Universität für Bodenkultur Wien
University of Natural Resources and Applied Life Sciences, Vienna

Department für Wasser-Atmosphäre-Umwelt
Institut für Siedlungswasserbau, Industriewasserwirtschaft und Gewässerschutz

Univ. Prof. DI Dr. Raimund Haberl

RELATIONSHIP BETWEEN HYDROPHOBICITY AND DISSOLVED ORGANIC CARBON IN NEW ZEALAND SOILS

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Handed in by:

HOLZINGER, URSULA

Supervisor: Dr. Andreas Klik, PhD

Co-Supervisor: Dr. Ranvir Singh, PhD

Student ID Number: 0248613

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Preface

The Master Thesis was conducted in the Department of Water, Atmosphere and Environment in the Institute of Hydraulics and Rural Management by the supervision of Andreas Klik of the University of Natural Resources and Applied Life Science in Austria and Ranvir Singh of the Soil Science Department of Massey University in New Zealand. My gratitude goes to all the people that provided support and help in the Department of Soil Science of Massey University, especially to Mike Bretherton, who helped me out with all the lab work and questions and Ranvir Singh who I could always turn to for issues concerning this paper. My thanks also goes to all the other wonderful people and friends that I have met during my stay overseas, making my life there amazing, and also my friends and family at home who provided support from the distance.

Table of Contents

1. Introduction ___ ***1***

2. Hydrophobicity ___ ***2***

2.1 What is Hydrophobicity ___ 2

2.2 State of the Art ___ 4

2.3 Hydrophobicity and its impacts in New Zealand ___ 7

2.3.1 Erosion ___ 8

2.3.2 Loss of Production ___ 9

2.3.3 Contamination of Rivers and Waterways ___ 10

2.4 Remediation of Soil Water Repellence ___ 10

2.5 Research Objectives ___ 11

3. Materials and Methods ___ ***13***

3.1 Geography and Soils of New Zealand ___ 13

3.1.1 Taranaki/Mt Egmont ___ 14

3.1.2 Soil Sampling ___ 14

3.2 Soils and Climate ___ 15

3.2.1 Organic Soil ___ 17

3.2.2 Gley Soil ___ 18

3.2.3 Brown Soil ___ 20

3.3 Soil Properties ___ 21

3.4 Water Droplet Penetration Time (WDPT) and Molarities of Ethanol Droplet (MED) Test 23

3.5 Organic Carbon Analyzer ___ 25

3.6 Soil sampling for field experiment ___ 25

3.7 Lab Experiment ___ 26

3.7.1 Trial Experiment ___ 26

3.7.2 Main Experiments – Hot and cold water washing treatments ___ 29

3.8 Statistical Data Analysis ___ 31

4. Results and discussion ___ ***33***

4.1 Soil Property Results (Appendix A) ___ 33

4.2 Trial Procedure (Appendix B) ___ 35

4.3 Field Experiments ___ 36

4.4 Results of Contact Angels and Water Droplet Penetration Time Test of Lab Experiments (Appendix D) ___ 41

4.5 Results of ANOVA Test for MED (Appendix E) ___ 44

4.5.1 Gley Soil ANOVA Results ___ 45

4.5.2 Organic Soil ANOVA Results ___ 46

4.5.3 Brown Soil ANOVA Results 48
4.6 Results of WDPT & CA vs DOC increase 50
4.6.1 Gley Soil WDPT & CA vs DOC Results 50
4.6.2 Organic Soil WDPT & CA vs DOC Results 52
4.6.3 Brown Soil WDPT & CA vs DOC Results 54
4.6.4 Combined results (hot&cold) of WDPT & CA vs DOC 57
5. Analysis of results 60
5.1 Field Experiment 60
5.2 Lab Experiment 60
5.3 Problems and Improvements for procedure 63
6. Conclusion 65
7. Bibliography 66
Appendix A - Soil Property Calculations 69
Appendix B - Trial Procedure 72
Appendix C - Field Experiments 74
Appendix D - Lab Experiment: WDPT & MED Test 83
Appendix E - Anova Results of MED 94
Appendix F - Change of WDPT & CA vs DOC increase 106

List of Figures

Figure 1 Schematic representation of the various degrees of hydrophobicity and the corresponding soil surface tensions. Θ=Contact Angle. 2
Figure 2 Potential sources causing hydrphobicity (Swansea, 2009) 4
Figure 3 Duration of soil water repellency in a soil with critical water thresholds (CWT) (Deurer et al, 2010)........ 6
Figure 4 Landforms of Taranaki (Council, 2004) 14
Figure 5 Location of soils used for this study: Red: Gley Soils; Purple: Organic Soils; Yellow: Brown Soils (Google Earth) 15
Figure 6 The formation of New Zealand's soils (Landcare, 2011) 16
Figure 7 Open Climate Stations NZ (NIWA)........ 16
Figure 8 Contact Angles of various soil types in New Zealand (Deurer et al, 2011) 17
Figure 9 Organic Soil Column (Landcare, 2011) 17
Figure 10 Humic Organic Soil (Landcare, 2011) 18
Figure 11 Organic Soil Sample Site (-39.39691, 174.37831; Slope: Flat) (Google) left: satellite picture (google maps) middle: hypsometric layer; right: photo of site........ 18
Figure 12 Gley Soil Column........ 19
Figure 13 Position of Recent Gley (Landcare, 2011) 19
Figure 14 Gley Soil Sampling Site (-39.32376, 174.41890) (Google) left: satellite picture; middle: hypsometric layer; right: photo of site........ 20
Figure 15 Brown Soil Column (Landcare, 2011) 20
Figure 16 Distribution of Orthic Brown Soil in NZ (Landcare, 2011) 20
Figure 17 Brown Soil Sample Site (-39.41775, 174.44301) (Google), left: satellite picture; middle: hypsometric layer; right: photo of site........ 21
Figure 18 Experiment setup for WDPT & MED in laboratory........ 23
Figure 19 WDPT Five water droplets on brown soil........ 23
Figure 20 Soil cylinder for sampling 25
Figure 21 Diagram of the Lab Experiment........ 28
Figure 22 ANOVA: Field Experiment Organic Soil 37
Figure 23 ANOVA: Field Experiment Gley Soil........ 38
Figure 24 ANOVA: Field Experiment Brow Soil 39
Figure 25 Average Gley Soil Leaching Hot & Cold Water 42
Figure 26 Average Organic Soil Leaching Hot & Cold Water........ 42
Figure 27 Average Brown Soil Leaching Hot & Cold Water........ 43
Figure 28 Correlation between MED & WDPT 44
Figure 29 ANOVA: Cold water treatment Gley Soil - CA vs Treatments........ 45
Figure 30 ANOVA: Hot water treatment Gley Soil - CA vs Treatments........ 45
Figure 31 ANOVA: Cold water treatment Organic Soil - CA vs Treatments 46
Figure 32 ANOVA: Hot water treatment Organic Soil - CA vs Treatments........ 47
Figure 33 ANOVA: Cold water treatment Brown Soil - CA vs Treatments 48
Figure 34 ANOVA: Hot water treatment Brown Soil - CA vs Treatments........ 49
Figure 35 Gley Soil cold water leaching: Decrease of WDPT&CA as DOC increases........ 51
Figure 36 Gley Soil hot water leaching: Decrease of WDPT&CA as DOC increases 52
Figure 37 Organic Soil cold water leaching: Decrease of WDPT&CA as DOC increases........ 53
Figure 38 Organic Soil hot water leaching: Decrease of WDPT&CA as DOC increases........ 54
Figure 39 Brown Soil cold water leaching: Decrease of WDPT&CA as DOC increases........ 55

Figure 40 Brown Soil hot water leaching: Decrease of WDPT&CA as DOC increases 56
Figure 41 BROWN SOIL: hot and cold water treatment - DOC vs WDPT vs CA.. 58
Figure 42 ORGANIC SOIL: hot and cold water treatment - DOC vs WDPT vs CA 59

List of Tables

Table 1 Overview of amount of soil replicates used per experiment 30
Table 2 General Soil Properties 33
Table 3 Change of Molarity of Ethanol used to infiltrate into the soil within 10sec 35
Table 4 ANOVA - Tukey Kramer Test: Field Experiment Organic Soil.. 37
Table 5 ANOVA - Tukey Kramer Test: Field Experiments Gley Soil 38
Table 6 Average Carbon Contents of Soils 39
Table 7 Precipitation Data Organic Soil... 40
Table 8 Precipitation Data Gley Soil 40
Table 9 Precipitation Data Brown Soil... 40
Table 10 ANOVA - Tukey Kramer Test: Cold Water Treatment Organic Soil 47
Table 11 ANOVA: Tukey Kramer Test - Hot Water Treatment Organic Soil... 48
Table 12 ANOVA: Tukey Kramer Test- Cold Water Treatment Brown Soil 49
Table 13 ANOVA: Tukey Kramer Test - Hot Water Treatment Brown Soil... 50
Table 14 GLEY SOIL cold water leaching: DOC vs WDPT vs CA... 51
Table 15 GLEY SOIL hot water leaching: DOC vs WDPT vs CA 52
Table 16 ORGANIC SOIL cold water leaching: DOC vs WDPT vs CA 53
Table 17 ORGANIC SOIL hot water leaching: DOC vs WDPT vs CA.. 54
Table 18 BROWN SOIL cold water leaching: DOC vs WDPT vs CA... 55
Table 19 BROWN SOIL hot water leaching: DOC vs WDPT vs CA 56
Table 20 BROWN SOIL: hot and cold water treatment - DOC vs WDPT vs CA 57
Table 21 ORGANIC SOIL: hot and cold water treatment - DOC vs WDPT vs CA....................................... 58
Table 22: Results of the pH analysis 69
Table 23 Water Content before winter 2011 69
Table 24 Water Contents after winter 2011 70
Table 25 Bulk Density of Soils.. 71
Table 26 Particle Density of soils.. 71
Table 27 Porosity and Pore Volume of Soils.. 71
Table 28 Trial Procedure in Laboratory, Results of DOC leached out 72
Table 29 Contact Angle Calculations before treatment (trial procedure) 73
Table 30 Contact Angle Calculations after hot water and lime application (trial procedure) 73
Table 31 Results of Field Experiment WDPT & MED 74
Table 32 Carbon Contents in initial Soils... 76
Table 33 ANOVA: Field Experiment- Raw Data - Organic Soil 77
Table 34 ANOVA: Results - Field Experiments Organic Soil 78
Table 35 ANOVA: Field Experiment- Raw Data - Gley Soil 79
Table 36 ANOVA: Results - Field Experiments Gley Soil... 80
Table 37 ANOVA: Field Experiment- Raw Data - Brown Soil 81
Table 38 ANOVA: Results - Field Experiments Brown Soil 82
Table 39 Gley Soil: Calculation of Contact Angles 84
Table 40 Organic Soil: Calculation of Contact Angles.. 85
Table 41 Brown Soil: Calculation of Contact Angles.. 86

Table 42 All results of WDPT and MED 87
Table 43 ANOVA: Raw Data - Cold Water Treatment Organic Soil 94
Table 44 ANOVA: Results - Cold Water Treatment Organic Soil 94
Table 45 ANOVA: Raw Data - Hot Water Treatment Organic Soil.. 96
Table 46 ANOVA: Results - Hot Water Treatment Organic Soil 97
Table 47 ANOVA: Raw Data - Cold Water Treatment Gley Soil.. 98
Table 48 ANOVA: Results - Cold Water Treatment Gley Soil 99
Table 49 ANOVA: Raw Data - Hot Water Treatment Gley Soil.. 100
Table 50 ANOVA: Results - Hot Water Treatment Gley Soil.. 101
Table 51 ANOVA: Raw Data - Cold Water Treatment Brown Soil 102
Table 52 ANOVA: Results - Cold Water Treatment Brown Soil... 103
Table 53 ANOVA: Raw Data - Hot Water Treatment Brown Soil 104
Table 54 ANOVA: Results - Hot Water Treatment Brown Soil 105
Table 55 All Soils: WDPT vs CA vs DOC.. 106

Abstract (English)

This diploma thesis was written within the course of a study at Massey University in Palmerston North, New Zealand, focusing on the increasing problem of hydrophobicity of soils in New Zealand pastures. Hydrophobicity has been a recognized problem by specialists for a long time; however, farmers are only recently becoming aware of its negative effects on the economy and the environment. Various studies led to the hypothesis that organic carbon compounds are the main reason for hydrophobicity. This thesis focused on the role of dissolved organic carbon (DOC).

