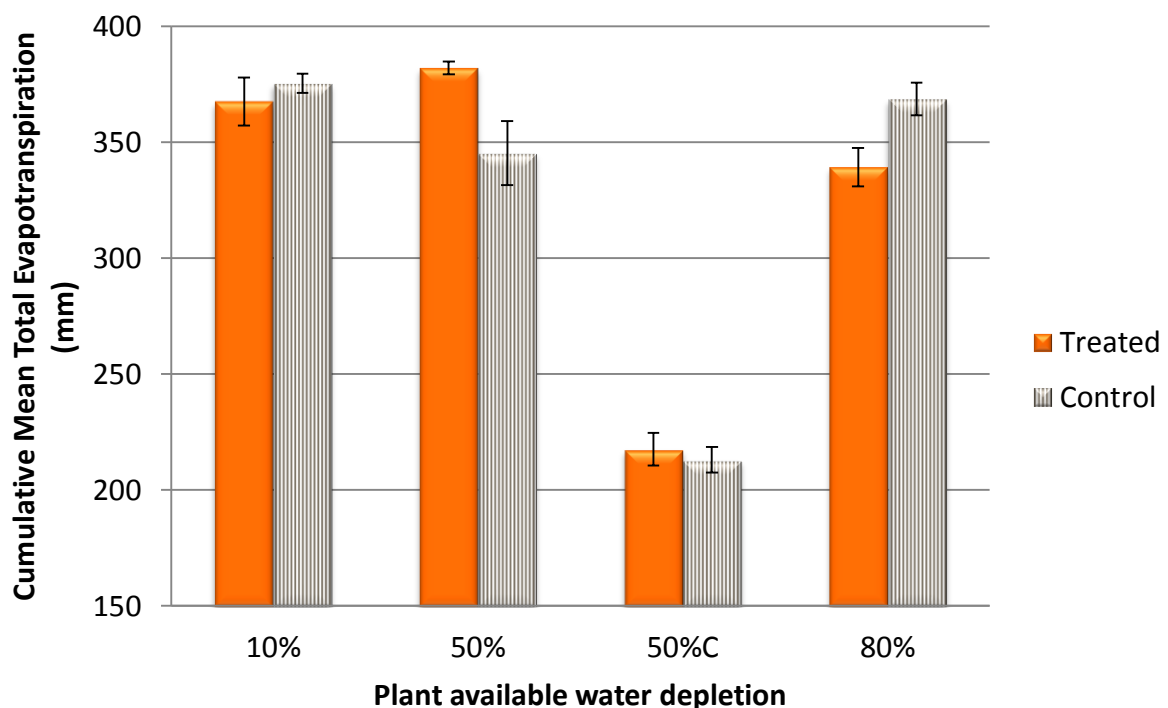


Figure 3.10: Cumulative mean evapotranspiration of the treated and control for each of the plant available water depletions.

Significant differences resulted for two of the four PAWDs (See Table 3.3). The ameliorant treated pots of the dry water regime, the 80% PAWD, had a significantly ($p = 0.0272$) smaller cumulative mean ET compared to the control. Therefore, the ameliorant reduced evaporative losses in the case of the soil that was depleted up to 80% of plant available water (PAW). In the case of the 50% PAWD, the ameliorant application increased evaporative losses ($p = 0.0321$) while that of the 80% PAWD resulted in the opposite effect ($p = 0.0272$).

Table 3.3: Means of the cumulative evapotranspiration over the nine-week period for the comparison of the treated and control within each of the PAWD.

Cumulative Evapotranspiration (mm)				
	10% PAWD Mean	50% PAWD Mean	50%C PAWD Mean	80% PAWD Mean
Treated	367.4 a	381.9 a	208.6 a	339.3 b
Control	375.3 a	345.2 b	201.2 a	368.2 a
<i>MSD</i>	<i>25.67</i>	<i>32.66</i>	<i>20.91</i>	<i>24.80</i>
<i>p-value</i>	<i>0.5006</i>	<i>0.0321</i>	<i>0.6199</i>	<i>0.0272</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

In Figure 3.12 it may be noted that the 50%C PAWD had a noticeably lower ET for both the treated and the control. This shows the benefit of using a mulch to reduce evaporative losses from the soil surface. The application of surfactants to the soil may decrease evaporative losses. If this is so there may be an alternative reason for the higher evaporative loss of the ameliorant treated 50% PAWD. According to Tschapek and Boggio (1981) the effect which the surfactant will have on ET is dependent on the method of application. That is, if the surfactant is applied on the soil surface, water evaporation is smaller, and if it is below the surface the evaporation is larger. This is due to the formation of a dry layer ("mulch") at the soil surface due to rapid initial evaporation for the soil with surfactant applied at the surface (Letey et al., 1962). The dry surface layer results in a discontinuity of the capillary action thereby hindering evaporation from the soil below. This is the same effect observed for that of a hydrophobic soil (Imeson et al., 1992).

Ameliorants containing surfactants can cause a decrease in the capillary rise in the soil (Shafran et al., 2003), this in turn decreases the extent of the vadose zone, and therefore decreases the FC. As the ameliorant was applied after the FC was determined, its application would affect the limits of the FC and drainage could occur more readily in the treated soils. Another hindrance to the evaluation of evaporative losses in this experiment is the restrictive volume of the pot, as this differs greatly to that of the effects expected in the field.

For the 80% PAWD in Figure 3.10, the application of the ameliorant reduced evaporative loss significantly. This may be why the beneficial effects of an ameliorant application are most apparent in the driest seasons where crop emergence is improved (Crabtree and Henderson, 1999).

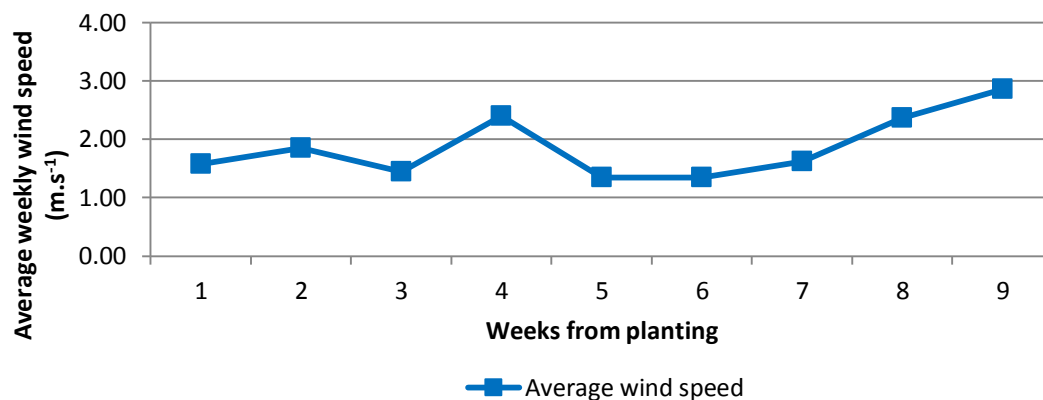


Figure 3.11: The average weekly wind speed outside the greenhouse in meters per second over the trial period of nine weeks

The average weekly wind speed is presented in Figure 3.11. These are the wind speed values outside of the greenhouse. The wind speed outside the greenhouse does affect evapotranspiration inside the greenhouse because the sides of the greenhouse are opened during the day to prevent the greenhouse from overheating. The wind speed is correlated to the ET, especially in week nine. Though the temperature decreases from week eight to nine there is an increase in the ET for all the treatments except the 80% PAWD, which decreases slightly. The wind speed is very high in week nine and this would accelerate ET as seen in Figure 3.12.

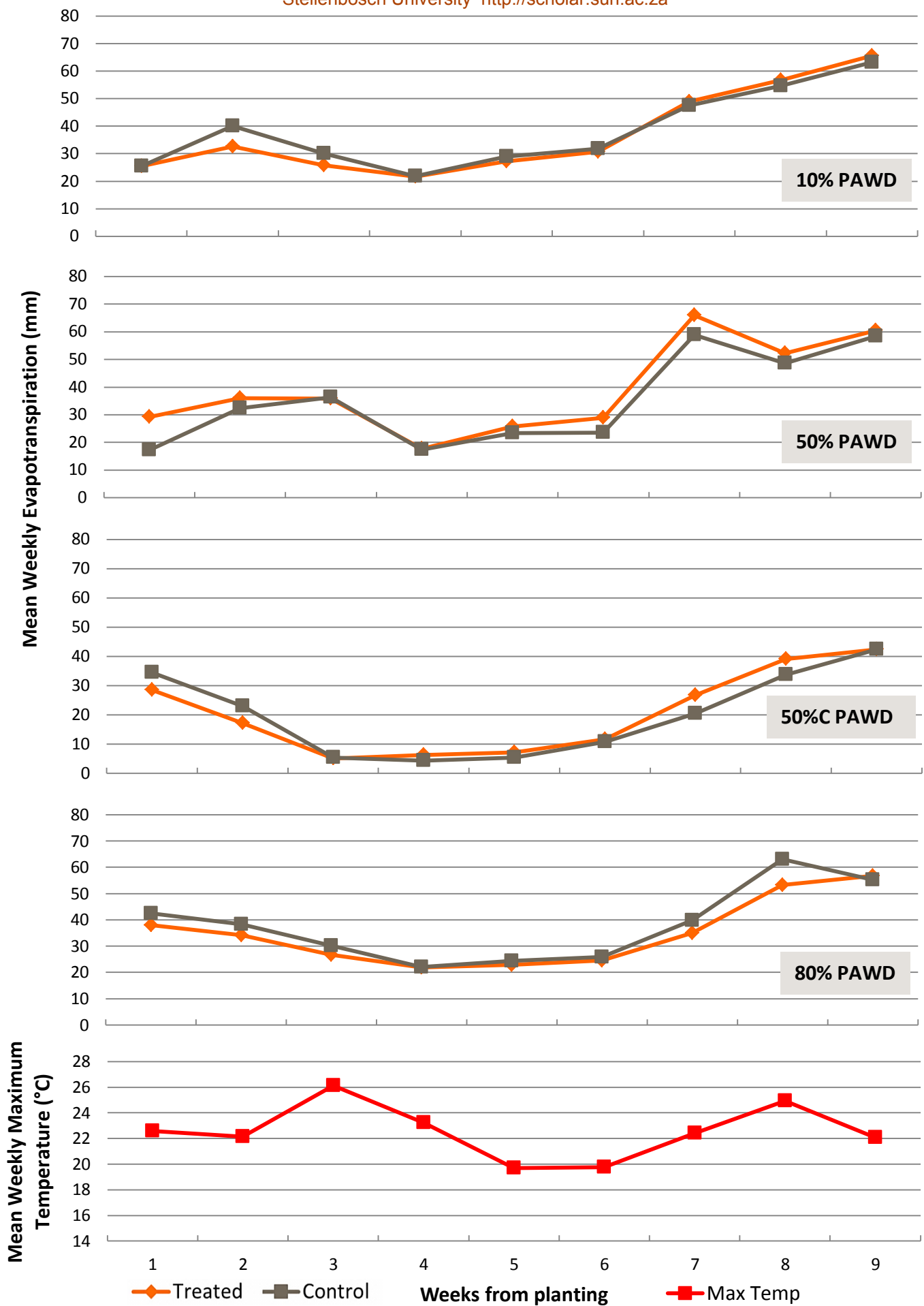


Figure 3.12: Evapotranspiration losses for all the plant available water depletions over a period of nine weeks and the mean weekly maximum temperature over the same period.

3.3.3. Bulk density

The data for the mean bulk density is presented in Figure 3.13. There were no statistical differences in the bulk densities overall. However, there is a trend in the 10%, 50%C and 80% PAWD indicating that the treated soil has a lower bulk density than that of the control, but these differences are too small to warrant enquiry.