Three different soil types in the North Island of New Zealand were examined by applying different amounts of hot and cold water and analysing the leachate for DOC. The persistence and degree of hydrophobicity were found by using the Water Droplet Penetration Time Test and the Molarity of Ethanol Droplet Test. The three soils used were gley soils, brown soils and organic soils. Only brown soils showed a significant exponential decrease in hydrophobicity as the dissolved organic carbon was leached out. The greatest difference was found between no application and the application of 400ml water. Hydrophobicity of gley soils was found to have no correlation with the leaching out of dissolved organic carbon. Organic soils had a changing hydrophobicity, however there was no clear pattern. It was further found that more dissolved organic carbon leached out using hot water in all three types of soils. Contrary to expectations, none of these applications turn the hydrophobic soils into hydrophilic soils.

Abstract (German)

Diese Arbeit war Teil einer Studie der Massey Universität in Palmerston North, Neuseeland, die sich schon seit Jahren mit den wachsenden Problemen von hydrophoben Böden im Neuseeländischen Weideland beschäftigt. Wasserabweisung (oder Hydrophobie) ist schon seit längerer Zeit ein anerkanntes Problem unter Spezialisten. Bauern hingegen fangen erst seit Kurzem an die negativen Auswirkungen auf die Landwirtschaft, im wirtschaftlichen und ökologischen Sinne, zu realisieren. In mehreren Studien wurden bereits Hypothesen aufgestellt, die besagen, dass organische Komponenten der Hauptgrund für Wasserabweisung in Böden sind. Diese Diplomarbeit konzentriert sich auf die Rolle von gelöstem organischem Kohlenstoff (DOC) auf hydrophobe Böden.

Es wurden drei verschiedene Bodenarten auf der Nordinsel in Neuseeland mit verschiedenen Mengen von kaltem und heißem Wasser behandelt und das DOC im Eluat analysiert. Dann wurde die Persistenz und der Grad der Hydrophobie untersucht, indem der „Water Droplet Penetration Time Test“ und der „Molarity of Ethanol Droplet Test“ angewandt wurden. Drei unterschiedliche Bodentypen wurden verwendet: Gley, Braunerde und Histosol. Die Versuche zeigten, dass nur Braunerde eine signifikante exponentielle Abnahme der Bodenhydrophobie aufwies, je mehr DOC herausfiltriert wurde. Die größte Veränderung ergab sich zwischen keiner Bodenbehandlung und einer Wasseranwendung von 400ml. Es wurde kein eindeutiger Zusammenhang zwischen Hydrophobie von Gley und dem gelösten organischen Kohlenstoff im Eluat gefunden. Die Wasserabweisung von Histosols änderte sich nur geringfügig/ nicht signifikant. Außerdem wurde festgestellt, dass sich mehr DOC im Eluat befand, wenn heißes Wasser verwendet wurde. Dies galt für alle drei Bodentypen. Im Gegensatz zu den Erwartungen wandelten keine der Anwendungen aus den Laborversuchen hydrophobe in hydrophile Böden um.

1. Introduction

The main purpose of this paper is to analyze the change of hydrophobicity of three different soil types in the North Island of New Zealand. This was done by finding a relationship between the amount of dissolved organic carbon (DOC) in the leachates that resulted from water application on the soil, and the water repellency in the soil by using the Water Droplet Penetration Time Test and the Molarity of Ethanol Droplet Test. The hypothesis was, that the more DOC leaches out of the soil, the less hydrophobic the soil becomes. Mitigating hydrophobic soils by using a "natural method" of irrigation could become handy where there is plenty of water to spare and where chemicals that can contaminate the water courses, need to be avoided. In a country such as New Zealand, where 55% of the land is used for agricultural production, the reduction of plant growth due to hydrophobic soils becomes a major issue for the economy, and therefore needs to be taken seriously.

As it has been observed in earlier studies, during prolonged wet periods hydrophobicity tends to disappear and after the soil dries out again over a period of time, it reappears (Doerr, 2007). This phenomenon encouraged the present research, which shows by means of experiments, the change in hydrophobicity depending on the availability of water in the soil and the decrease of DOC within the soils. In this thesis the dissolved organic carbon which, due to its size and charge, is believed to be the hydrophobic carbon compounds that surround the soil particles occupying the diffuse layer, making the soil hydrophobic, will be analyzed.

The following study is based on experiments performed from July to September 2011 at the Institute of Natural Resources of Massey University in New Zealand, using brown, organic and gley soils from the North Island of New Zealand in the area around Taranaki Mountain.

2. Hydrophobicity

2.1 What is Hydrophobicity

Hydrophobicity, also known as soil water repellency (SWR), is a phenomenon that occurs when the soil does not wet up spontaneously. It is said to have its origin in the drying of soil below its critical water content. Once the soil is provided with water again, however, the hydrophobicity sometimes reverses and the soil can become hydrophilic again (Mueller et al). Most soils have the ingredients to become hydrophobic, as chemical analysis have shown that hydrophobic and wettable soils both contain organic compounds that could form hydrophobic coatings (Doerr, 2007). Molecules with hydrophobic properties can be found everywhere in the environment. For example, plants produce these hydrophobic compounds which are relatively resistant to physical and chemical degradation, in order to protect the leaf surface from desiccation, and to repel insects and microbes. Therefore, they are relatively common in vegetated soils and are believed to cause water repellency (Doerr, 2000; (Doerr et al, 2009)). SWR occurs in all kinds of soil textures in over 50 countries worldwide and in a wide variety of climatic conditions ranging from tropical to subtropical (Mueller & Deurer, 2011).

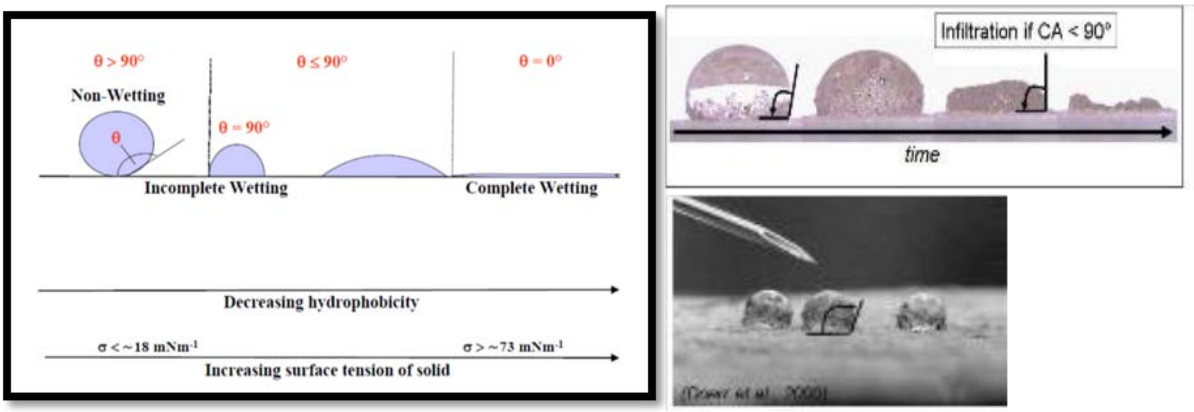

Figure 1 Schematic representation of the various degrees of hydrophobicity and the corresponding soil surface tensions. Θ=Contact Angle.

Calling soils that resist wetting water repellent is, according to Roy and McGill (2002), not completely accurate, as they are not actually water repellent, but attract water too weakly due to their low-energy surfaces. However, as in the textile and coating industry, the term “water repellent” is commonly used and as it give a clear picture, the term is also used to describe hydrophobic soils. Usually in dry and fine-textured soils the forces that act on water in a hydrophilic soil are capillary forces, whereas in coarse textured and wet soils, the forces dominating the water infiltration result from gravity. Soil hydrophobicity abolishes these capillary forces that would take up water or any other substance into the soil particle, creating a layer around the soil particle that prevents any contact with the soil. This in turn impairs the physical filtering process of the soil (Aslam et al., 2009). Coarse textured soils are more susceptible to developing SWR as they have a much smaller particle surface area than finer textured soils. Thus the number of potential adsorption sites for organic molecules is reduced (Doerr et al., 2009). Under certain conditions, all soils may show some signs of water repellency, but usually it only becomes a critical issue once it interferes with plant growth and hence in the case of New Zealand, reduces the grazing areas for the livestock (Roy & McGill, 2002).

In hydrophilic soils the rate of infiltration is only limited to the texture and structure of the soil, whereas in hydrophobic soils the texture does not seem to be a determining factor. Sorptivity, which is the soils ability to take up water, and capillary rise, are not present in an extreme water repellent soil. As a result, infiltration rates are reduced and overland flow is promoted (Deurer & Bachmann, 2007). Water drops pending on the soil often evaporate before they can infiltrate (Hallett, 2007). A certain ponding height of water is required to allow the water to start infiltrating into the hydrophobic soil. However, even then the water would take a preferential path towards the pores with greater diameter produced by animal activity or root channels. Preferential flow, however, does not permit the wetting of the entire soil particle surfaces and would not wash out all the hydrophobic substances covering the particles (Deurer & Mueller, 2010).

It is not yet certain what exactly causes a perfectly sound soil to suddenly become hydrophobic, as this phenomenon occurs in all types of soils. In some areas wildfires, which can vaporize and alter organic material have been found to be the initiation of water repellency, in other cases it was the introduction of certain plant species that release organic material rich in lipids such as surface waxes of plant leaves and fungal hyphae that have introduced hydrophobicity into a soil. Nevertheless, the effects this has on the surface of the soil are countless; inhibited plant growth, increased overland flow, soil erosion, uneven spatial and vertical wetting patterns, reduced evaporation and enhanced risk of water pollution (groundwater as well as river) are only a few examples of the impacts hydrophobicity has on the environment (Swansea, 2009).

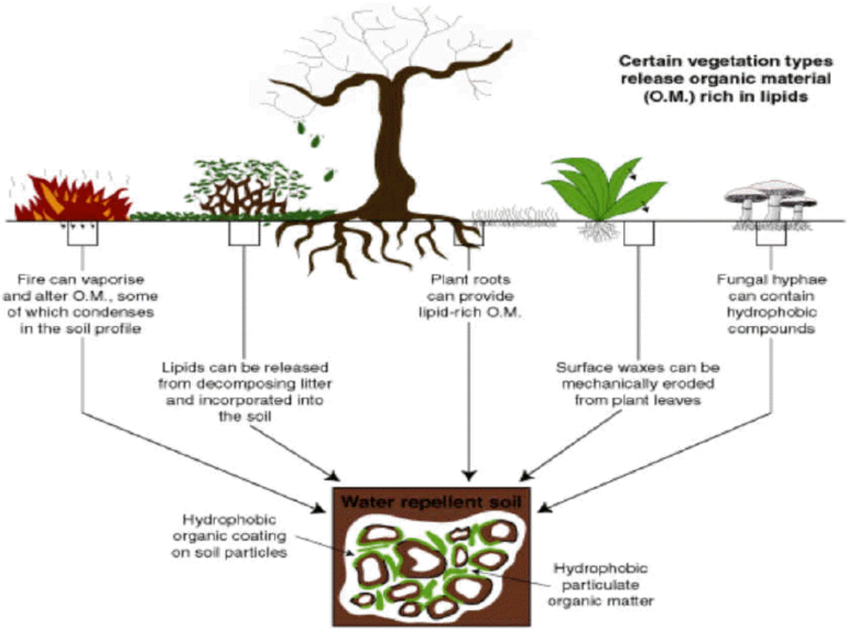

Figure 2 Potential sources causing hydrphobicity (Swansea, 2009)

2.2 State of the Art

Soil water repellency (SWR) is a result of an “accumulation of hydrophobic organic substances relative to the soil’s specific surface area” (Mueller & Deurer, 2011). It is thought to be caused primarily by a coating of long-chained hydrophobic organic molecules on individual soil particles (Swansea, 2009).

Since the 1950s, research on amelioration of soil water repellency has mainly been driven by the golf course industry (Mueller & Deurer, 2011). Studies to determine whether SWR and soil organic matter have any correlation, were conducted in the past but have not shown any obvious results. According to past researches, SWR has to do with the composition and nature of the outmost organic layer of organic matter. These components surrounding the soil particles are believed to be the reason for impeding the soil to take up water, forming a water repellent layer.

Soil hydrophobicity is not necessarily dependent on the amount of organic matter, but rather the hydrophobic material in the soil, which was found to cause non-wetting problems at as little as 3-6% of the soil matrix (Slay, 2007). Studies in Australia have found soils with exceptionally low organic matter content to have some of the highest levels of SWR worldwide. Therefore the degree of hydrophobicity is not necessarily proportionate to the total amount of organic material (Slay, 2007). Water repellency results from hydrophilic ‘ends’ of molecules to be oriented towards the pore space of the soil (Doerr et al., 2009). Aliphatic hydrocarbons, including insoluble, non-polar carbon chains and amphiphilic polar substances that have a hydrophilic end are these compounds believed to be responsible for water repellent soils. These organic compounds are derived from living or decomposing organisms (Hardie et al., 2011).

There are many suggestions for what might be the origin of these hydrophobic substances in the soil. Vegetation might be one of the causes, as certain plant or grass species have appeared to promote soil water repellency, possible due to plant-microbial community associations (Deurer & Mueller, 2010). Evergreen tree types, mainly those with resins, waxes or aromatic oils are the plants that are usually associated with soil hydrophobicity. Root exudates might be a source for hydrophobic organic acids due to their allelopathic functions. Long term contribution of woody underground rhizomes associated with grasses such as agrostis spp., poa pratensis etc. along with poor microbial activity could also have contributed to SWR in hill country of permanent pasture (Slay, 2007). In general, microbial organisms themselves, even when microbial activity is high, can also cause SWR as they decompose organic litter which can result in hydrophobic substances.

The land use activity is another aspect that affects hydrophobicity, as according to a study of Aslam et al. (2009) the contact angles, which represent the degree of hydrophobicity, are higher on lands that sheep use as campsite to rest the whole night, compared to the ones that they only use for daytime pasture. This is probably due to the compaction of the soil, when a lot of weight by the animal is placed on one spot for a long time, reducing the pore sizes for water infiltration and hence hindering the rearrangements of the hydrophobic substances.

Fires are also found to be a source for hydrophobic substances, since they can cause the volatilization of hydrophobic organic substances in the litter and topsoil. Some of these compounds are then being driven upwards into the atmosphere whereas others condense onto soil particles in cooler layers at or below soil surface where they settle in a higher concentration (DeBano et al., 1976; (Doerr et al, 2009)). Very hot fires, on the other hand, can destroy these organic compounds and make soils wettable again (Doerr et al, 2009). As many pastures in New Zealand have been created by burning down the native bush, this source of hydrophobicity should also be considered, however, this aspect has not yet been studied in detail (Deurer & Mueller, 2010). Wild fires that occurred in California, Australia and Portugal have been found to induce hydrophobicity and hence it has become a recognized finding in the 1960's and 70's that heat changes and intensifies SWR. Hydrophobicity increases at heating temperatures of 50-150°C and it is believed that at these temperatures the bond of hydrophobic substances to the soil particles improves. On the contrary, at temperatures higher than 250-300°C, hydrophobicity is destroyed or moved deeper into the soil (Slay, 2007). A different study showed the increase of hydrophobicity at temperatures of 175-270°C and combustion of hydrophobic compounds at temperatures 270-400°C, going as high as 500-600°C, if there is insufficient oxygen. The duration of the heating process also affects the degree of hydrophobicity (Doerr et al., 2009).

According to laboratory studies, heating at low temperatures of 40°C as opposed to 60°C increases the WDPT by a factor of 6 (Hardie et al, 2011), which is believed to be a key factor for the increasing hydrophobicity in summer, as the pastures exposed to direct sunlight (usually the north side of the hills) can easily reach these temperatures (Slay, 2007). During a study in Australia it was found that the persistence of SWR actually increased from summer to winter due to an accumulation of hydrophobic substances such as hydrophobic waxes that probably resulted from increased biological processes due to an increase in temperature and minimal leaching (Hardie et al., 2011).

Possible major culprits in the formation of water repellent soil are fungi that produce large quantities of hydrophobic material in order to protect themselves against desiccation and stress. Bacidiomycete are common fungi that decompose litter, especially lignin, in soils. As they move through the soil they leave waxy mycelium making the soil water repellent. Another possible source of SWR is pasture pests, such as the mealybug, which is wide spread in Hawke's Bay region in New Zealand. They produce wax-like substances that cover the soil aggregates and may impede infiltration (Slay, 2007).

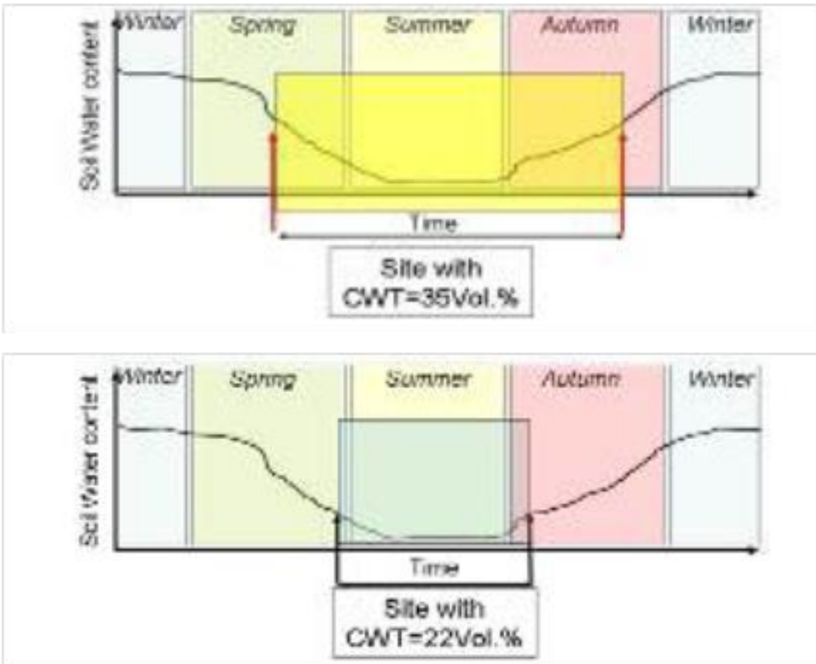

Figure 3 Duration of soil water repellency in a soil with critical water thresholds (CWT) (Deurer et al, 2010)

Various studies have found that once the water content falls below a certain threshold; in medium textured soils this is reached when water occupies 20-30 percent of the total soil volume; soils can switch rapidly from hydrophilic to hydrophobic (Doerr et al, 2007). Figure 3 shows the effect of certain critical water contents to the duration of hydrophobicity in a soil (Deurer et al, 2010). In a different study the maximum contact angle was calculated at the permanent wilting point and as the soil rewets, the CA decreases and reaches a minimum at water content close to field capacity (Deurer & Bachmann, 2007). However, even though soil moisture was found to be correlated to soil water repellency, it cannot be considered as the only factor influencing the rapid change of wettability, as there are always other temporally variable factors such as root and microbial activity that play along with it (Doerr et al, 2007). Water repellency occurs from a few days to a few weeks after constant dry periods of no precipitation depending on the land use and on which kind of studies were done. When looking at the study on modeling water movement in water repellent soil, it took 3 weeks of intensive evaporation for a soil at field capacity to become water repellent (Deurer & Bachmann, 2007). In a study in Portugal with soils of sandy texture and Eucalyptus plantations the amount of time taken for the soil to become water repellent was significantly higher, with three to up to nine weeks of dry weather (Deurer & Bachmann, 2007). In another study, the time taken for water repellency to set in was only 6-9 days (Deurer & Bachmann, 2007).

As for dissolved organic carbon (DOC), various studies have been performed to find a relationship between DOC and water repellency. In a study done in 2004, repeated wetting and drying cycles caused hydrophobicity to increase, due to higher DOC concentration on the surface soils. Here the quality rather than the quantity correlates with water repellency. This was confirmed in a study in 2009, when it was found that hydrophobic acid DOC is the reason for increasing hydrophobicity, not the total DOC. However, again in another study, it was found that when adding DOC to hydrophobic sand, the repellency decreased rather than increased (Hardie et al, 2011). To find conclusions for these uncertainties, it is important to perform further studies on the relationship between DOC and water repellency. Most of the dissolved organic carbon is made up of fulvic and humic acids, which are humic substances, organic materials that is most resistant to microbial attack. As they are relatively stable in soils, they are considered for the present thesis to be the main factor of hydrophobicity in the soils (Brady & Weil, 2002).

Soil pH, bulk density and soil water content might also be factor for the degree of hydrophobicity. Some previous studies have suggested that these physical soil properties are of significance to a certain extent, and should not be neglected when analyzing soils for water repellency.

2.3 Hydrophobicity and its impacts in New Zealand

For up to 100 years, hill country in New Zealand has been under predominantly permanent pasture and subject to low management inputs compared to the lowlands, which made gradual build up of hydrophobic material possible (Slay, 2007). Hydrophobicity was first recognized as a problem in New Zealand in 1959 by van't Woudt, whereas in 1990s workers were finding it to be a norm, rather than an exception for many soils (Ibid.). The main problem with hydrophobic soils is, however, that according to J. Morgan (2007), it is a transient phenomenon that is quickly forgotten once the pastures regain their green colour (Deurer & Mueller, 2010).

In a survey recently done by Deurer et al. (2011) in the North Island of New Zealand, ten dominant soil orders of New Zealand's classification scheme were used for SWR analysis. The five remaining ones were omitted as they do not occur in the North Island or they are associated with high mountains, braided rivers, beaches or tidal estuaries and only cover 1% of New Zealand. All of these soils showed moderate to high potential persistence of SWR after they were dried and analyzed (Ibid.). Hawke's Bay, a region where farm gate returns from the sheep and beef sector alone contribute to 15% of the regional GDP, is situated in the East Coast of the North Island. This region, which is dominated by agricultural production, has been studied in detail, and was found to have GDP reduction from 2007 to 2009 by about NZ$ 1 billion due to drought and prolonged dry conditions into autumn (Deurer & Mueller, 2010).

Threatening key ecosystem services of soils such as plant growth for food production, water retention, quick infiltration to avoid flooding and erosion, and filtering of agrichemicals to provide clean drinking water (Mueller & Deurer, 2011), hydrophobicity is becoming a bigger issue the more research is done and the more people become aware of it. When soils develop hydrophobicity; flooding and erosion; loss of fertility in the soil due to enhanced nutrient and agricultural chemical transfer into the groundwater; and reduction of plant growth, are some of the negative impacts concerning the environment (Doerr, 2007).