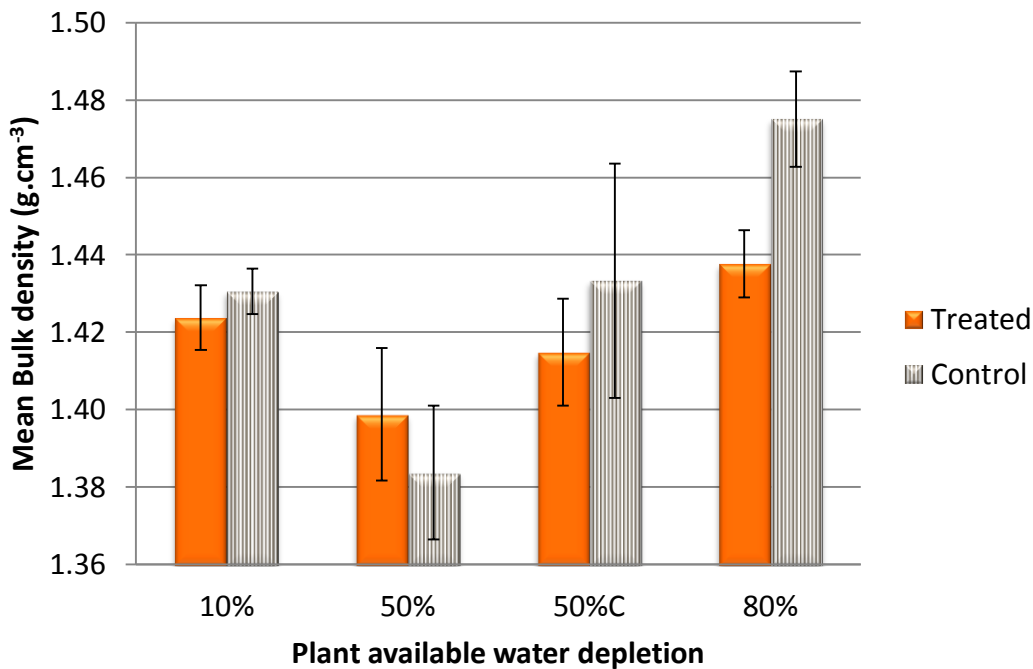


Figure 3.13: Mean bulk density of the treated and control for each of the plant available water depletions.

When considering the effect of the different irrigation regimes on the bulk density there are significant differences between the different PAWDs (Table 3.4). The bulk density of the 80% PAWD was significantly larger compared to the 50% PAWD ($p = 0.0045$). This shows that the soil which was allowed to dry to 80% of PAWD on a regular basis has a higher bulk density. The 50% and 50%C PAWD did not differ from either the 10% or the 80% PAWD. The wetting and drying cycles of the clay soil may have amplified the process leading to higher bulk density. The relatively high bulk density of the 10% PAWD could have resulted from the process of consolidation as these pots were irrigated most frequently.

Table 3.4: Means of bulk density for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

Bulk density (g.cm⁻³)	
Treatment	Mean
Treated	1.419a
Control	1.431a
<i>MSD</i>	<i>0.0234</i>
<i>p-value</i>	<i>0.3069</i>
PAWD	Mean
10%	1.427 ab
50%	1.391 b
50%C	1.424 ab
80%	1.456 a
<i>MSD</i>	<i>0.0441</i>
<i>p-value</i>	<i>0.0045</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

3.3.4. pH Measurements

There are no significant differences in pH values for the treated versus the control pots for any of the water depletion regimes as shown in Table 3.5. This shows that there is no negative effect on the pH of the soil when an ameliorant application is made.

Table 3.5: pH of the soil samples in H₂O and KCl for treatment and control for all plant available water depletions.

	pH H₂O		pH KCl	
	Treated	Control	Treated	Control
10%	5.52	5.35	4.58	4.45
50%	5.53	5.53	4.62	4.57
50%C	5.50	5.48	4.51	4.50
80%	5.42	5.48	4.55	4.61

3.3.5. Aggregate Stability

The results for the aggregate stability data are presented in Figure 3.14. The linear model ANOVA for aggregate stability showed that there is interaction between the treatment and the PAWD. As the main effects of the linear model, namely treatment and PAWD, cannot be evaluated separately due to interaction a new model was analysed (Section 2.3.2). The means for the statistical analysis are presented in Table 3.6.

Examining the results, there are two differences to take note of for aggregate stability. The pots that remained moist for longer periods, that is the 10% and the 50% PAWD, showed an increase in the percentage of water stable aggregates formed for the pots that received the ameliorant treatment. Conversely, the 50% and 80% PAWD of the control had the highest percentage of water stable aggregates while the ameliorant treated were considerably less.

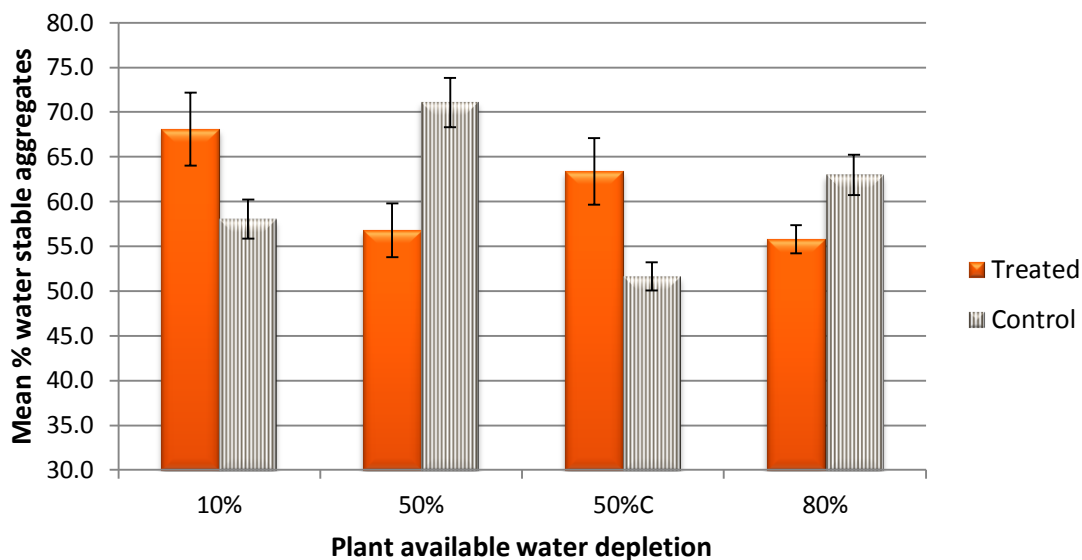


Figure 3.14: Aggregate stability for the treated versus control for each of the PAWDs.

The higher value for the aggregate stability of the treated for both the 10% and 50% PAWD is correlated with a higher dry root biomass for the treated of the same PAWDs. The more root biomass per pot, the more root mucilage would have been produced. Root mucilage is a key chemical component for the stabilising of aggregates (Morel et al., 1991 and Traore et

al., 2000). The control of the 50% and 80% PAWD also had high aggregate stability percentages, but these do not correlate with the dry root biomass. Another mechanism by which aggregates are formed may be more physical nature, such as the alternate wetting and drying cycles of irrigation and evaporation, as well as the drying action of roots (Amézketa, 1999). The 50% and 80% PAWDs had more intense wetting and drying cycles than those of the 10% and 50%C that remained moist for longer periods. Thus, it is likely that aggregates were formed in this way. The question now is; why do the treated of the 50% and 80% PAWDs not have such high aggregate stabilities?

There is corroboration in the literature showing that the application of surfactants to soil decreases the aggregate stability (Mbagwu et al., 1993) mostly that of anionic surfactants and occasionally nonionic surfactants, but also that surfactant application increases the aggregate stability (Brandsma et al., 1999, Lehrsch et al., 2012), The action of the anionic surfactant present in the ameliorant may be why the treated for the 50% and 80% PAWD had such a low aggregate stability. Having proposed that, to explain the high aggregate stability of the treated for the 10% and 50%C PAWD, the stimulating effect of the root mucilage must have dominated the effect of the anionic surfactant. Unfortunately, these assumptions cannot be confirmed, as we do not have measurements for root mucilage production or the concentration of anionic surfactant present in the soil.

Table 3.6: Means of the aggregate stability for the comparison of the treated and control within each of the PAWD.

Aggregate Stability (%)				
	10% PAWD Mean	50% PAWD Mean	50%C PAWD Mean	80% PAWD Mean
Treated	68.08 a	56.78 b	63.35 a	55.78 b
Control	58.03 a	71.10 a	51.66 b	62.98 a
<i>MSD</i>	<i>10.69</i>	<i>9.41</i>	<i>9.301</i>	<i>6.305</i>
<i>p-value</i>	<i>0.062</i>	<i>0.008</i>	<i>0.020</i>	<i>0.030</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

3.3.6. Dry Root biomass

The results of the mean dry root biomass are presented in Figure 3.15. Statistically there was no interaction between the treatment and the PAWD, therefore the main effects were evaluated separately. There was a significant difference between the treated and control over all the PAWDs ($p = 0.0416$). Therefore, the application of the ameliorant significantly increased the root biomass produced. It may be conjectured that, either the ameliorant had an effect on the soil environment such that the roots responded favourably, or that the ameliorant may have had a direct effect on the root growth, or both.

The 10% PAWD showed the largest root biomass while the 80% PAWD shows the smallest biomass, indicating that more frequent irrigation produces a greater root biomass, better growing conditions. Considering Figure 3.15, the greatest differences between treated and control was for the 10% and 50%C PAWD. Thus, the ameliorant improved root biomass production especially for pots which remained wet for longer periods of time.

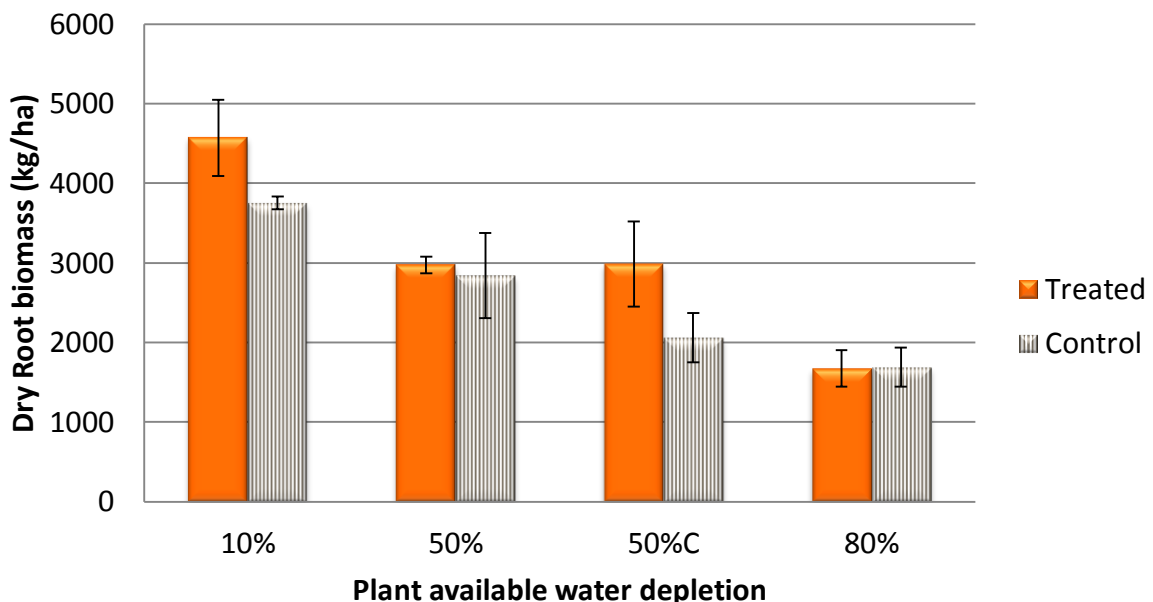


Figure 3.15: Mean dry root biomass for the treated and control for each of the plant available water depletions.