Soil water repellency, however, when looking at it from a positive perspective, can sustain the stability of aggregates, sequester organic carbon, reduce the loss of soil water by evaporation and provide water for deeper rooted plants. Greater pore channels can create preferential flow, which allows the water to pass through the shallow rooted plants directly into the deep root zone, to provide water for plants that would have not have been reached by water otherwise (Mueller & Deurer, 2011). For example, splash erosion rates were reduced due to repellence as the aggregate stability was increased, and slaking was reduced (Doerr et al, 2007).

2.3.1 Erosion

The main hydrologic and erosion effects of hydrophobicity include lower infiltration rates and along with it an increased overland flow, higher susceptibility to wind erosion as soils are dryer, more surface erosion due to the overland flow and greater spatial variability in infiltration and soil moisture fluxes, causing an uneven distribution of soil moisture (Doerr et al., 2009). When the rate of rainfall exceeds the rate of infiltration, water accumulates on the surface of the soil and puddles are formed on surface depression. Once these puddles overflow, surface run-off starts. The rate of surface runoff depends on the degree of soil water repellency (Deurer & Mueller, 2010).

Erosion processes are more pronounced under burnt forestlands than for permanently vegetated areas. This is due to the loss of interception and storage in the vegetation and litter, which can also make the surface less rough and in turn increase the velocity of overland flow and with it increase erosion. When overland flow concentrates in small rivulets, rill erosion can result and through topographic convergence of water at large scales, gully, bank and channel erosion are created. When the mineral soil surface is exposed to rain splash, sheet wash, and rill erosion, soil sealing that can further reduce infiltration rates, can be induced (Doerr et al, 2009). Slopes are prone to landslides in areas where the water infiltrates through cracks, route ways or macro-pores causing a preferential flow and with it an enhanced transfer of water into the subsoil occurs, causing the surface soil layer to slide down (Deurer & Mueller, 2010).

In areas which are dominated by snowmelt, SWR is rarely a problem, since compared to rainfall intensities, snow melts much slower. Initially the snowmelt would wet the soil beyond the critical soil moisture threshold, which is the reason why in the Rocky Mountains, for example, even though some areas were severely burned, there is hardly any surface runoff or erosion during the winter and spring months (Benavides-Solorio et al., 2005;Doerr et al., 2009). Under very dry conditions, when the soil moisture gets below a critical threshold, SWR has an even greater effect on infiltration and runoff, as according to a study done in an Australian eucalypt forest in 1989, the overland flow coefficient increased from 5 to 15% under extremely dry conditions (Burch et al., 1989;Doerr et al., 2009).

As SWR decrease surface soil moisture, which reduces soil particle cohesion and lowers the threshold wind velocity that is needed to detach the particles from the soil, particles are more prone to wind erosion (Whicker et al., 2002;Doerr et al., 2009).

On the contrary, however, soil water repellence can also mitigate erosion by reducing sorptivity of soil aggregates and making the soil more stable from slaking (Deurer & Mueller, 2010).

2.3.2 Loss of Production

As 55% of New Zealand's land is used for agricultural purposes of which 75% are under pasture, the condition of soils is of high importance for the agricultural industry. On the North Island, which consists of about 7 million ha, 69% of the land is used as grassland (Deurer et al, 2011). Due to a reduction in infiltration, germinations and hindering of vegetation growth, pasture productivity is affected in the long run. Even though until today, it is not considered a major concern for farmers, however, it will become an issue soon.

Since in New Zealand pasture production is strongly correlated with stock production, losses of about NZ$180-260/ha were calculated by Slay in 2008 with gross margins being NZ$600-1200/ha. According to initial pasture production measurements; SWR caused a loss of 50% pasture production in dry patches within 4 months of measurement, where these covered 30% of the pasture . According to Statistics New Zealand, 2009, dairy farming made up the largest export in the country which generated a revenue of NZ$ 9 billion. The 'Dry Patch Syndrome' which is associated with the SWR and has been identified in pastures of Hawke's Bay, in the north-east of the North Island, has caused an estimated 30-40% of loss in pasture production in

2007 which is a loss of about NZ$ 420 per hectare (Deurer & Mueller, 2010). If climate continues to change, summer droughts will occur on a more regular scale, and SWR will become a major issue for New Zealand's pastures (Slay, 2008; (K. Mueller 2010)).
To point out other examples, where SWR made an economic impact, is for example in many recreational areas in the United Kingdom. There the annual treatment of patches of reduced grass growth on golf greens alone cost an estimated €10 million. Also in Western Australia, where around 2 million ha of land are water repellent, an estimated €100 million of agricultural production is lost (Münziger & Rodriguez, 1999).

2.3.3 Contamination of Rivers and Waterways

Fresh water quality is of widespread concern in New Zealand, and these problems need to be addressed, where they occur. Increased overland flow due to hydrophobicity has become an issue and needs much further investigation. According to a study done recently, the surface runoff that occurs on water repellent soils mobilises the fertilizers used on the pastures and carries them into the river systems, causing contamination of these rivers (Deurer & Mueller, 2010). In an experiment performed in that study on organic soils, these runoffs were analyzed. With the help of bromide and chloride simulating fertilizers that are lost to surface runoff, the ROMA (Runoff Measurement Apparatus) designed by the Plant and Food Research New Zealand to serve as a tool for understanding the impact of SWR on runoff, was used to find the quantity of these two substances after simulated rainfall on certain undisturbed slabs of soil. Even though in that experiment by losing 96% of water to surface runoff, only around 13% of the bromide were actually washed away. Nevertheless, it is still very important to consider the effect fertilizers might have on the waters they enter, as they can also aggravate the eutrophication of lakes and waterways (Deurer & Mueller, 2010). A significant amount of chloride was lost, not as run-off but as leachate, by using a 30% ethanol solution which is not affected by SWR and infiltrates the soil in a very similar way as water in hydrophilic soils. In a study done in the Netherlands, the risk of ground water pollution increased after a prolonged dry period, as the soils became water repellent (Münziger & Rodriguez, 1999). Much more research on the nutrient and pesticide losses and the effects on water courses, is still needed however to draw up a valid conclusion (Jeyakumar & Deurer, 2011).

2.4 Remediation of Soil Water Repellence

There are many methods that have been used to reduce water repellency in soils. They can be divided into direct and indirect treatments. Direct remediation abolishes the cause of water repellence whereas indirect strategies choose a site that is already hydrophobic and treat the symptoms that occur. Indirect treatment includes surfactants, claying, vegetations, soil aeration, cultivation or compaction. Surfactants are surface-active substances that reduce surface tension of the liquid in which they are dissolved in and increase the adsorption of water by the water repellent soil. Clay is used to cover the soil particles that are object to hydrophobicity as most clay minerals are hydrophilic, have a large specific surface area, and a negative charge. They increase the specific surface area of the soil and reduce the effectiveness of hydrophobic compounds present (Münziger & Rodriguez, 1999).

Choosing plants that adapt to water repellent soils are part of the indirect treatments dealing with vegetation cover. To assist the breakdown of surface thatch, soil aeration can be used. Cultivation strategies set off the abrasion of soil particles, which remove the hydrophobic coatings making the soil non-repellent. The surface roughness can be reduced by compaction, which also makes the soil less water repellent. Direct methods involve treatments such as slow release fertilizers, liming which raises the pH and increases the activity of microbial populations and fungicides. Bio-remediation that uses bacteria that degrade waxes and irrigation to keep the soil moist are also being used to counter SWR.

Another direct method is the stimulation of earthworms which mix the water repellent topsoil with the non-water repellent subsoil. Their casts produce organic matter of high quality that increase microbial activity and their channels decrease the surface runoff and help water to infiltrate into the soil (Mueller & Deurer, 2011). Earthworms play an important role in aerating the soil and mixing the topsoil with the mineral layers in the subsoil. They are the dominant group of microorganisms in pastures. Soil microorganisms decompose most plant and animal wastes and release nutrients that are taken up by plant roots (Molloy, 1998). In an average topsoil, the microorganisms make up about 5% of the organic matter whereas the remaining 95% consist of inanimate humus. Wetting agents are used in some industries, such as horticulture and turf grass to increase the wettability of the soil (Doerr, Shakesby & MacDonald, 2009).

2.5 Research Objectives

The objectives of this research were:

- to investigate the effect of different amounts of water infiltration on hydrophobicity of three selected soils;
- to investigate the effect of different temperatures of infiltration water on the reduction of hydrophobicity in these soils, and whether temperature has an impact.[1]

[1] It was expected that organic carbon would detach from the soil particles faster in higher temperatures than in cooler ones, increasing the DOC in the leachate and reducing soil hydrophobicity at an increased rate. If this was

- to analyse the correlation between dissolved organic carbon (DOC) leached through the soil and whether this reduces the hydrophobicity left in the soil. It is assumed that the dissolved organic components are a major factor impeding the soil to take up water as these compounds are complex and resistant to microbial attack. As DOC is the organic carbon that passes through a filter with pores of ≤ 0.45 μm diameter, it is assumed that they eluviate through macropores and attach to the walls of the soil aggregates around, making them water repellent (Zhang et al., 2004).
- to investigate the transient property of soil water repellency, by using WDPT and MED tests data collected over different times and seasons in the past few years and correlating it with official rainfall data in these areas (field monitoring). The main purpose here was to find out if hydrophobicity changes in relation with the natural precipitation entering the soil, and how that overland flow might also have an influence.[2]

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the case, another important question could have been answered such as, how temperature interacts with or changes organic compounds.

[2] It was expected, that the soils would be more hydrophobic after summer, as this is the drier and hotter season with less precipitation. Then they would reduce their degree of hydrophobicity during the wetter winter months so they eventually become hydrophilic again. This would demonstrate on a broader scale the interactions of hydrophobic soil in a natural environment, and from here they could be correlated with the laboratory findings to find an overall solution to mitigate SWR

3. Materials and Methods

To predict the phenomenon of soil water repellency three key properties of climate, soil and site are needed: the contact angle of the air-dry soil which calculates the degree of SWR; the time that the water needs to infiltrate into the soil (WDPT) that demonstrates the persistence of the SWR; and the critical water content (Mueller & Deurer, 2011). Aliphatic hydrocarbon, which are made up entirely of hydrogen and carbons, and amphiphilic molecules that possess hydrophilic and lipophilic properties which makes them have an affinity to aqueous and non-aqueous media are believed to be the organic carbon compounds that cause SWR. According to a recent study, hydrophobic soils are formed where there is either an increase of residues or a decrease of the decomposition rate of hydrophobic substances, hence an accumulation of an inferior quality of organic matter (Mueller & Deurer, 2011).

The hypothesis of this project was that as more water leaches through the soil, the dissolved organic carbon will loosen its grip from the soil particles and leach out. With this, there will be more dissolved organic carbon in the leachate each time and as DOC disappears from the soil the degree of hydrophobicity in the soils will reduce. Since up till now, however, it is not at all clear how hydrophobicity even comes to be, basic investigations need to be done; here using water to infiltrate into the soil without any chemical interactions will give a very basic understanding of whether water can mitigate this problem.

Natural methods are the preferred method to avoid any negative impacts on the environment, such as contamination of rivers by using chemicals in addition to water. Using water is however only an environment friendly method as long as water is applied from the very beginning, before soil dries out and overland flow is encouraged.

3.1 Geography and Soils of New Zealand

New Zealand, consisting of an area of 270,000 square kilometers, has a huge variety of landscapes and land formations. From the rounded volcanic hills of Dunedin; the moist lowlands of the Southland Plains; to the glaciated schist mountains of Mt Aspring as well as the humid, densely forested coastal lowlands of South Westland. There are many regional climatic differences from subtropical Aupouri Peninsula of Northland to the subantarctic wilderness of southern Steward Island (Molloy, 1998). New Zealand is located on the junction of the Pacific Plate and the Indian-Australian Plates which resulted in the formation of high mountains that have been moved up and are still rising 10mm a year as the plates override and grind past each other. Volcanic activities, mainly in the North Island have formed the landscape in the past 2 million years. 70 per cent of the country is either hilly land (12°-28°), mainly in the North Island or steep land (>28°), mainly in the South Island (Molloy, 1998).

3.1.1 Taranaki/Mt Egmont

The region of this study is a sparsely populated, deep dissected hill country at eastern Taranaki (also known as Mt Egmont), which has a complex network of streams. The landscape is completely different to the one in western Taranaki where many soils are stony and suffer impeded drainage as supposed to free-draining tephra soils in the eastern part (Molloy, 1998). In the past 100.000 years, 30m of tephra has accumulated in the area. The westerly and southerly winds of Taranaki have resulted for the thickest airfall tephras to be deposited in the northern and eastern sector of the mountain. Here, common soils found are Stradford soils, also known as "Stratford Ash", which have developed on coarse tephras. These have erupted around 7000 years ago and due to their free draining effect they are ideal for dairy farming (Molloy, 1998).

There are four different landforms that make up Taranaki which are distinguished in Figure 4: the volcanic landscape and ring plain centered on the mountain; the Taranaki hill country (frontal and inland) where the soil samples of this study originate; the coastal and inland marine terraces; and the costal marine environment. The hill country starts in the east of the ring plain, where the frontal hill country, which corresponds with the area where soils were taken, is of pronounced rolling topography. The underlying strata of the hill country consists of tertiary age sedimentary rocks, locally known as papa which are mudstones, siltstones and sandstones, all which are non volcanic. In the area east of Toko, where the gley soil that was used for this study originates, the ground still carries a covering andesitic tephra (Molloy, 1998).

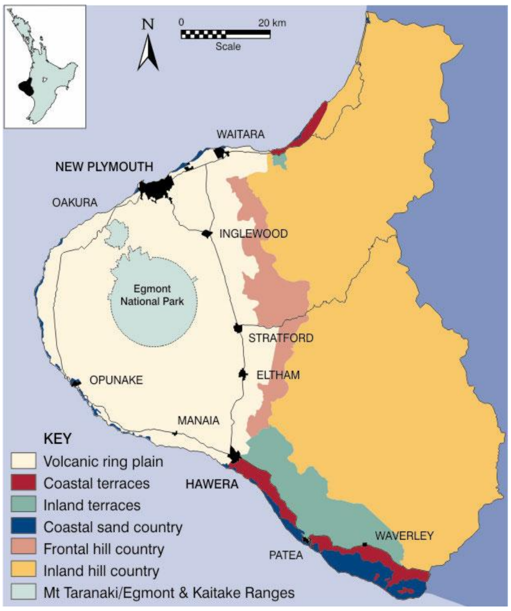

Figure 4 Landforms of Taranaki (Council, 2004)

The soils in the hill country are mostly shallow soils that have developed on steep unstable slopes and are also referred to as 'steepland soils'. Depending on the topography, age, climate, the proportion of siltstone, mudstone and sandstone, there is great variability in composition and depth of the soils. Pastoral farming and commercial forestry are both manageable in this area even though the hill country is prone to erosions (Council, 2004).

3.1.2 Soil Sampling

In April 2011, twenty-one different soil rectangles (7 from each site: organic, brown and gley site) of about 60cm x 40cm and 10cm depth were carefully dug out of the sampling sites in the areas on the east side of Taranaki. These areas are described in more detail in 3.2. The rectangles were stored in the cold room of the Soil Science Building at Massey University in closed plastic bags. This way the water content remained relatively constant until the soils were used for investigation. From these samples the soil properties were measured (see section 3.3), and they were used for the lab experiments that are described in section 3.7.

3.2 Soils and Climate

Egmont soils which have been used for this study are considered loamy, as they consist of 22% clay, 23% silt and 55% sand. The black or dark brown A horizon (probably originating from fire induced flax / Pteridium fern vegetation during Polynesian settlement) of about 25cm depth lies above a friable, loamy, brown upper B horizon (around 45cm). Underneath that, a paler yellowish-brown lower B horizon of silt loam texture can be found (Molloy, 1998). The locations where the soils have been taken can be found in Figure 5.

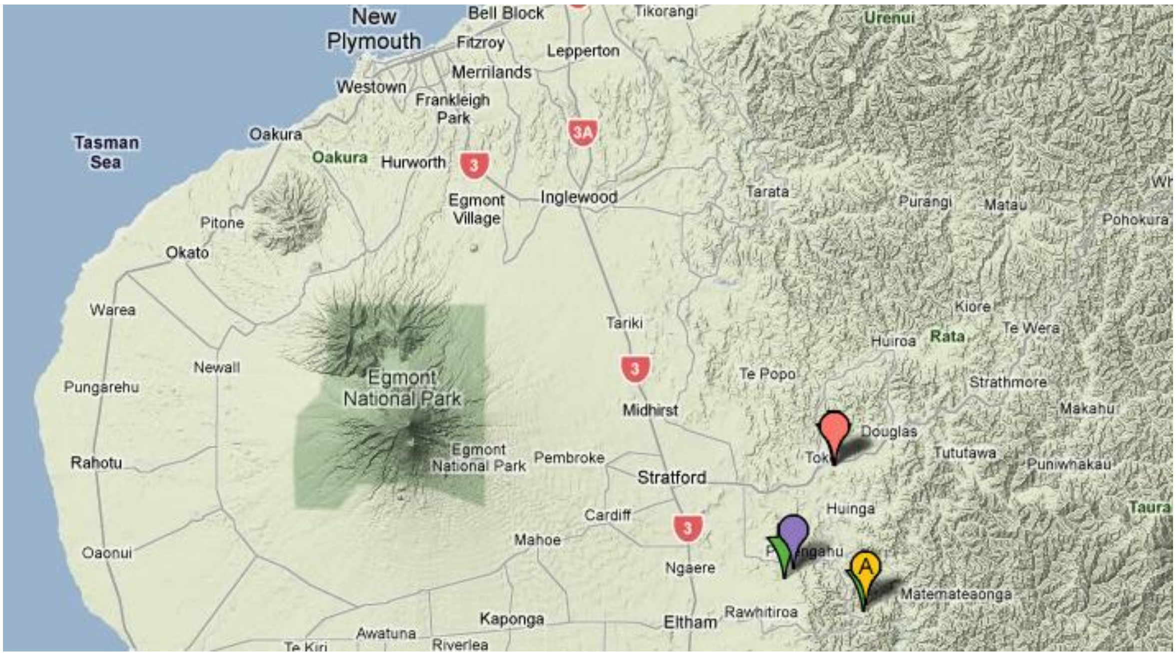

Figure 5 Location of soils used for this study: Red: Gley Soils; Purple: Organic Soils; Yellow: Brown Soils (Google Earth)

Below, the formation of the organic, the gley and the brown soils are represented. Judging from this diagram, organic soil originates from organic parent material which is made up of plant materials. Mineral parent material with a persistent high water table develops into gley soil, whereas brown soil form from mineral parent material that are well to imperfectly drained. The raw soil is dominated by quartz, feldspar and mica which develop into recent soils. Through humid and wetter conditions this recent soil turns into brown soil.

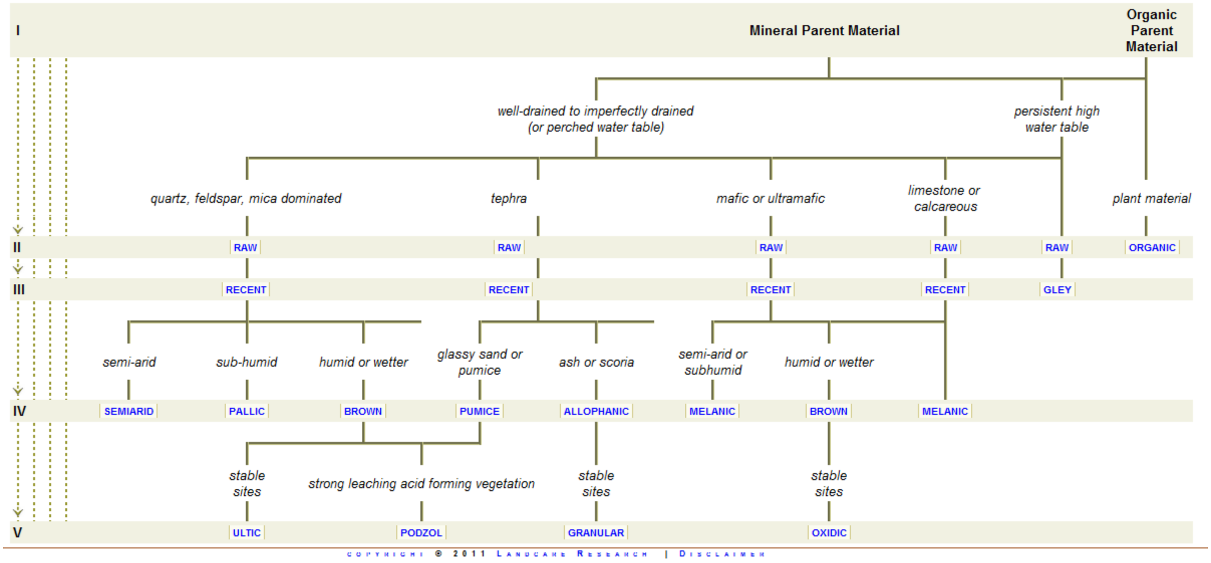

Figure 6 The formation of New Zealand's soils (Landcare, 2011)

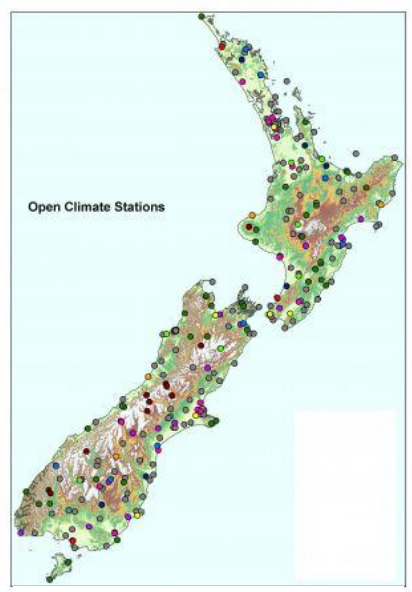

Figure 7 Open Climate Stations NZ (NIWA)

To understand the overall conditions of the soils that were investigated, climatic conditions were closely followed and compared to the changes in soil condition and data. Using information by the National Institute of Water and Atmospheric Research (NIWA) and through this the 1992 created National Climatic Database, which archives climatic data of New Zealand, the Pacific Islands and Antarctica some dating back to the 1850s, the exact rainfall data could be found for the years and months of interest for this study. Every day the database is updated from data of 260 climate stations consisting of data on temperature, rainfall, solar radiation, soil moisture, earth temperature etc. At the end of each month, data from manual climatic stations that are operated by voluntary observers are digitalized and uploaded (NIWA).

As the three areas that were studied do not lie within a close distance to any of the stations set up by NIWA, a Virtual Climate Network was used. This service, which is also provided by NIWA, was used to find three virtual climate stations (of the 11500 virtual climatic stations showing daily interpolated data) within a radius of 2 km from each of the sites (NIWA). The daily precipitation rates could be derived from here and the amount of water that the soils were exposed to between the sampling-taking could be calculated. As the soils have been collected three times in the past 2 years, and the precipitation within these dates can be calculated and analyzed, the changes in soil hydrophobicity can be correlated with the rainfall and soil moisture content.