The ameliorant alters the soil environment by lowering the surface tension of water. Cohesive forces between soil and water are decreased, lowering the matric potential, thus the roots are able to take-up water more readily and growth would be improved (see Section 1.1.6). Another possibility is that the ameliorant treatment improves the aeration of the soil, facilitating infiltration (Feng et al., 2001) and thereby improving the root growth. There is a correlation between the root growth and the bulk density substantiating this observation. The ameliorant treated soil has a lower bulk density than that of the control for all the PAWD, except the 50% PAWD, corresponding to the higher dry root biomass (Figure 3.13).

The comparison between the various PAWDs showed significant differences with regard to mean root biomass ($p < 0.0001$). The pots that received the most frequent irrigation, the 10% PAWD, had the greatest dry root biomass production. The dry root biomass of the 50% PAWD was second largest, but did not differ significantly from the 50%C PAWD. Studies on the effects of surfactants, or bio-surfactants and root exudates, on the rhizosphere are few.

Table 3.7: Mean of the Dry Root Biomass for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

Dry Root Biomass (kg.ha⁻¹)	
Treatment	Mean
Treated	305.3 a
Control	258.6 b
<i>MSD</i>	<i>44.81</i>
<i>p-value</i>	<i>0.0416</i>
PAWD	Mean
10%	416.3 a
50%	290.7 b
50%C	252.3 bc
80%	168.3 c
<i>MSD</i>	<i>84.46</i>
<i>p-value</i>	<i><0.0001</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

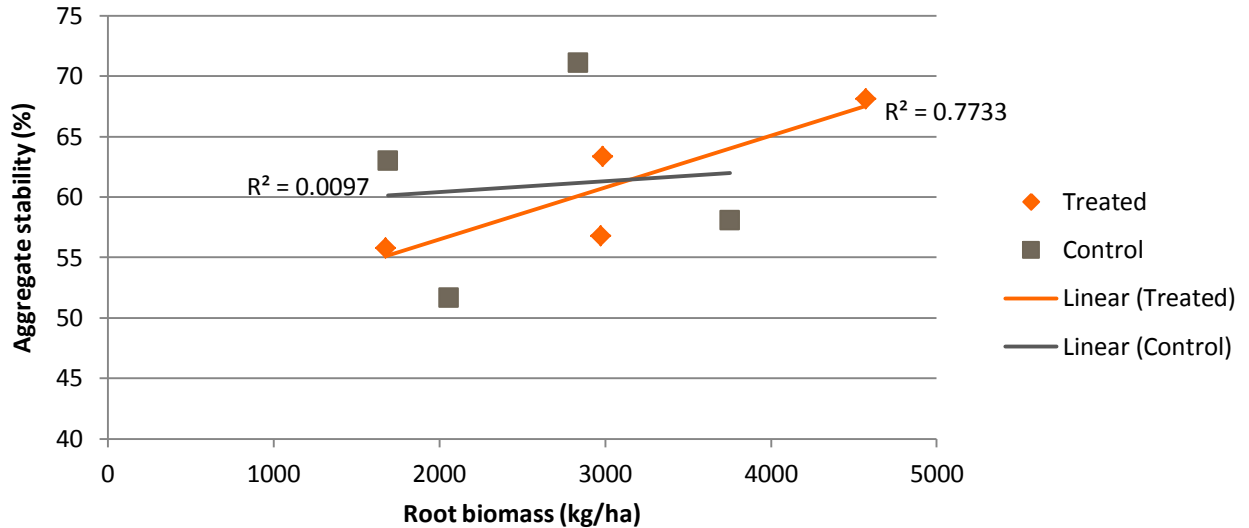


Figure 3.16: Linear correlation of dry root biomass and aggregate stability.

Research shows that the physical and chemical properties of the rhizosphere are greatly modified by the application of a surfactant, resulting in significant effects (Read et al., 2003 and Dunbabin et al., 2006). To substantiate this, a linear correlation was done for the dry root biomass versus the aggregate stability. From Figure 3.16 it is evident that there is a correlation between the dry root biomass and the aggregate stability of the treated soil with an R^2 -value of 77% while the correlation for the control is below 1%.

3.3.7. Dry Shoot biomass

The results for dry shoot biomass are presented in Figure 3.17. The statistical analysis, presented in Table 3.7, shows that there are no significant differences between the treated and control for all the PAWDs combined. The trend, however, indicates that the ameliorant treated plants performed better than the control. There is no doubt that the ameliorant application does improve plant growth. The reason for an increase in dry shoot biomass for the treated plants may be a secondary effect because of the improved root system.

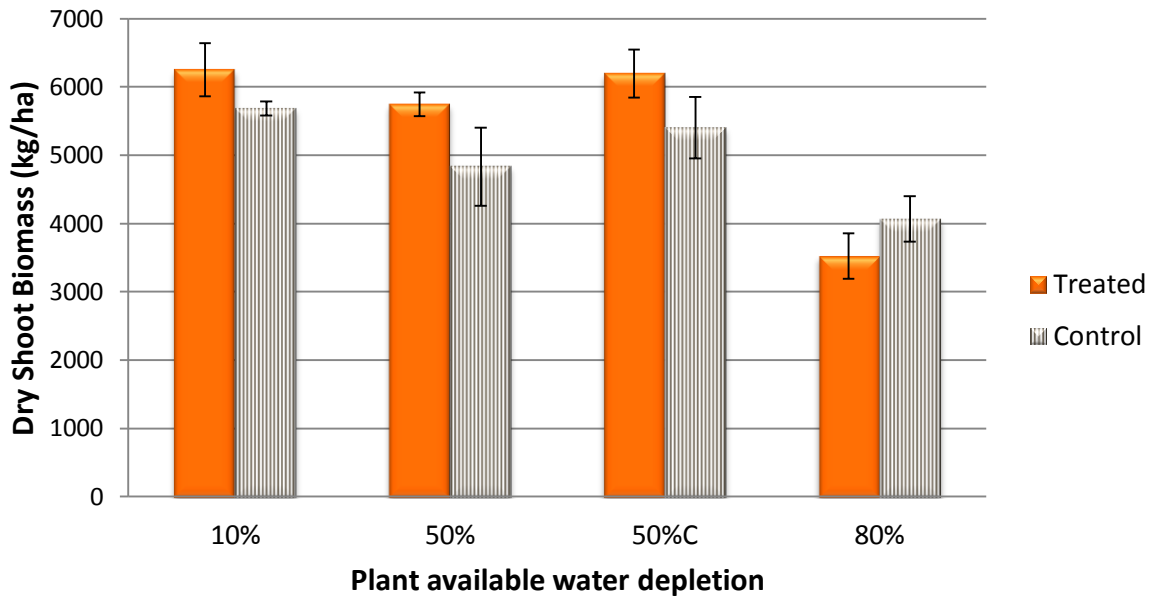


Figure 3.17: Mean dry shoot biomass for the treated and control for each of the plant available water depletions.

On evaluation of the effect of the PAWDs on shoot biomass, a significant difference is apparent; that of the 80% PAWD compared to the other three PAWD, which do not differ from one another. The 80% PAWD showed stunted and poor growth due to the low irrigation levels applied.

Table 3.8: Means of the Dry Shoot Biomass for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

Dry Shoot Biomass (kg.ha ⁻¹)	
Treatment	Mean
Treated	543.0 a
Control	499.7 a
<i>MSD</i>	<i>50.76</i>
<i>p-value</i>	<i>0.918</i>
PAWD	Mean
10%	596.8 a
50%	529.0 a
50%C	579.9 a
80%	379.6 b
<i>MSD</i>	<i>95.68</i>
<i>p-value</i>	<i><0.0001</i>

Means with different letters are significantly different according to Tukey’s studentised range test ($P < 0.05$)

3.3.8. Total Plant Biomass

The total biomass is presented in Figure 3.18 to give an indication of the contribution of each of the components, shoot and root biomass, to the total biomass. The statistical analysis shows that over all the PAWDs the treated had a significantly higher mean total dry biomass compared to the control ($p = 0.0465$). The effect of the PAWDs on the mean total dry biomass shows significant differences ($p < 0.0001$).

The largest mean total dry biomass is that of the 10% PAWD. Not surprisingly, as these pots received the most frequent irrigation. The total dry biomass of the 50% and 50%C PAWD did not differ significantly. The 80% PAWD had the smallest mean total dry biomass due to the very low quantity of water received, causing stunting of plant growth.

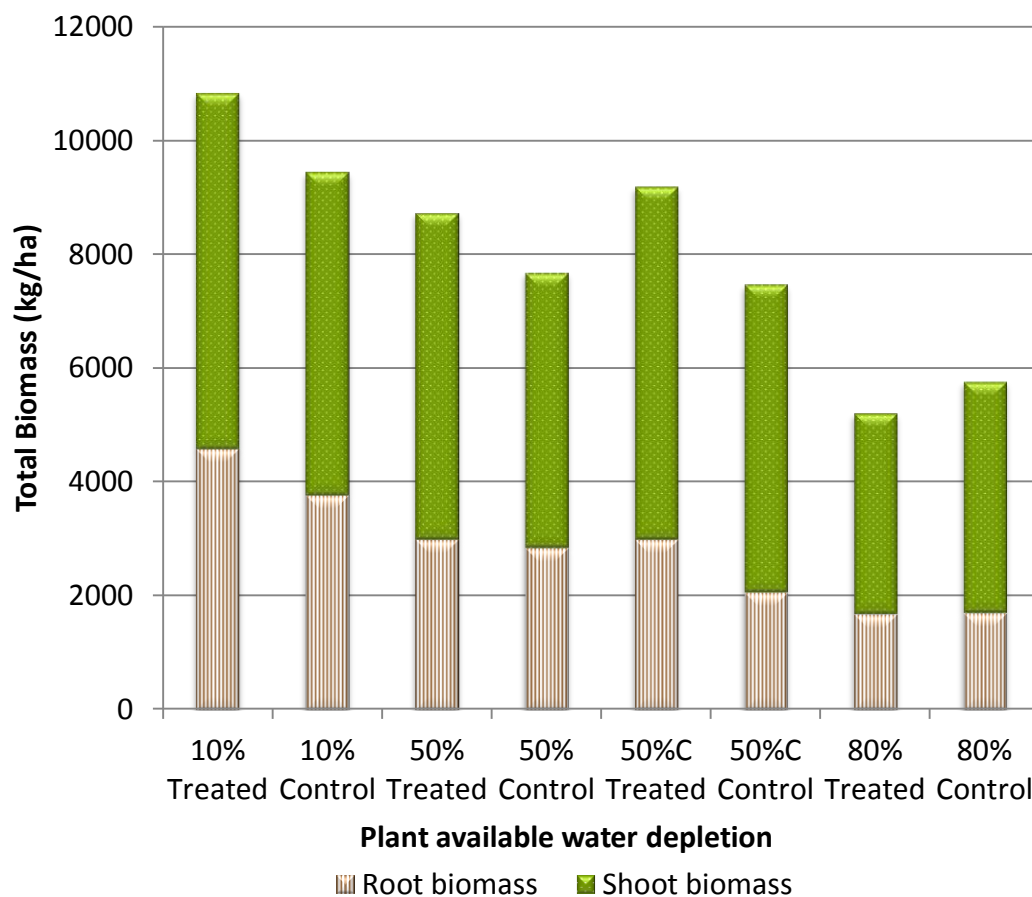


Figure 3.18: Mean total biomass for the treated and control for each of the plant available water depletions as components of shoot and root biomass.

Plants treated with the ameliorant had a greater total biomass than that of the control. This is indicative of an improvement in the overall plant growth with the application of the ameliorant. From Figure 3.18 it may be noted that the increase in biomass for the ameliorant treated plants is predominately from the contribution of the root biomass, especially that of the 10% and 50%C PAWD.