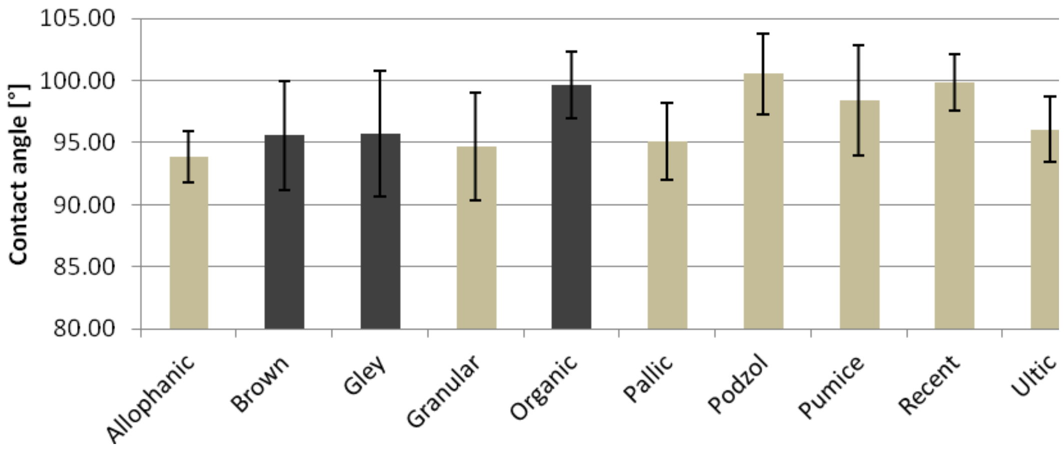

Figure 8 Contact Angles of various soil types in New Zealand (Deurer et al, 2011)

The above diagram points out the three soils that were analyzed and compares it to other soil types that are found to be hydrophobic in previous studies of the North Island. These previous data were used for the field data analysis. This is mainly to show that there is a variation of degree of hydrophobicity depending on the soil type.

3.2.1 Organic Soil

Organic soils, (Figure 9 shows a column of these soils) or in the World Reference Base also called Histosols, occupy around 325-375 million ha of the world. Most of the Histosols that are located in the southern hemisphere can be found in temperate lowlands and cool montane areas. They consist of incomplete decomposed plant remains sometimes mixed with sand, silt or clay as its parent material. According to their properties on organic material such as packing density, mineral admixtures, wood content and their type of peat bog they are used for diverse purposes. The oxidation of sulphuric minerals, which might occur when Histosols are drained, can accumulate anaerobic conditions, and productivity is destroyed if lime is not sufficiently applied. Organic soils usually have a bulk density of 0.04-0.4 T/m^3 (WRB, 2006).

Figure 9 Organic Soil Column (Landcare, 2011)

Organic soils cover around 1% of New Zealand's area. They can take up to 20 times their weight of water. These soils which are dominated by organic matter are formed in the partly decomposed remains of wetland plants also known as peat, or forest litter. According to the New Zealand soil classification, they can be divided into four different groups of organic soils: Litter Organic, Fibric Organic, Mesic Organic and Humic Organic. Usually organic soils have a low bulk density, low bearing strength, when dried out they have a high shrinking potential and a high total available water capacity. Due to anaerobic conditions, soil organisms are restricted and due to a high carbon/nitrogen ratio the decomposition is slow. Figure 10 provides a map of the distribution of humic organic soils in the area where the organic soil for this study was taken.

Figure 10 Humic Organic Soil (Landcare, 2011)

The organic soils, used for this study, were sampled from a dairy farm. The sampling field is flat and the topsoil depth is about 100mm. The annual water deficit is zero and the profile readily available water is at a depth of 50mm -74mm (Deurer et al, 2011). Figure 11 shows the satellite picture of the field and a photo taken on site while soil samples were taken.

Figure 11 Organic Soil Sample Site (-39.39691, 174.37831; Slope: Flat) (Google) left: satellite picture (google maps) middle: hypsometric layer; right: photo of site

3.2.2 Gley Soil

Gleysols (Figure 12) are wetland soils that occupy around 720 million ha of the earth’s surface. They can be found in almost every climatic zone. They are usually saturated with groundwater forming a gleyic colour pattern as they appear in low landscape areas or depressions (WRB, 2006). Segregation of Fe compounds can be found within the upper 50cm due to reduction processes. Using Gleysols for agricultural purposes is complex, since installing a drainage system to lower the groundwater table is necessary, otherwise the soil structure will be destroyed when cultivated in a too wet stage. However, after draining, they can be used for multiple purposes such as cropping, dairy farming or horticulture (WRB, 2006). Gley soils can become water logged during wet seasons, and even though they usually have enough plant nutrients, the lack of soil structure and aerations during these seasons impairs plant growth (Molloy, 1998).

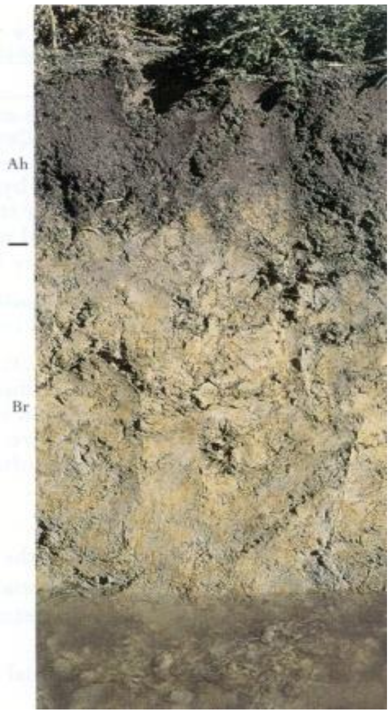

Figure 12 Gley Soil Column

The bulk density of gley soils is usually 1.1-1.6 T/m^3.
Gley soils cover around 3% of New Zealand and can be divided into six different soil groups, which are, sulphuric gley, sandy gley, acid gley, oxidic gley, recent gley and orthic gley. The gley that was used for this research is classified by Landcare Research as “recent gley” and its location can be seen in Figure 13. Gley soils have light grey subsoils usually with reddish brown or brown mottles. They have been chemically reduced and are strongly affected by water logging. This usually happens in spring and winter, can however also be present all year round. They have high groundwater tables, shallow potential rooting depth and a relatively high bulk density. Due to anaerobic conditions, soil organism activities are limited (Landcare, 2011). Applying lime on gley soils that have high organic matter content creates a better habitat for micro- and meso-organisms and enhances the decomposition rate of soil organic matter (WRB, 2006).

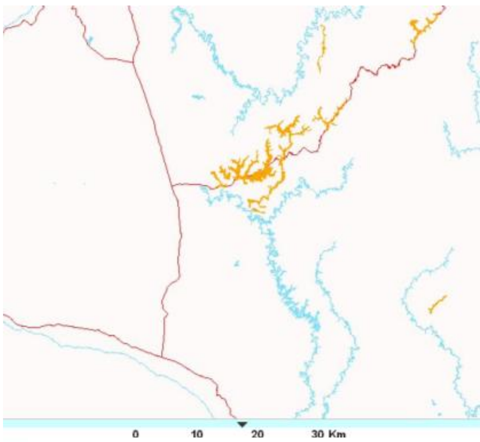

Figure 13 Position of Recent Gley (Landcare, 2011)

Figure 14 shows the satellite picture of the field and a photo taken on site while soil samples were taken.

Figure 14 Gley Soil Sampling Site (-39.32376, 174.41890) (Google) left: satellite picture; middle: hypsometric layer; right: photo of site

The gley soils used for this study were sampled from a dairy farm. The sampling field is flat and the topsoil depth is about 100 mm. The annual water deficit is 0mm and the profile readily available water is 50-75mm (Deurer et al, 2011).

3.2.3 Brown Soil

The brown soil analyzed in this study comes from the soil class Cambisols, according to the World Reference Base of Soil Resources. Cambisols are relatively young soils and have no to very little profile development. They cover around 1500 million ha worldwide and are generally used for agricultural purposes, often intensively. They are amongst the most productive soils in the world when there is high base saturation in temperate zones. Acidic Cambisols, and ones that are found in hilly terrain are, as in this case, used for grazing land. The name is derived from the Italian word cambiare, which means change, referring to the horizon differentiation in the subsoils, changing structure, colour, clay content or carbonate content (WRB, 2006). The parent material is made up of medium and fine textured materials that are derived from a wide range of rocks. Cambisols can be found in all

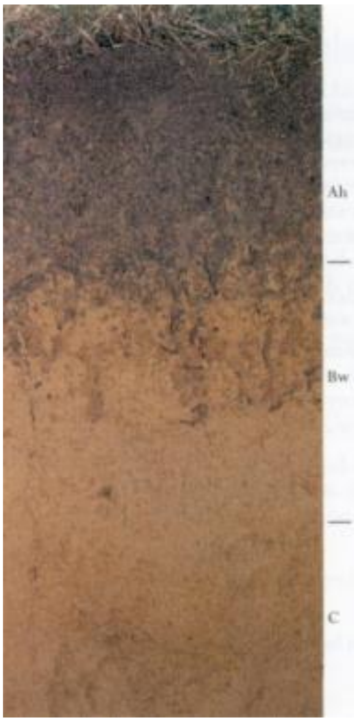

Figure 15 Brown Soil Column (Landcare, 2011)

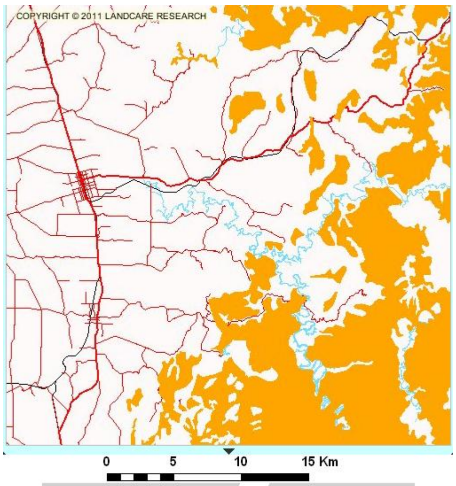

Figure 16 Distribution of Orthic Brown Soil in NZ (Landcare, 2011)

climates, in many types of vegetations and anywhere from level to mountainous terrain (WRB, 2006).

Brown soils cover about 43% of New Zealand and occur at areas where drought is not common in summer and the ground is not waterlogged in winter (Landcare, New Zealand Soil Portal, 2011). They have brown and yellow-brown subsoil underneath dark grey-brown topsoil. The brown colour comes from a thin coating of iron oxides which is created by weathering of the parent material. The topsoils are relatively stable with very well developed polyhedral or spherioidal structure. They have a low to moderate base saturation. They generally contain a large and active population of soil organisms, usually earthworms, which were also observed in the soils used for analysis.

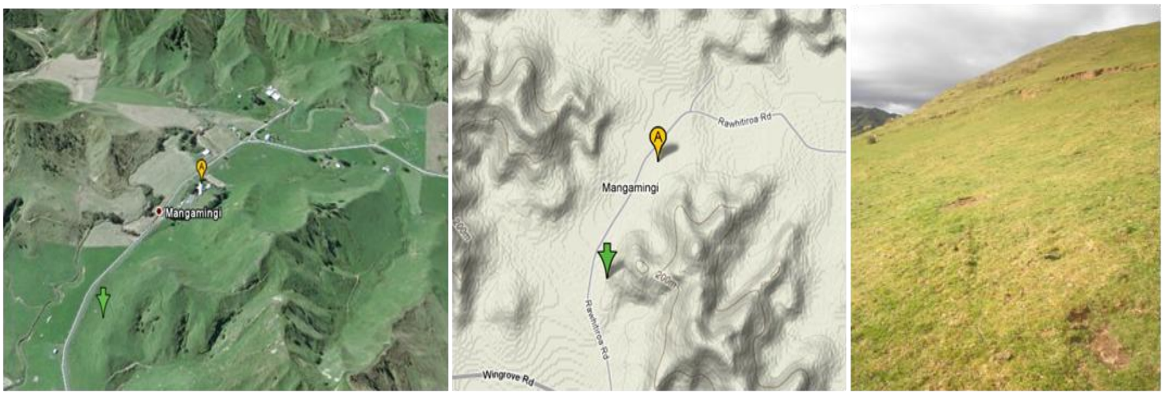

Figure 17 Brown Soil Sample Site (-39.41775, 174.44301) (Google), left: satellite picture; middle: hypsometric layer; right: photo of site

According to Landcare Research, the soil used for the experiments is placed within the orthic brown soil. This name refers to the New Zealand classification scheme where brown soil can be separated into allophanic brown, sandy brown, oxidic brown, mafic brown, acid brown, firm brown and orthic brown (other brown soil). Figure 16 shows the distribution of orthic brown soil in the area around Stratford, which overlaps with the area the samples were taken. Figure 17 shows the satellite picture of the field and a photo taken on site while soil samples were taken.

The brown soil used for this study was sampled from a cattle and sheep farm. The sampling field is at a slope of 14°W and the top soil depth is 80mm. The annual water deficit is 0mm and the profile readily available water is 50-75mm (Deurer et al, 2011).

3.3 Soil Properties

Before preparing the soils for the hydrophobicity tests, general soil property measurements were performed to get a better understanding for the physical properties of the specific soil used in the experiments. The soils pH, the bulk density and the soil water content were analyzed.

The first property measured was the pH of the soils. This was done by sieving each soil through a 2mm sieve and leaving it to air-dry until the next day. Then 10g of subsample was used to be mixed with 25ml of water. After letting it settle for 17 hours a pH meter was used to measure the pH-value.

The gravimetric water content (SWC) for the field experiments was determined before (April) and after (August) winter of 2011 as it usually rains much more in winter and soil water repellency is expected to decrease as the soil water content increases. Results can be found in Table 2.

SWC could be an additional indication for hydrophobicity. This was done by first weighing the mass of wet soil, then drying it in the oven until constant mass at 105°C, and weighing the mass of dried soil once again. The mass of dried soil was subtracted from the mass of wet soil to get the mass of water, which was then divided by the mass of just the dry soil (Θm=mw/ms).The water content of soils affects the plant growth and influences soil properties such as aeration, temperature, consistence, and others (McLaren & Cameron, 1996) which could then affect the activity of microorganisms.

The bulk density ρ_b was determined by taking three undisturbed soil samples using cylinders of 5 cm height and 5 cm diameter. The ratio of the weight of dry soil and the volume of the cylinder is the bulk density measured in g/cm³.

To determine the particle density, a volumetric flask was filled with 100 ml of water, weighed and recorded. After that, 25g of air dried soil was weighed into a beaker. 50ml of water was added and boiled until the air, trapped within the soil was expelled. After cooling, the soil suspension from the beaker was put into the empty 100ml flask, and additional water was poured into the flask until the mark of 100ml was reached. The flask was weighed once again. By assuming the density of water is 1g/ml and masses are measured in grams, the volume of the soil is then calculated. The soil particle density is determined using the common formula (Klute, 1986):

$$\rho s = \frac{\text{mass of soil}}{\text{volume of soil}}$$

From the bulk density and the particle density, the porosity of soil was determined with the formula: Porosity of soil = 1-(ρ_B/ρ_S). This provides the percentage of pores in the soil which can be filled with water. As for the lab experiments, it was important to find out the pore volume; that is the amount of water necessary to saturate the soil, which occurs when all the pores are filled with water. Since at the beginning of the experiment it was assumed that only by saturating the soil could all the organic compounds start to mobilize and dissolve, it was important to use at least this amount of water. The pore space is usually occupied by air and water. This can provide information for other important soil properties, such as, how much water can be stored in the soil. This then gives indication for the potential of flooding or drought in the area and how fast water, heat and roots can move through the soil.

3.4 Water Droplet Penetration Time (WDPT) and Molarities of Ethanol Droplet (MED) Test

Figure 18 Experiment setup for WDPT & MED in laboratory

Soil water repellency is a function of the free energy of the solid/gas interface in soil. Since this energy cannot be measured directly in the laboratory, parameters related to thermodynamics are being used instead. These parameters are the initial advancing contact angle or the work of wetting (Roy & McGill, 2002). The most common tests to assess soil water repellency are the Water Droplet Penetration Time (WDPT) Test and the Molarity of Ethanol Droplet (MED) Test which, compared to other methods are less time-consuming and easier to handle. The WDPT measures the persistence of SWR, while the strength/degree of SWR is measured by the MED test. The persistency and degree of SWR are often related, but the relationship is not always clear or consistent (Dekker and Ritsema, 1994; (Doerr, 2009)). Also, the classification of the quantitative data derived from the WDPT and the MED test vary with the perception of the investigator of what constitutes low or high water repellency (Doerr, 2009).

Figure 19 WDPT Five water droplets on brown soil

Using the WDPT test, the persistency, which is the time it takes for water to be absorbed by the soil, can be analyzed by placing 5 water droplets on a soil which was previously sieved using a 2mm sieve. Then the sieved soil is placed inside an oven of 65°C temperature and dried for 48 hours. After taking the soil out of the oven, it is put into sealed plastic bags and stored at room temperature for 24 hours, in order to re-equilibrate. Each soil is then placed into an aluminum petri-dish covered with about 1cm of soil depth and the surface is smoothed before the droplets are applied. The time it takes for the droplets to infiltrate into the soil is recorded. A longer duration indicates highly persistent water repellency (Doerr, 2009). The threshold used to determine that the soil is water repellent as supposed to wettable or ‘normal’ for this study is chosen to be 10 seconds according to Roy and McGill, (2002). This defines every soil water repellent that would hold the water droplet on the surface for over 10 seconds. In other studies such as that of Deurer et al (2011) a threshold of 5 seconds was used according to Bisdom et al. (1993). Due to the fact that the soils used for this study are extremely water repellent, a higher threshold was used, also as there is no common regulation as to how many seconds of water pending actually define the water repellency of a soil. Up to four hours were measured until the last droplet infiltrated the most persistent soil type. The average time of the five droplets was calculated and recorded.

Five classes of persistence of SWR were chosen, using a combination of the definition of Deurer et al. (2011) and the own time frames:

- class 0 wettable/hydrophilic: 0-10sec
- class 1 slightly persistent: 10sec-5min
- class 2 strongly persistent: 5min-30min
- class 3 severely persistent: 30min-1hr
- class 4 extremely persistent: 1hr-3hrs
- class 5 extreme persistent: >3hrs

The WDPT is a useful empirical test, but it provides little information about the soils affinity to water over shorter solid/liquid contact times (Roy & McGill, 2002). It can also be defined as the time of a liquid-solid contact angle to change from its original value to one that is approaching 90 degrees, however, it mainly indicates the stability of water repellency (Hardie, Cotching, Doyle & Lisson, 2011). The negative aspect of WDPT is that it consumes a great amount of time, since for each droplet that is placed on the soil surface the time can take up to 4 hours until it can finally be recorded. On the other hand it is a very simple measurement which does not require too much equipment and expertise.

To determine the degree of hydrophobicity, the Molarity of Ethanol Test (MED) is used. This method is much faster than the WDPT test as each droplet is placed on the soil for a maximum of only 10 seconds. In this experiment, the soil is prepared using a 2mm sieve and dried for 48hrs in the oven in the same way as is done for the WDPT test. After re-equilibration the dried soil is once again placed in a petri-dish and the surface is smoothened before droplet application. Instead of using distilled water as in the WDPT, different concentrations of Ethanol are used. To prepare these solutions Ethanol is added to water in different amounts in order to create different concentrations. About 20 different solutions are prepared. The lowest molarity in this experiment is 0.171 and the highest 6.496 which never had to be applied. When a droplet enters the soil just after 10 seconds, the next higher concentration of Ethanol which is the Ethanol solution of a lower surface tension is used. Another droplet is placed on a different spot of the soil. If then the droplet infiltrates into the soil before 10 seconds, the same experiment is performed two more times. After all three droplets of Ethanol enter into the soil within 10 seconds the concentration is used to calculate the contact angle between the drop and the soil surface. The formulas used are as follows:

$$\% \text{ of Ethanol} = \frac{\text{Average of Molarity of Ethanol}}{17.096} * 99.5$$

$$\text{Surface tension} = 61.05 - 14.75 * \text{LN}(\text{Average of Molarity of Ethanol} + 0.5)$$

$$\text{Contact Angle} = \arccos\left(\sqrt{\text{Surface tension}/71.27} - 1\right) * \left({}^{180}/_{\pi}\right)$$

It is important that the surface of soil is big enough to perform a complete MED Test. A spot that is used for placing a droplet should not be used twice, since the spot would already have a certain moisture level which would encourage the droplet to infiltrate much faster. Leveling the soil in order to place the droplets, can be done smoothly by using a finger or device, but not by shaking the soil as in this way the greater aggregates would move up to the top.

3.5 Organic Carbon Analyzer

Dissolved Organic Carbon (DOC) that was in the leachate from lab experiment was collected and analyzed in the Landcare Research Lab. Since for this experiment, only DOC was of importance, about 20ml of the leachate was taken and filtered through a 0.45-µm-pore-filter as this is the threshold where only **dissolved** organic carbon can go through the filter. The amount of total carbon and inorganic carbon was investigated for analysis, whether the dissolved organic carbon content has a correlation with the degree of hydrophobicity. The instrumentation used in the laboratory was an Elementar Hi-TOC. Here the water sample is combusted at high temperature in the presence of a cerium dioxide catalyst to produce CO_2.This is measured in an infrared cell. Inorganic carbon is measured separately. Total organic carbon can then be determined by calculating the difference of total carbon and inorganic carbon. This method, known as “Method 5310 B, Total Organic Carbon/High Temperature Combustion Method”, is also the standard method for analyzing water and wastewater (Landcare, 2012).

3.6 Soil sampling for field experiment

Figure 20 Soil cylinder for sampling

At the end of winter, in August 2011, the sites were visited once again. The 15 cylinders were already prepared to be taken to the field to gather undisturbed soil samples. For each soil 5 replicates were taken from the fields to get analyzed for their hydrophobicity in the lab. The WDPT test and the MED test were performed once again. Also the water content of the soils was calculated to compare the results with those of the water content and hydrophobicity before the winter in April 2011. All together for the second field trip 15 soil cylinders were put into labeled plastic bags which were sealed to prevent the soil from drying out until analysis.

3.7 Lab Experiment

3.7.1 Trial Experiment

Before the actual experiment was done, a trial procedure was performed to first of all find out if hydrophobicity of the soil does actually change with treatment. This is done in order to avoid performing an experiment that might take up to months and at the very end finding out that nothing changes during the process of experiment. To perform this trial experiment, the equipment used were 9 cylinders of 83mm bore diameter and 50mm height, 9 specially cut out mesh, a scale, a sharp knife, a hammer, a cutting cylinder (of 3cm height) and 9 jointing cylinders. The soils that were used were the ones with soil properties described in section 3.3. Three replicates of each of the soil types (gley, organic and brown) were taken using 9 plastic cylinders which were especially prepared for this experiment. Only the top few centimeters of the soil are of relevance in this study, as this is where the soil would be most hydrophobic.