Table 3.9: Means of the Total Biomass for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

Total Biomass (kg.ha⁻¹)	
Treatment	Mean
Treated	8482 a
Control	7582 b
<i>MSD</i>	<i>884.9</i>
<i>p-value</i>	<i>0.0465</i>
PAWD	Mean
10%	10131 a
50%	8197 b
50%C	8323 b
80%	5479 c
<i>MSD</i>	<i>1668</i>
<i>p-value</i>	<i><0.0001</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

3.3.9. Leaf Area Index

The data for the Leaf Area Index (LAI) is presented in Figure 3.19. As there was no interaction between treatment and the PAWD, only the main effects will be considered as presented in Table 3.10. There was a significant difference overall between the mean of the treated and that of the control ($p=0.0172$). Therefore, the LAI of the ameliorant treated pots showed improved crop growth.

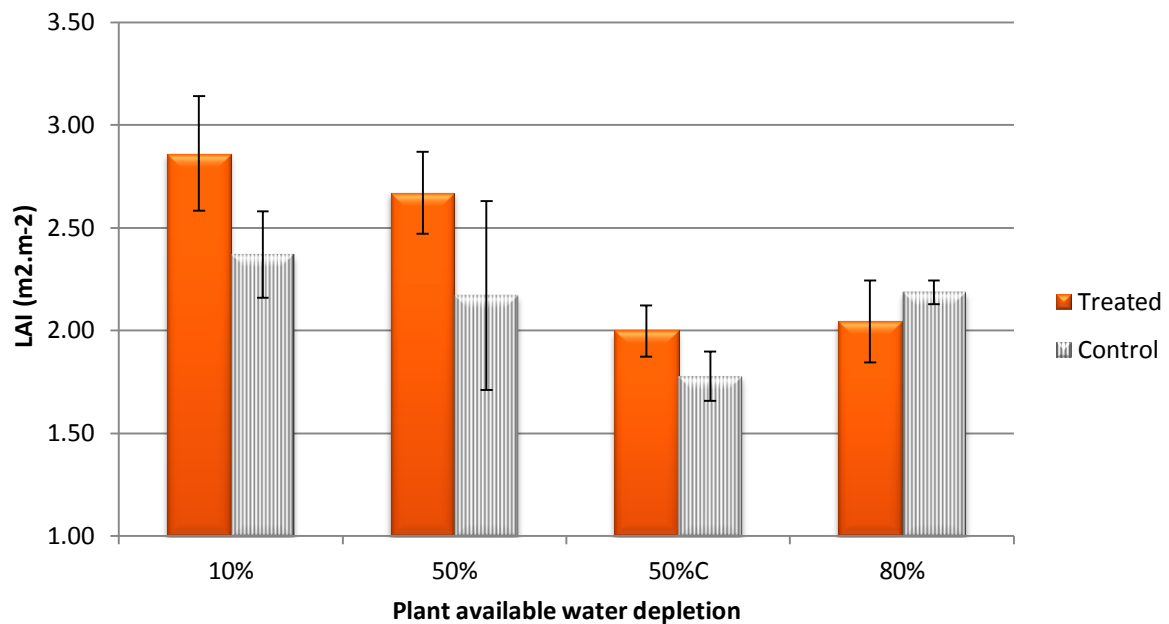


Figure 3.19: The Leaf Area Index for the treated and control for each of the plant available water depletions.

The LAI is used here as a measure of the crop growth and the primary photosynthetic production. The treated plants for each of the PAWD show a greater LAI, except for the 80% PAWD where the means are similar.

A larger LAI provides the plant with the advantage because of greater light interception and greater photosynthetic capacity (Burstall and Harris, 1983). Hence, the improvement in total dry biomass production for the ameliorant treated plants.

Table 3.10: Means of the Leaf Area Index for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

Leaf Area Index	
Treatment	Mean
Treated	2.440 a
Control	1.980 b
<i>MSD</i>	<i>0.277</i>
<i>p-value</i>	<i>0.0019</i>
PAWD	Mean
10%	2.529 a
50%	2.308 ab
50%C	1.844 b
80%	2.160 ab
<i>MSD</i>	<i>0.521</i>
<i>p-value</i>	<i>0.0099</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

The LAI for the various PAWDs showed statistical differences between the 10% and the 50%C PAWD. The 50%C PAWD had the smallest LAI and this may be due to stocky growth as a result of a decrease in the soil temperature, as discussed more fully in Section 3.3.10.

3.3.10. Plant height

The results for the plant height data are presented in Figure 3.20. The linear model ANOVA for plant height showed that there is interaction between the treatment and the PAWD and the alternate statistical model was used as per Section 2.3.2. The means for the statistical analysis are presented in Figure 3.20.

For three of the four PAWD the ameliorant treated pots showed significantly taller plants than that of the control. Only in the case of the 80% PAWD was the mean of the control larger than that of the treated. It was visually noted that the plants that received the ameliorant treatment grew better. Although the mean plant height of the 50%C PAWD is small, the plants had a greater total biomass than that of the 50% or 80% PAWD. Hence, the

maize plants of the 50%C PAWD had stocky or compact growth. Stocky growth may be caused by low soil temperature (Atkin et al., 1973). As the soil of the 50%C PAWD remained moist for longer periods, this could cause decrease in soil temperature during the day. The 10% PAWD, which was also wet, did not have stocky growth. The possibility exists that the 50%C had a greater production of vascular bundles than that of the other plants due to its great mass in comparison to its height.

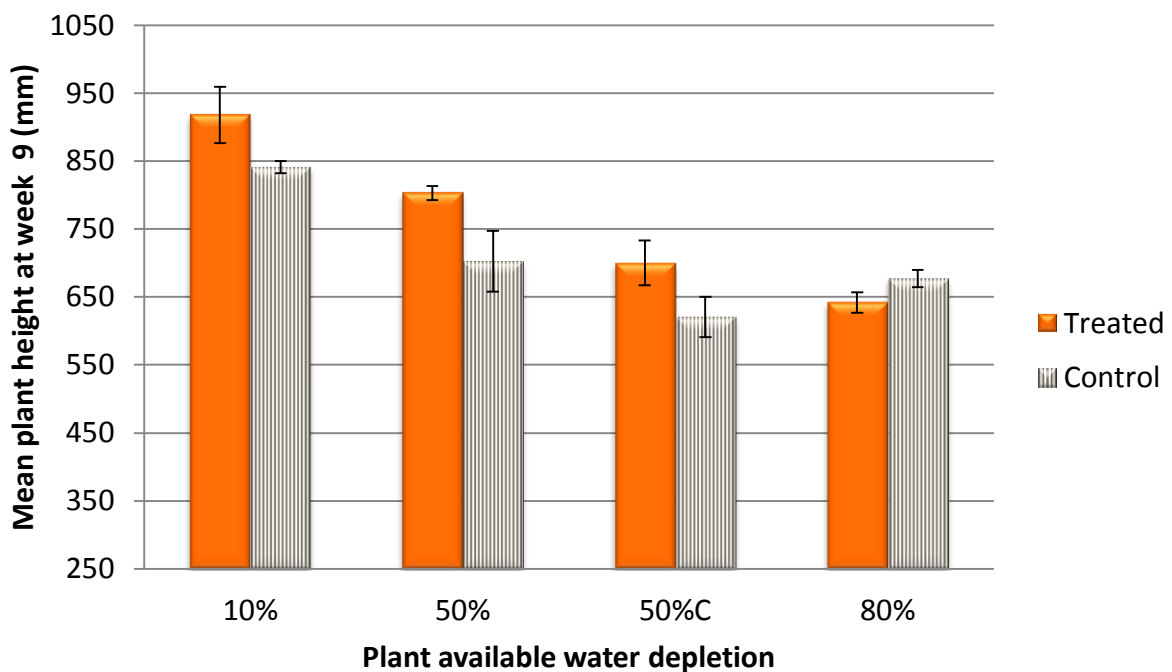


Figure 3.20: Plant height for the treated versus control plants for each of the plant available water depletions.

The most likely reason for the overall improvement in plant height for the treated is that the application of the soil ameliorant provided a favourable soil environment resulting in an increase in root biomass, hence improved plant vigour. There is a correlation between the LAI and that of the plant height. The enhanced photosynthetic capacity, greater leaf area allocation of the ameliorant treated plants, increased growth rate yielding taller plants (Kocacinar and Sage, 2005). A comparison of the LAI with that of the plant height shows a linear correlation for the treated and control plants, with R^2 -values of 88.2% and 74.4% respectively.

Table 3.11: Means of the plant height for the comparison of the treated and control within each of the PAWD.

Plant Height (mm)				
	10% PAWD Mean	50% PAWD Mean	50%C PAWD Mean	80% PAWD Mean
Treated	917.5 a	803.8 a	720.0 a	642.5 b
Control	841.3 b	703.8 b	621.3 b	676.3 a
<i>MSD</i>	72.00	71.70	75.46	23.87
<i>p-value</i>	0.0390	0.0123	0.0734	0.0098

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

3.3.11. Chlorophyll content

The data obtained for the measurement of the Chlorophyll Content Index (CCI) is presented in Figure 3.21. The statistical analysis (Table 3.12) shows that there is no significant difference between the treated and control. The trend observable in Figure 3.21 is that the CCI is higher for the control than for those treated with the soil ameliorant.

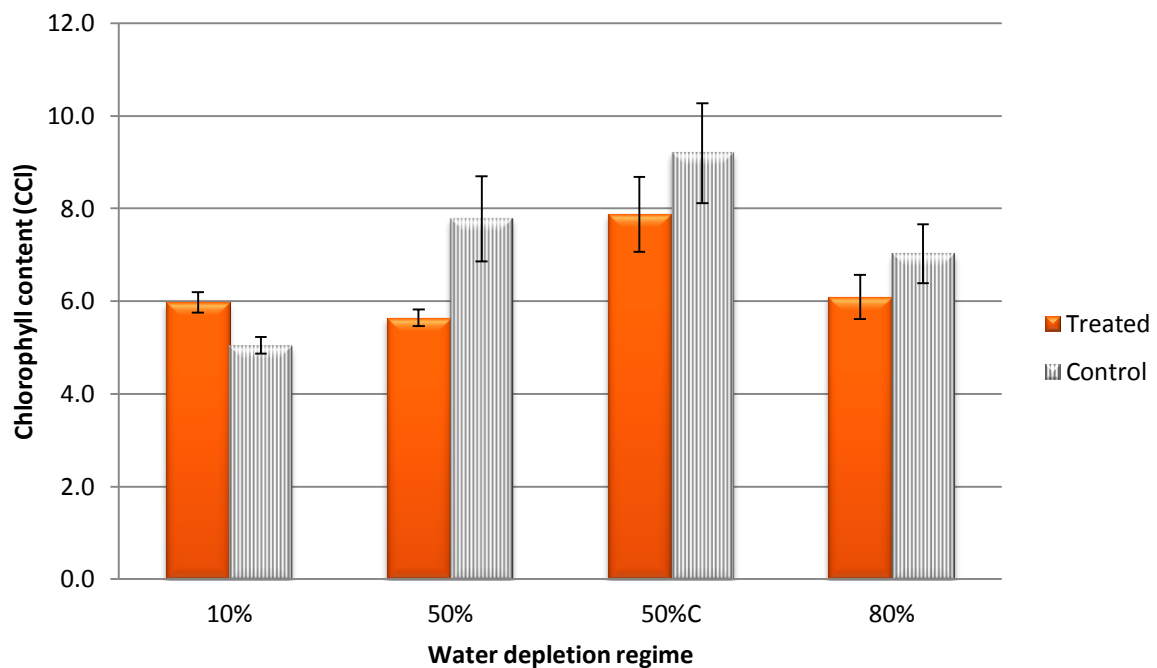


Figure 3.21: Chlorophyll content of the treated versus the control for each of the plant available water depletions as a Chlorophyll Content Index (CCI)

There is a significant difference between the CCI of the 50%C PAWD and the other PAWD's. The 50%C has the highest CCI. This may be because the plants of the 50%C PAWD were stocky and thus there is no dilution effect on the chlorophyll content due to large leaf surface area. Therefore the 50%C PAWD should have a relatively small leaf area. This is confirmed in Figure 3.19, which shows that the 50%C PAWD did have the lowest mean LAI.

The CCI tended to be opposite to the LAI and plant height indicating that chlorophyll content is lower in plants with larger LAI and plant height. A study by (Széles et al., 2012) showed that the chlorophyll content in the leaves of maize was less for the plants that had lower soil water content at the closing of the vegetative stage.

Table 3.12: Means of Chlorophyll Content Index for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

Chlorophyll Content Index	
Treatment	Mean
Treated	6.393 a
Control	7.261 a
<i>MSD</i>	<i>0.904</i>
<i>p-value</i>	<i>0.0589</i>
PAWD	Mean
10%	5.508 b
50%	6.710 b
50%C	8.533 a
80%	6.558 b
<i>MSD</i>	<i>1.704</i>
<i>p-value</i>	<i>0.0005</i>

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

3.3.12. Leaf Chemical Analysis

The data obtained for the leaf chemical analysis is presented in Table 3.13 as mg per plant, using the dry shoot biomass of the plant. The data is also presented graphically in Figure 3.22 to Figure 3.29. No statistical analysis was performed as a single composite sample was collected of all the replicates for each of the treatment combinations.

The leaf chemical showed few trends and even those present are very nondescript. The trend for Ca though very minor, is similar but inverse to that of the aggregate stability. That is, treatments with higher Ca content in their leaves correlated with a lower aggregate stability in each of the PAWD. Though this correlation is not significant, it may be said that Ca does play an integral role in the formation and stabilization of aggregates (Muneer and Oades, 1989 and Amézqueta, 1999).

There was no apparent trend for the K content of the leaves evaluated (Figure 3.25). Two of the four PAWD, 50% and 80% showed a decrease in the K content compared to the control. A study by Bujtás et al. (1988) found that the net potassium influx to roots of wheat seedlings was decreased with the application of a nonionic surfactant. The results for the leaf chemical analysis of the pot experiment show no concrete evidence to substantiate the observation by Bujtás et al.

The trend for the Mg concentration in the leaves shows an increase in Mg content for the treated plants. The leaf concentrations of Na, Ca and Mn show similar trends. When comparing the treated to the control, the higher or lower values are grouped according to the PAWD, where the 50% and 80% are similar and the 10% and the 50%C are the similar. This indicates that the hydrology of the system has a noticeable effect of the on the outcome of the ameliorant effect. The Cu and Zn content, both show increased concentrations in the control leaves for all the PAWDs. The Fe content is highly variable.

The results for the various cation concentrations present in the leaf is highly variable, with few exceptions. There are no very obvious trends and hence no concrete deductions can be made to the effect of the ameliorant, if any, on leaf chemistry.

Table 3.13: The Macro- and Micro-nutrients for the soil ameliorant treated and control pots for each PAWD in milligrams nutrient per plant.

		Ca (mg/plant)		Mg (mg/plant)		Na (mg/plant)		K (mg/plant)	
PAWD	Treated	Control	Treated	Control	Treated	Control	Treated	Control	
10%	22.71	24.10	21.55	21.04	0.74	0.73	486.20	363.22	
50%	30.74	24.57	25.91	20.34	0.87	0.72	381.68	392.13	
50%C	40.04	38.18	29.82	24.36	0.83	0.87	443.36	380.32	
80%	17.43	17.38	14.82	15.74	0.53	0.57	280.67	338.52	

		Fe (mg/plant)		Cu (mg/plant)		Zn (mg/plant)		Mn (mg/kg)	
PAWD	Treated	Control	Treated	Control	Treated	Control	Treated	Control	
10%	1.85	1.17	0.05	0.06	0.35	0.36	0.97	1.05	
50%	1.37	1.16	0.08	0.08	0.33	0.33	1.12	0.68	
50%C	1.19	1.38	0.04	0.05	0.42	0.38	1.44	1.47	
80%	0.81	0.82	0.05	0.07	0.05	0.25	0.85	0.86	

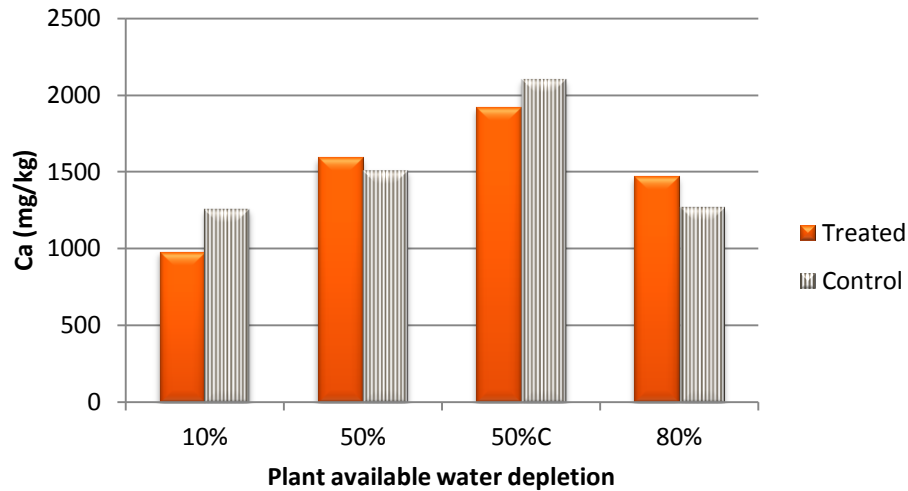


Figure 3.22: Ca content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

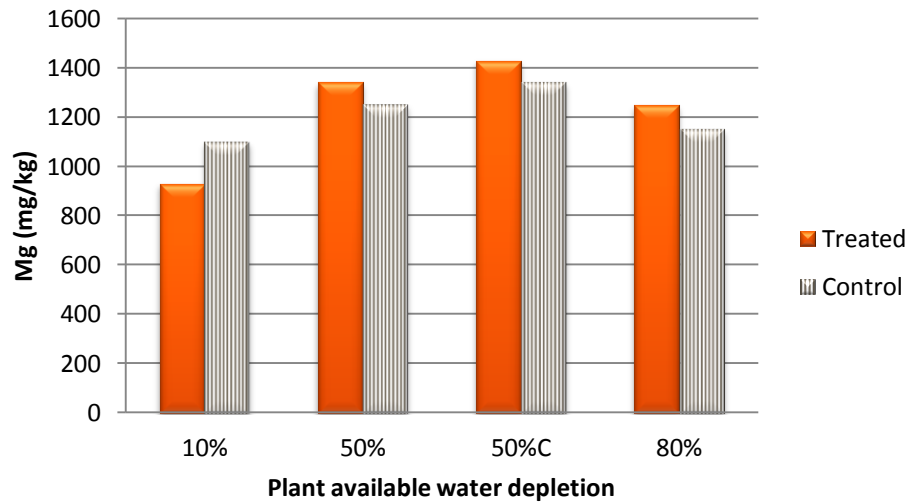


Figure 3.23: Mg content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

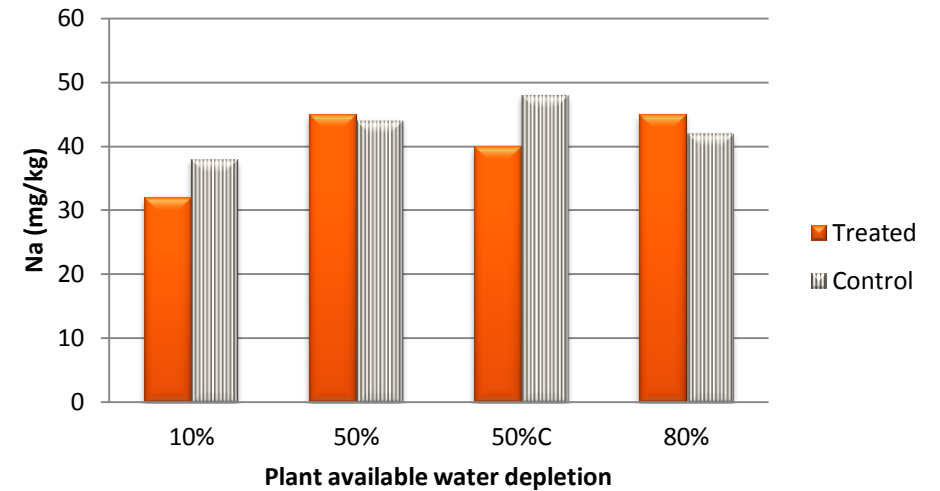


Figure 3.24: Na content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

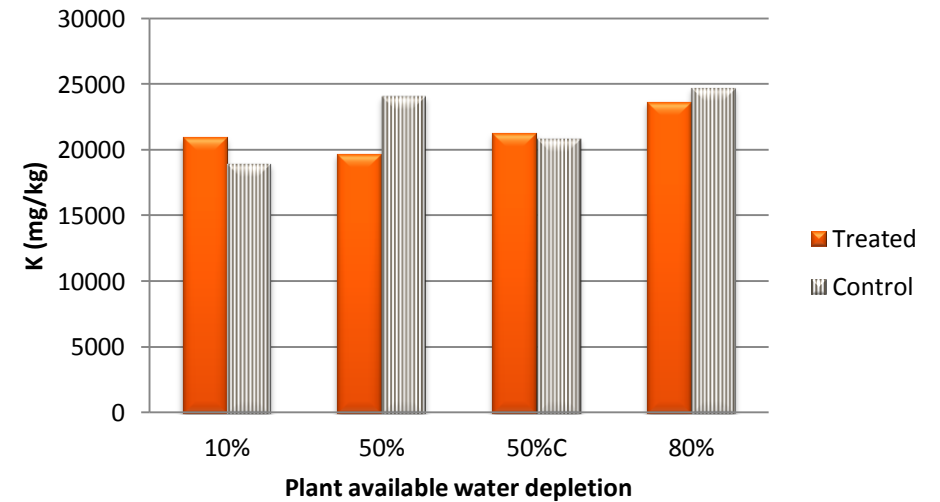


Figure 3.25: K content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

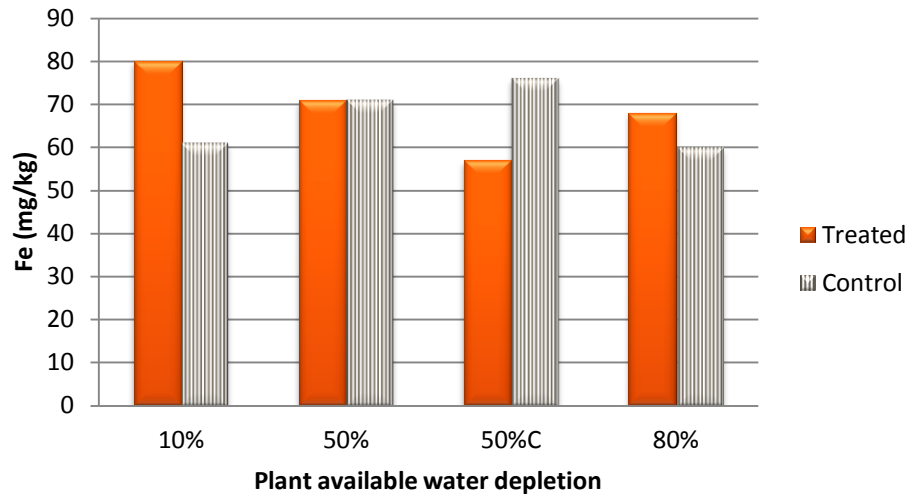


Figure 3.26: Fe content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

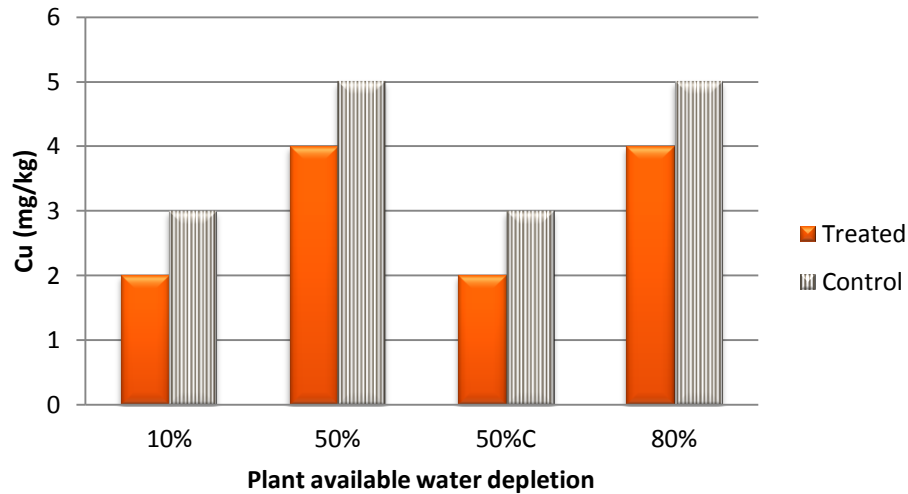


Figure 3.27: Cu content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

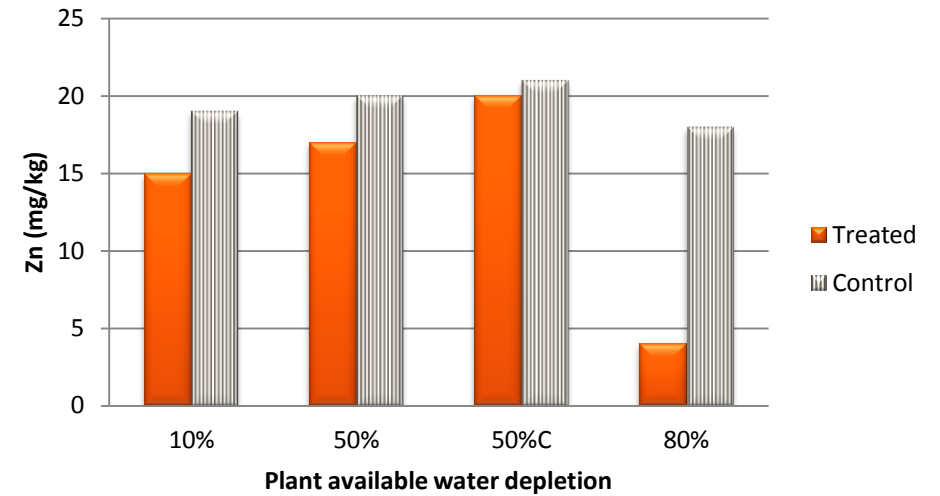


Figure 3.28: Zn content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

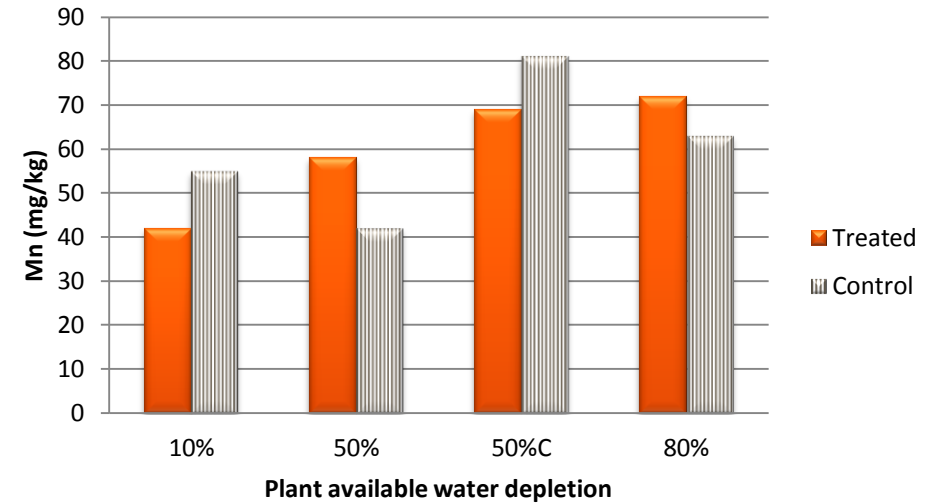


Figure 3.29: Mn content for the leaf analysis of the treated versus the control plants for each of the plant available water depletions.

3.3.13. Biomass Water Use Efficiency

The mean calculated values for the Biomass Water Use Efficiency (BWUE) are presented in Figure 3.30. The statistical analysis (Table 3.14) shows that the treated pots had a significantly higher BWUE than that of the control ($p=0.0469$). This shows that the ameliorant application improved the BWUE.

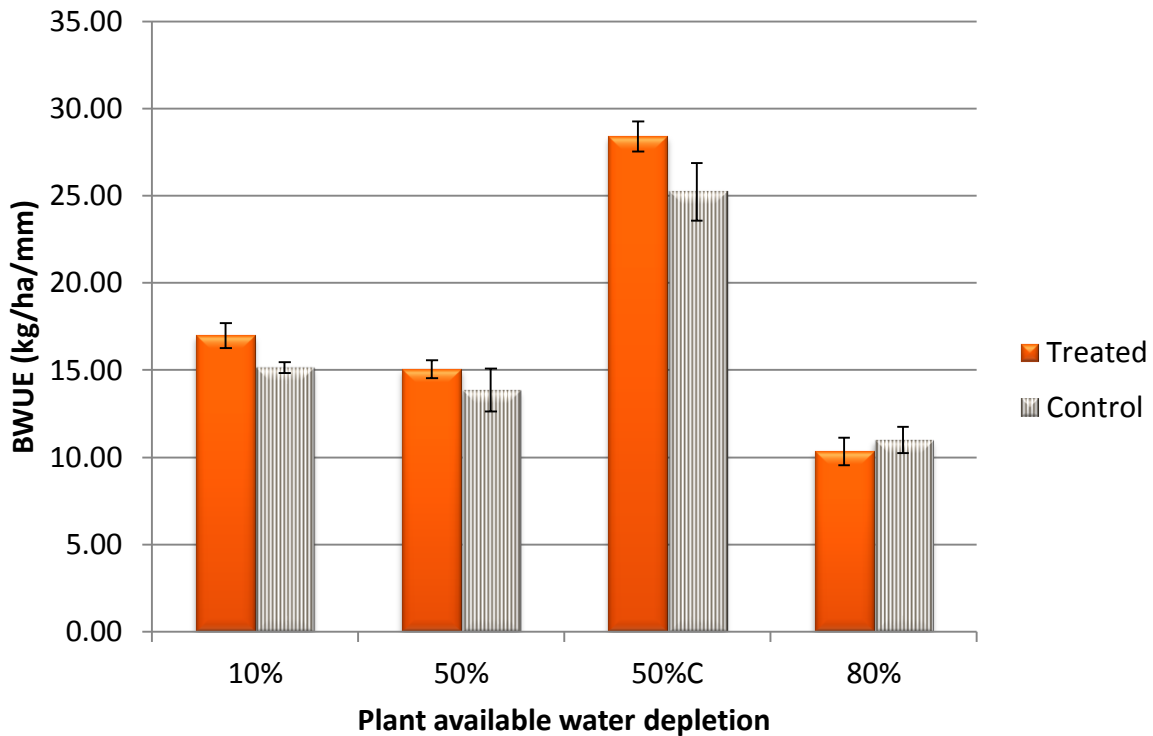


Figure 3.30: The mean Biomass Water Use Efficiency of the treated versus the control for each of the PAWDs

The PAWDs show significant differences ($p<0.0001$) where the 50%C PAWD had the highest significant BWUE. The 10% and 50% PAWD have similar trends while that of the 80% PAWD performed very poorly. The highest BWUE is for the 50%C PAWD where the treated showed a further improvement of 13% over the control (Table 3.15). The benefit of a mulch for water conservation is shown by the 50%C PAWD. Reduced surface evaporation for the 50%C PAWD allows for the efficient use of water for biomass production, less wastage for a greater biomass production.

Table 3.14: Means of the BWUE for the comparison between the treated and control over all PAWD and the comparison between different PAWD for the treated and control combined.

BWUE (kg.ha ⁻¹ .mm ⁻¹)	
Treatment	Mean
Treated	17.69 a
Control	16.31 b
<i>MSD</i>	1.366
<i>p-value</i>	0.0469
PAWD	Mean
10%	16.06 b
50%	14.45 b
50%C	26.82 a
80%	10.66 c
<i>MSD</i>	2.574
<i>p-value</i>	<0.0001

Means with different letters are significantly different according to Tukey's studentised range test ($P < 0.05$)

The theoretical evaluation of WUE in crop production by Sinclair et al. (1984) outlines five options for improving water-use efficiency namely; biochemical alterations, stomatal physiology, alteration of the cropping environment, improved harvest index and increased proportion of transpired water. Of these options, the one that may apply with the application of the ameliorant is that there was an increased proportion of transpired water. Although there are no measurements were taken for transpiration, the results for increased overall growth show that the plant was more productive. Yet, considering that the effect of the ameliorant, as shown in the literature (Leinauer et al., 2001, Read and Gregory, 2008 and Lehrsch et al., 2011) and the Sandbox experiment (Section 3.2), the reduction in matric potential would allow the plant to take up water more readily.

A evaluation of the Soil-Plant-Atmosphere Continuum (SPAC) by Cowan (1965) showed that the rate of transpiration decreases with an increase in the matric potential. The matric potential was illustrated as a point of resistance to transpiration stream through the SPAC when using an analogue of Ohm's Law (Van den Honert, 1948). Reducing that resistance would allow greater transpiration potential. To conclude, Sinclair et al. (1984) stated that "crop production is inextricably linked to crop transpiration. To increase crop biomass more water must be used in transpiration."

3.4. The percentage increase from control to treated for selected properties

A summary of the key differences in the Pot experiment are presented in Table 3.15. These values show the percentage increase from the control to the treated for the various soil and plant parameters evaluated. For the 10%, 50% and 50%C PAWD almost all the properties showed an increase or improvement with the application of the ameliorant. The 80% PAWD was added to the evaluation as an extreme case and here the ameliorant did not always improve the particular property.

Table 3.15: The percentage increase from the control to the treated for some selected soil properties and plant traits.

Soil property/Plant trait	10% PAWD	50% PAWD	50%C PAWD	80% PAWD
ET(mm)	-2%	11%	2%	-8%
BWUE(kg.ha ⁻¹ .mm ⁻¹)	12%	9%	13%	-6%
Shoot Biomass (kg.ha ⁻¹)	10%	19%	15%	-13%
Root Biomass (kg.ha ⁻¹)	22%	5%	45%	-1%
LAI (m ² .m ⁻²)	-1%	52%	13%	9%
Aggregate stability (%)	17%	-20%	23%	-11%

*Negative percentages indicated a decrease in the treated relative to the control.

Conclusions

The Firgrove field trial showed very promising results for the management of water-repellent sandy soils where even wetting of the soil and water-holding capacity can be improved with the application of the ameliorant. As Soil A was well-drained, whereas Soil B had a high water-table thus the effect of the ameliorant application is better represented by the results for Soil A. Soil A showed both an increase in the water retention, as well as a more uniform water content over the nine week period for the ameliorant treated soil compared to the control. As the water measurements were taken between drippers the increase in water content measured for the ameliorant treated soil, may be better explained as an improvement in the soil water distribution or lateral movement of the water in the soil. This effect would be due to the presence of the surfactant in the soil lowering the surface tension of water and enabling the water to infiltrate into smaller pores than would otherwise be possible. Improved water distribution, especially with drip irrigation systems, would make available a larger volume of wetted soil for root growth.

The Sandbox experiment showed a change in the soils matric potential, in which the soil had higher water retention for the ameliorant treatment at all suctions tested in comparison with the control. A shift in the Water Characteristic Curve for the Sandbox experiment is indicative of effects on the soil water system where modification of the water retention properties of a sandy soil has an effect on the matric potential. These effects may be attributed to the lowering of the soil-water contact angle due to the presence of surfactants and orange-oil. This shift in the matric potential has potential to shift the boundaries of plant available water thereby improving plant growth. More available water is especially beneficial in cases where there are fluctuations in soil water content, which may result in plant stress.

The results of the Pot Experiment show that there are significant effects on plant growth and to a lesser extent on soil properties. Plant response to the application of the ameliorant was very favourable and improvements in plant growth specifically dry root and shoot biomass production, LAI and, especially, BWUE were realised. The dry root biomass was increases significantly for the ameliorant application compared to the control, where the dry

shoot biomass showed a trend where the ameliorant treatment was greater than that of the control. The LAI and the plant height were significantly improved for the ameliorant application in comparison to the control.

Bulk density at the end of the pot experiment had not changed significantly for the ameliorant treated soil in comparison to the control. There was an increase in the percentage water-stable aggregates for the ameliorant treatment of the moist regimes, 10% and 50% C PAWD. The overall improvement in the percentage water-stable aggregates is positively correlated ($R^2=77\%$) to the dry root biomass.

There were no effects observed on soil pH or the leaf chemical composition at the end of the Pot experiment. In most cases the ameliorant treatment of the 80% PAWD did not differ from that of the control, but the trend shows that the ameliorant treatment had a slightly negative effect on the plant traits evaluated. The 80% PAWD is however, an extreme case and as such, this discrepancy is minor.

The improvements in plant response, be it biomass, LAI or plant height, are difficult to relate to the soil properties evaluated for the Pot experiment. Thus, there is a strong inclination that the improvements may be attributed to more intricate changes in the soil-water relations, such as the effects on the rhizosphere. However, examining the effect of soil ameliorants on the rhizosphere is challenging as it would require special and costly research tools.

The possible effects of the ameliorant on the rhizosphere are of great importance. Small changes due to the application of the ameliorant in the bulk soil have an amplified effect in the rhizosphere. As no specific research has been done in this study on the rhizosphere, it would be an opportunity for important future research in this field. The application of the ameliorant had a marked effect on the root growth, which would suggest that the ameliorant did have an effect on the rhizosphere.

Other areas of research which may be of interest to explore is the effect of the ameliorant on microbial activity in the soil and the effect of the ameliorant in other soil textures and different organic matter contents. The longevity of the ameliorant in the soil and the

permanency of the changes effected by the ameliorant application may be of use to ensure effective utilisation of the ameliorant in the agricultural industry.

The key objective was to evaluate certain soil properties and plant responses as affected by the application of the soil ameliorant. In light of the results of this study the hypotheses postulated in the Introduction may accordingly be rejected or not rejected.

1. The water holding capacity of the soil increases when the soil has been treated with the ameliorant – Do not reject, as the results of the Field Trial and the Sandbox experiment show that there is an increase in the water holding capacity and water retention of a sandy soil with the application of the ameliorant.
2. The aggregate stability of the soil improves when the soil has been treated with the ameliorant – Do not reject, as the aggregate stability of the soil in the Pot experiment was increased with ameliorant application in certain cases.
3. The bulk density decreases with a concomitant increase in the porosity of the soil treated with the ameliorant – Reject, as the bulk density was not affected by the application of the ameliorant in either the Field Trial or the Pot Experiment.
4. The root system is improved with the application of the ameliorant – Do not reject, as the Dry root biomass of the maize plants in the Pot experiment were significantly increased with the application of the ameliorant.
5. The overall plant growth (shoots, LAI, plant height) is improved with the application of the ameliorant – Do not reject, as the overall plant growth was significantly increased with the application of the ameliorant in the Pot experiment, specifically dry shoot biomass, LAI and plant height were improved.
6. The chlorophyll content increased in the plants grown in the soil that received the ameliorant application –Reject, as the results from the Pot experiment show a decrease in the chlorophyll content of the plants that received the ameliorant application.
7. The BWUE is improved with the application of the ameliorant – Do not reject as the BWUE was significantly improved with the application of the ameliorant.

References

- Abraham, D., Braguini, W., Kelmer-Bracht, A.M., Ishii-Iwamoto, E.L., 2000. Effects of four monoterpenes on germination, primary root growth, and mitochondrial respiration of maize. *Journal of Chemical Ecology*. 26, 611–625.
- Abu-Zreig, M., 2003. Effect of Application of Surfactants on Hydraulic Properties of Soils. *Biosystems Engineering*. 84, 363–372.
- Allred, B., Brown, G.O., 1996. Anionic Surfactant Transport Characteristics in Unsaturated Soil. *Soil Science*. 161, 415–425.
- Amézketa, E., 1999. Soil Aggregate Stability : A Review. *Journal of Sustainable Agriculture*. 14, 83–151.
- Ang, C.C., Abdul, A.S., 1992. A laboratory study of the biodegradation of an alcohol ethoxylate surfactant by native soil microbes. *Journal of Hydrology*. 138, 191–209.
- Arneodo, C., Baszkin, A., Benoit, J.P., Fellous, R., Thies, C., 1988. Interfacial Studies of Essential Oil-Water Systems. *Colloids and Surfaces*. 34, 159–169.
- Arriaga, F.F.J., Lowery, B., Kelling, K.A., 2009. Surfactant impact on nitrogen utilization and leaching in potatoes. *American Journal of Potato Research*. 86, 383–390.
- Atkin, R.K., Barton, G.E., Robinson, D.K., 1973. Effect of Root-growing Temperature on Growth substances in Xylem Exudate of *Zea mays*. *Journal of experimental botany*. 24, 475–487.
- Bachmann, J., Deurer, M., Arye, G., 2007. Modeling Water Movement in Heterogeneous Water-Repellent Soil: 1. Development of a Contact Angle–Dependent Water-Retention Model. *Vadose Zone Journal*. 6, 436.
- Bisdorn, E.B. a., Dekker, L.W., Schoute, J.F.T., 1993. Water repellency of sieve fractions from sandy soils and relationships with organic material and soil structure. *Geoderma*. Elsevier. 56, 105–118.
- Blake, G.R., Hartage, K.H., 1986. Bulk density, in: Klute, A. (Ed.), *Methods of Soil Analysis*. ASA and SSSA, Madison, Wisconsin, pp. 363–376.
- Bowen, E., 1975. Potential by-products from microbial transformation of D-limonene. *Florida State Horticultural Society*. 304–308.
- Brandsma, R., Fullen, M., Hocking, T., 1999. Soil conditioner effects on soil structure and erosion. *Journal of soil and water conservation*. Soil and Water Conservation Society. 54, 485.

- Brownawell, B.J., Chen, H.U.A., Zhang, W., Westall, J.C., 1997. Sorption of Nonionic Surfactants on Sediment Materials. 31, 1735–1741.
- Bujtás, C., Cserhádi, T., Szigeti, Z., 1988. Effects of some nonionic tenzides on potassium influx in roots of wheat seedlings. *Biochemie und Physiologie der Pflanzen*. 183, 277–281.
- Burstall, L., Harris, P.M., 1983. The estimation of percentage light interception from leaf area index and percentage ground cover in potatoes. *The Journal of Agricultural Science*. 100, 241–244.
- Chan, K., Sivapragasam, S., 1996. Amelioration of a degraded hardsetting soil using an anionic polymeric conditioner. *Soil Technology*. 9, 91–100.
- Cid-Ballarín, C., Muñoz-Carpena, R., Socorro-Monzón, A., González-Tamargo, G., 1998. Wetting Agent Effects on Peat Properties Related to Nutrient Solution Losses and Plant Growth. *Acta Horticulturae*. 458, 161–169.
- Connolly, R., 1998. Modelling effects of soil structure on the water balance of soil–crop systems: a review. *Soil and Tillage Research*. 48, 1–19.
- Cornelissen, J.H.C.A., Lavorel, S.B., Garnier, E.B., Díaz, S.C., Buchmann, N.D., Gurvich, D.E.C., Reich, P.B.E., Steege, H.F., Morgan, H.D.G., A, M.G.A.V.D.H., Pausas, J.G.H., Poorter, H.I., 2003. A handbook of protocols for standardised and easy measurement of plant functional traits worldwide. 335–380.
- Cowan, I.R., 1965. Transport of water in the soil-plant-atmosphere system. *Journal of Applied Ecology*. 2, 221–241.
- Crabtree, W.L., Henderson, C.W.L., 1999. Furrows , press wheels and wetting agents improve crop emergence and yield on water repellent soils. *Plant and Soil*. 214, 1–8.
- Cristani, M., D'Arrigo, M., Mandalari, G., Castelli, F., Sarpietro, M.G., Micieli, D., Venuti, V., Bisignano, G., Saija, A., Trombetta, D., 2007. Interaction of Four Monoterpenes Contained in Essential Oils with Model Membranes: Implications for Their Antibacterial Activity. *Journal of Agricultural and Food Chemistry*. American Chemical Society. 55, 6300–6308.
- DeBano, L.F., 1981. Water repellent soils: a state-of-the-art. US Dept. of Agriculture, Forest Service, Pacific Southwest Forest and Range Experiment Station.
- Dekker, L.W., Ritsema, C.J., 1996. Uneven moisture patterns in water repellent soils. 70, 87–99.
- Doerr, S.H., Shakeby, R.A., Dekker, L.W., Ritsema, C., 2006. Occurance prediction and hydrological effects of water repellency amongst major soil and land-use types in a humid temperate climate. *European Journal of Soil Science*. 57, 741–751.

- Dunbabin, V.M., McDermott, S., Bengough, a. G., 2006. Upscaling from Rhizosphere to Whole Root System: Modelling the Effects of Phospholipid Surfactants on Water and Nutrient Uptake. *Plant and Soil*. 283, 57–72.
- Federle, T.W., Schwab, B.S., 1989. Mineralization of Surfactants by Microbiota of Aquatic Plants. *Applied and environmental microbiology*. 55, 2092–2094.
- Feng, G.L., Letey, J., Wu, L., 2001. The Influence of Two Surfactants on Infiltration into a Water-Repellent Soil. *Geoderma*. 361–367.
- Fernández-Gálvez, J., Mingorance, M.D., 2010. Vapour and liquid hydrophobic characteristics induced by presence of surfactants in an agricultural soil☆. *Geoderma*. Elsevier B.V. 154, 321–327.
- Francis, C.A., Rutger, J.N., Palmer, A.F.E., 1969. A Rapid Method for Plant Leaf Estimation in Maize (*Zea mays* L.). *Crop Science*. 9, 537–539.
- Friedly, E.C., Crandall, P.G., Ricke, S.C., Roman, M., O’Bryan, C., Chalova, V.I., 2009. In vitro antilisterial effects of citrus oil fractions in combination with organic acids. *Journal of food science*. 74, M67–72.
- Hallett, P., Gordon, D., Bengough, A., 2003. Plant influence on rhizosphere hydraulic properties: direct measurements using a miniaturized infiltrometer. *New Phytologist*. 597–603.
- Hallett, P.D., Baumgartl, T., Young, I.M., 2001. Subcritical Water Repellency of Aggregates from a Range of Soil Management Practices. 65, 435–439.
- Hamme, J.D. Van, Singh, A., Ward, O.P., 2006. Physiological aspects Part 1 in a series of papers devoted to surfactants in microbiology and biotechnology. *Biotechnology Advances*. 24, 604–620.
- Henry, E.J., Smith, J.E., 2003. Surfactant-Induced Flow Phenomena in the Vadose Zone : A Review of Data and Numerical Modeling. *Vadose Zone Journal*. 2, 154–167.
- Hillel, D., 1998. *Environmental Soil Physics*. Academic Press, San Diego, CA, p. 590.
- Ibrahim, M., Oksanen, E., Holopainen, J., 2004. Effects of limonene on the growth and physiology of cabbage(*Brassica oleracea* L) and carrot(*Daucus carota* L) plants. *Journal of the Science of Food and Agriculture*. 84, 1319–1326.
- Imeson, A.C., Verstraten, J.M., Van Mulligen, E.J., Sevink, J., 1992. The effects of fire and water repellency on infiltration and runoff under Mediterranean type forest. *Catena*. 19, 345–361.
- Isman, M.B., 2000. Plant essential oils for pest and disease management. *Crop Protection*. 19, 603–608.

- Jarvis, N., Etana, a., Stagnitti, F., 2008. Water repellency, near-saturated infiltration and preferential solute transport in a macroporous clay soil. *Geoderma*. 143, 223–230.
- Karagunduz, A.P., Young, K.D., Michael, H., 2001. Influence of a nonionic surfactant on the water retention properties of unsaturated soils. *Soil Science Society of America Journal*. Soil Science Society. 65, 1392.
- Kemper, W.D., Rosenau, R.C., 1986. Aggregate stability and size distribution. Klute, A. (Ed.). ASA and SSSA, Madison, Wisconsin, pp. 425–442.
- Klute, A., Weaver, R.W., Mickelson, S., Sparks, D.L., Bartels, J.M., Dane, J.H., Topp, G., Ulery, A.L., Drees, L., 2005. *Methods of Soil Analysis: Part 3, Third*. Soil Science Society of America, Madison, Wisconsin, pp. 160–161.
- Kocacinar, F., Sage, R.F., 2005. *Vascular Transport in Plants*. Holbrook, N.M., Zwieniecki, M.A. (Eds.). Elsevier Academic Press, Burlington, MA., pp. 517–518.
- Kostka, S., 2000. Amelioration of water repellency in highly managed soils and the enhancement of turfgrass performance through the systematic application of surfactants. *Journal of Hydrology*. 231-232, 359–368.
- Law, J.P.J., Kunze, G.W., 1966. Reactions of Surfactants with Montmorillonite: Adsorption Mechanisms. *Soil Science Society of America Proceedings*. 30, 321–327.
- Lehrsch, G. a., Sojka, R.E., 2011. Water quality and surfactant effects on the water repellency of a sandy soil. *Journal of Hydrology*. Elsevier B.V. 403, 58–65.
- Lehrsch, G. a., Sojka, R.E., Koehn, a. C., 2012. Surfactant effects on soil aggregate tensile strength. *Geoderma*. Elsevier B.V. 189-190, 199–206.
- Lehrsch, G. a., Sojka, R.E., Reed, J.L., Henderson, R. a., Kostka, S.J., 2011. Surfactant and irrigation effects on wettable soils: runoff, erosion, and water retention responses. *Hydrological Processes*. 25, 766–777.
- Leinauer, B., Rieke, P.E., Vanleeuwen, D., Sallenave, R., Makk, J., Johnson, E., 2001. Effects of Soil Surfactants on Water REtention in the Rootzones in Turfgrass. *Society*. 9, 542–547.
- Lemon, E.R., 1956. The potentialities for decreasing soil moisture evaporation loss. *Soil Science Society of America Proceedings*. 20, 120–125.
- Letey, J., Osborn, J., Pelishek, R.E., 1962. The influence of the water-soild contact angle on water movement in the soil. *Bulletin International Association Scientific Hydrology*. 3, 75–81.
- Liu, Z., Edwards, D., Luthy, R., 1992. Sorption of non-ionic surfactants onto soil. *Water Research*. 26, 1337–1345.

- Lui, M., Roy, D., 1995. Surfactant-induced interactions and hydraulic conductivity changes in soil. *Waste Management*. 15, 463–470.
- Mbagwu, J., Pocolo, a, Mbila, M., 1993. Impact of surfactants on aggregate and colloidal stability of two tropical soils. *Soil Technology*. 6, 203–213.
- Mingorance, M.D., Gálvez, J.F., Peña, a., Barahona, E., 2007. Laboratory methodology to approach soil water transport in the presence of surfactants. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 306, 75–82.
- Misra, G., Pavlostathis, S.G., Perdue, E.M., Araujo, R., 1996. Aerobic biodegradation of selected monoterpenes. *Applied microbiology and biotechnology*. 45, 831–8.
- Morel, J., Habib, L., Plantureux, S., Guckert, A., 1991. Influence of maize root mucilage on soil aggregate stability. *Plant and soil*. 136, 111–119.
- Muneer, M., Oades, J.M., 1989. The Role of Ca-Organic Interactions in Soil Aggregate Stability . III . Mechanisms and Models. *Australian Journal of Soil Research*. 27, 411–423.
- Paavolainen, L., Kitunen, V., Smolander, A., 1998. Inhibition of nitrification in forest soil by monoterpenes. *Plant and Soil*. Kluwer Academic Publishers. 205, 147–154 LA – English.
- Park, D.M., Cisar, J.L., Williams, K.E., Snyder, G.H., 2004. ALLEVIATION OF SOIL WATER REPELLENCY IN SAND BASED BERMUDAGRASS IN SOUTH FLORIDA. *Acta Horticulture*. 661, 111–115.
- Parr, J.F., Norman, a G., 1964. Effects of Nonionic Surfactants on Root Growth and Cation Uptake. *Plant physiology*. 39, 502–7.
- Penman, H.L., 1941. Laboratory experiments on evaporation from fallow soil. *The Journal of Agricultural Science*. 31, 454–465.
- Read, D., Gregory, P., 2008. Surface tension and viscosity of axenic maize and lupin root mucilages. *New phytologist*. 137, 623–628.
- Read, D.B., Bengough, a. G., Gregory, P.J., Crawford, J.W., Robinson, D., Scrimgeour, C.M., Young, I.M., Zhang, K., Zhang, X., 2003. Plant roots release phospholipid surfactants that modify the physical and chemical properties of soil. *New Phytologist*. 157, 315–326.
- Ritsema, C.J., Dekker, L.W., 1996. Water repellency and its role in forming preferred flow paths in soils. *Australian Journal of Soil Research*. 34, 475–487.
- Rodríguez-Cruz, M.S., Sanchez-Martin, M.J., Sanchez-Camazano, M., 2005. A comparative study of adsorption of an anionic and a non-ionic surfactant by soils based on physicochemical and mineralogical properties of soils. *Chemosphere*. 61, 56–64.

- Rosegrant, M.W., Ringler, C., Zhu, T., 2009. Water for Agriculture : Maintaining Food Security under Growing Scarcity. *The Annual Review of Environment and Resources*. 34, 205–222.
- Rosen, M.J., 2004. *Surfactants and Interfacial Phenomena*, Third. John Wiley and Sons Inc., pp. 1–4.
- Scamehorn, J., Schechter, R., Wade, W., 1982. Adsorption of surfactants on mineral oxide surfaces from aqueous solutions III. Binary mixtures of anionic and nonionic surfactants. *Journal of Colloid and Interface Science*. 85, 494–501.
- Shafran, A.W., Gross, A., Ronen, Z., Weisbrod, N., Adar, E., 2003. Effects of Surfactants Originating from Reuse of Greywater on Capillary Rise in the Soil.
- Sharma, N., Tripathi, A., 2006. Fungitoxicity of the essential oil of *Citrus sinensis* on post-harvest pathogens. *World Journal of Microbiology and Biotechnology*. 22, 587–593.
- Shaw, P.E., Coleman, R.L., 1974. Quantitative composition of cold-pressed orange oils. *Journal of Agricultural and Food Chemistry*. 22, 785–787.
- Sinclair, T.R., Tanner, C.B., Bennett, J.M., 1984. Water-Use Efficiency Crop Production. *Bioscience*. 34, 36–40.
- Skopp, J.M., 2002. Further uses for bulk density, in: Warrick, A.W. (Ed.), *Soil Physics Companion*. CRC Press, New York, pp. 14–15.
- Smolander, A., Ketola, R.A., Kotiaho, T., Kanerva, S., Suominen, K., Kitunen, V., 2006. Volatile monoterpenes in soil atmosphere under birch and conifers: Effects on soil N transformations. *Soil Biology and Biochemistry*. 38, 3436–3442.
- Soldat, D.J., Lowery, B., Kussow, W.R., 2010. Surfactants Increase Uniformity of Soil Water Content and Reduce Water Repellency on Sand-Based Golf Putting Greens. *Soil Science*. 175, 111–117.
- Subba, M.S., Soumithri, T.C., Rao, R.S., 1967. Antimicrobial Action of Citrus Oils. *Journal of Food Science*. 32, 225–227.
- Sutherland, R.A., Ziegler, A.D., 1998. The influence of the soil conditioner “ Agri-SC ” on splash detachment and aggregate stability.
- Széles, A.V., Megyes, A., Nagy, J., 2012. Irrigation and nitrogen effects on the leaf chlorophyll content and grain yield of maize in different crop years. *Agricultural Water Management*. Elsevier B.V. 107, 133–144.
- Tillman, D.R., Scotter, M.G., Wallis, M.G., Clothier, B.E., 1989. Water-repellency and its measurement by using intrinsic sorptivity. *Australian Journal of Soil Research*. 27, 637–644.

- Traore, O., Groleau-Renaud, V., Plantureux, S., Tubeileh, A., Bêuf-Tremblay, V., 2000. Effect of root mucilage and modelled root exudates on soil structure. *European Journal of Soil Science*. 51, 575.
- Tschapek, M., Boggio, L., 1981. Surfactants and soil water evaporation and migration. 144, 112–120.
- Ussawarujikulchai, A., Laha, S., Tansel, B., 2008. Synergistic Effects of Organic Contaminants and Soil Organic Matter on the Soil-Water Partitioning and Effectiveness of a Nonionic Surfactant (Triton X-100). *Bioremediation Journal*. 12, 88–97.
- Uys, D.C., 2011. Personal communication.
- Van den Honert, T.H., 1948. Water transport in plants as a catenary process. *Discussions of the Faraday Society*. The Royal Society of Chemistry. 3, 146–153.
- Van Roon, A., Parsons, J.R., Krap, L., Govers, H. a J., 2005a. Fate and transport of monoterpenes through soils. Part II: calculation of the effect of soil temperature, water saturation and organic carbon content. *Chemosphere*. 61, 129–38.
- Van Roon, A., Parsons, J.R., Te Kloeze, A.-M., Govers, H.A.J., 2005b. Fate and transport of monoterpenes through soils. Part I. Prediction of temperature dependent soil fate model input-parameters. *Chemosphere*. 61, 599–609.
- Visser, J., Verhoog, S. -a., 2007. Water management and planning in a semi-arid country: the South African situation. *Sustainable Development and Planning III*. WIT Press, Southampton, UK. II, 913–920.
- Wallace, J.S., 2000. Increasing agricultural water use efficiency to meet future food production. *Agriculture, Ecosystems and Environment*. 82, 105–119.
- Wang, H., Liu, C., Zhang, L., 2002. Water-saving Agriculture in China: An Overview. *Advances in Agronomy*. 75, 135–171.
- White, C., 1994. Monoterpenes: Their effects on ecosystem nutrient cycling. *Journal of Chemical Ecology*. Kluwer Academic Publishers-Plenum Publishers. 20, 1381–1406 LA – English.
- White, C.S., 1991. The Role of Monoterpenes in Soil Nitrogen Cycling Processes in Ponderosa Pine : Results from Laboratory Bioassays and Field Studies. *Biogeochemistry*. 12, 43–68.
- Xu, Q., Vasudevan, T., Somasundaran, P., 1991. Adsorption of anionic—nonionic and cationic—nonionic surfactant mixtures on kaolinite. *Journal of Colloid and Interface Science*. 142, 528–534.
- Yang, X., 2008. Effect of nonionic surfactant on plant growth and physiology. Ph. D Thesis. Auburn University, Alabama, pp. 34–87.

Zartman, R.E., Bartsch, R.A., 1990. Using Surfactants to enhance Drainage from a Dewatered column. *Soil Science*. 149, 52–55.

Zunino, M., Zygadlo, J., 2004. Effect of monoterpenes on lipid oxidation in maize. *Planta*. Springer-Verlag. 219, 303–309.

Zunino, M.P., Zygadlo, J. a., 2005. Changes in the Composition of Phospholipid Fatty Acids and Sterols of Maize Root in Response to Monoterpenes. *Journal of Chemical Ecology*. 31, 1269–1283.