As the roots were thick and hard to cut, even when using the cutting cylinder which had a cutting edge on one side, a knife was needed to cut along the walls of the cylinder. This way the cylinder entered the soil more easily and the soil was not disturbed too much. The 5cm high sample cylinder was then set on top, and together they were forced into the soil. Once the surface of the soil reached the top of the cylinder and the cylinder was filled with soil, a knife was used to cut away the lower part of the soil that filled the cutting cylinder. Caution needed to be taken so no soil was lost from the sample cylinder and the bottom end was neatly cut to avoid any unevenness. Then the cylinder pieces were joined back together, with a mesh between cutting and sample cylinder, so that soil particles did not fall through into the leachate. The jointing cylinder connected the cutting cylinder with the sample cylinder.

Hydrated lime (Calciumhydroxyd) was applied on the sample cylinders to speed up the process of leaching organic carbon, as according to Deurer (personnel comm.) the slow decomposition of organic matter, which also causes hydrophobicity, can be caused by low pH levels. Usually 750kg of $Ca(OH)_2$ are applied on the surface of the pastures. To apply it on the surface of the cylinders, a calculation was performed for the exact amount of hydrated lime. 0.38 g of $Ca(OH)_2$ was used for a surface area of 0.005027m^2 (or 0.5*10-6ha). The incubation time took 2-3 days. The calculation can be followed in Appendix B.

The lime was evenly spread out on the surface of the soil in the cylinder. To encourage the lime to infiltrate quicker into the soil, 10ml of water was evenly spread on top of the lime each day for 3 days. This amount of water (20ml) that was added to the soil can be neglected in the

calculation, as the soil water content was not affected that much, since at the same time, when leaving the soil standing for a day, this amount would have evaporated again.
The pore volume was determined according to the calculations described in section 3.3. It was then used to find the amount of water that is needed to completely fill up all the pores in the soil with water, to ensure all the carbon compounds, with focusing mostly on those that cover the soil particles as thin hydrophobic layer, have a chance to dissolve and loosen. The amounts of water that saturate the soils are recorded in Table 2. As for the trial experiment, the most effective and quickest method known to get rid of the carbon in the soil was used. Instead of using cold water, hot water was used in addition to lime. Pressure was also applied in order to get quicker leaching results, as otherwise, due to the soils hydrophobicity, the water would have been ponding on the soil surface for a long time. The main reason for choosing hot water over cold water was due to the fact that hot water carbon is labile in nature and is thus highly available to microbial biomass (Ghani, Dexter & Perrott, 2003). Hence, it was expected that DOC would detach quicker and leach out at a faster rate than when using cold water.
For the first leachate 179ml of tap water was heated up to 80°C and put into the cylinder of brown soil sample. The lowest negative gauge pressure was applied for the first leaching round. All lids were closed airtight above the holes, leaving one hole for the cylinder with the soil. It is important to check that all are sealed, so no air is being sucked in from anywhere other than the cylinder with the soil. After about a minute, the pressure was turned off and the beaker that was placed underneath the cylinder was weighed. This is to find out how much water actually leached through the soil, and how much stayed inside. To double check the results, the soil and cylinders were weighed as well, before and after the application. As most of the water was leached out, for later experiments these weighing was neglected as it was of no relevance. The weight of the beaker needed to be subtracted to get the amount of leachate. Then, a sample of this leachate was filtered through 0.45µm which assured that only the dissolved organic carbon stays in the leachate. This was then taken to the Landcare Research lab at Massey University campus to get analyzed, using an Elementar Hi-TOC analyzer to find the amount per liter of DOC in the leachate (as described in the section 3.5).
The same procedure was followed using the other soils, whereas for the organic soil 193 ml of heated tap water was applied and for the gley soil 134 ml was used. Only later an error in the pore volume calculation was discovered, and the real values for the pore volume of the cylinder can now be found in Table 2.
In order to get a better understanding of what kind of equipment was used for the experiment, the sketch below shows the method and equipment used.

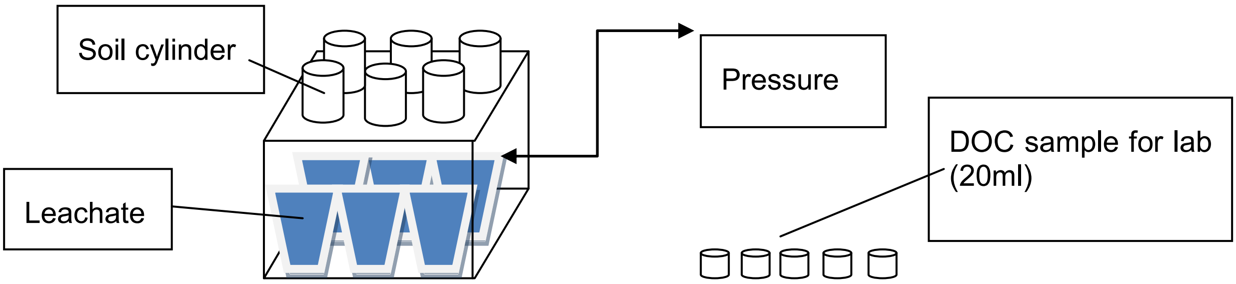

Figure 21 Diagram of the Lab Experiment

The second round of leaching was done the same way, with exactly the same amount of water. Again all values were recorded, and leachate samples were taken from each soil leachate to get analyzed for DOC. In the third round the negative gauge pressure was reduced to allow the water to infiltrate at a slower rate in order to give the dissolved carbon more time to detach. However, even here the rate of infiltration was still very fast, and it is not sure if there actually was enough time for the organic carbon to break free from the soil particles and leach out with the water. For this reason the fourth round of leaching procedure was done without applying any pressure.

In the fourth round all soil samples were placed on the box at the same time, since this time no pressure was applied and the cylinder did not need to be connected to the box in an airtight manner. The water was again applied with a temperature of 80°C, for each soil the amount of water as calculated for the pore volume was applied again. After several minutes, when no more water leached out, pressure was applied again to encourage the last bit of water to leach through the soil.

In this experiment the preferential flow was easy to observe, since for some soils it took a much longer time to leach (there was pending of water on the surface) and for some the water leached through very fast. For example, gley soil sample G#2 had seemingly no preferential flow, whereas G#1 & G#3 had a lot. O#2 had little preferential flow, O#3 had a lot. B#1 had a lot whereas B#3 had less. These assumptions were made according to the time of water ponding on the surface of the soil. Longer water ponding is interpreted as less preferential flow, but this could also be due to differences in the infiltration and soil water repellency. However, in this present experiment, there was no difference in the initial degree of hydrophobicity of B#1 and B#3, so this assumption does not apply here. By the end, 12*3 leachate samples were taken to the lab to get analyzed for DOC.

The leachate needed to be filtered through a 0.45µm filter, mainly to get out only the DOC but also in order to prevent bigger particles from disturbing the TOC analyzer. As the trial experiment was only designed to get an overview that something does happen, it was performed in the least time-consuming way as possible, analyzing only the extreme values. Therefore, only the first and the fourth wash were sent into the lab for analysis to find out the DOC. For O#1 all four washes were taken to the lab, just to see the changes in DOC concentration for an entire experiment. A minimum of 15ml of each leachate sample was required for the DOC analysis; therefore, around 20ml of each sample were filtered, just to be on the safe side.

The leachate was weighed for the purpose to find out how many milliliters actually leached out of the soil. As the DOC concentration was given in mg/L, the DOC had to be multiplied with the actual amount of leachate that made its way through the soil to find the loss of total DOC of the soil, as this then was correlated with the changes in soil water repellency, WDPT and MED measurements.

The results of this trial experiment are summarized in Appendix B. These results suggest that there is an increase in leached dissolved organic carbon as the soil was leached with more water. Some sample results do not show the same increase in DOC, however if the DOC is added up, there is an increase of leached out DOC for each soil. When comparing this to the results of the WDPT and the MED test which are also summarized in Table 28 of Appendix B, it is obvious that the hydrophobicity decreases as more water was used to leach the soils. Even though through this experiment, the soil still did not become hydrophilic as it was expected at first, there was an obvious positive change for each of the replicates becoming less hydrophobic. These results are visualized in Table 3.

3.7.2 Main Experiments – Hot and cold water washing treatments

The main experiment with ‘hot and cold water washing’ was performed after finding out that the trial procedure showed obvious changes in the degree of hydrophobicity. The soil sampling for the further experiment took place the same way as for the trial experiment described above in section 3.7.1. As only 10 cylinders can be used for leaching at a time, depending on the number of experiments performed previously, the soil cylinders were taken from brown, gley and organic soils to perform hot or cold water leaching with the according amount of water.

For the pore space in the cylinders used, which are of 8.3cm diameter with the height of 5cm, the pore volume was calculated by multiplying the porosity of the soil with the volume of the cylinder, which in this case was 270.53cm³. To simplify the lab experiments, the maximum amount of water necessary to saturate one of the three soils was important, which in this case was the amount needed to saturate the organic soil with 210ml of water. However, as it was only necessary to use at least this amount, 400ml which was defined as about two washings (W2),was used for the first round which was then multiplied for the following leaching applications. This way the water application for the experiments were divided into 5 different steps, starting with 0ml water added to the soil, then 400ml, 800ml, 1600ml and 2400 ml.

Usually for each water amount five replicates of a soil for cold water leaching and four replicates of a soil for hot water leaching was used. By the end of the experiment, as time was running out, the number of replicates decreased for the hot water leaching with the increase of water amount as it seemed that there was not much difference between hot and cold water leaching at that time.

During soil sample taking with the cylinders it was important to try not to disturb the soil too much. As the blocks of soils were quite small for the amount of replicates that were needed to reach a valid conclusion, it was inevitable to change the compactness of the soil, as the more soil was used, the looser it got. Trying to stamp the cylinders not too close to the edge into the soil (as here, after some time of storage moisture of the initial soil decreases) it was tried to maintain a certain similar compactness for all soils. Each time the cylinder was taken from one of the rectangular soil cuboids, the block was placed back into the plastic bag to avoid it from drying out, and put back into the cold room. Usually 2 cylinders per experiment, one for cold and one for hot water leaching, were stamped into one soil block. The experiments were divided into the amounts of water that were being used. Such that, for the first experiment, no water was used; for the second experiment 400ml water was used; the third 800ml; the fourth 1600ml and the final one had 2400ml water applied on the soil.

Table 1 Overview of amount of soil replicates used per experiment

Water application	**Cold Water Brown**	**Hot Water Brown**	**Cold Water Organic**	**Hot water Organic**	**Cold Water Gley**	**Hot water Gley**
0ml	B1, B2, B3, B4, B5, B6, B7	B1, B2, B3, B4, B5, B6, B7	O1, O2, O3, O4, O5, O6, O7	O1, O2, O3, O4, O5, O6, O7	G1, G2, G3, G4, G5, G6, G7	G1, G2, G3, G4, G5, G6, G7
400ml	B1, B2, B4, B6, B7	B1, B4, B6, B7	O1, O3, O4, O5, O6	O1, O3, O4	G1, G2, G3, G5, G7	G1, G2, G3, G7
800ml	B1, B2, B3, B5, B7	B2, B3, B5	O1, O2, O3, O4, O5	O2, O3, O4, O5	G1, G2, G4, G5, G6, G7	G2, G4, G6, G7
1600ml	B2, B3, B4, B5, B6, B7	B3, B6, B7	O2, O3, O5, O6, O7	O2, O3, O7	G1, G2, G4, G5, G6, G7	G1, G2, G6
2400ml	B2, B4, B6, B7	B6, B7	O5, O6, O7	O7	G3, G4, G7	G7

The same equipment which was used for the trial procedure and which can be followed in the diagram of 3.7.1 was used for the actual experiment. Underneath the holes where the water leaches through, beakers were placed inside the box to collect the leachate. When having the ten cylinders filled with soils, usually three, three and four, they were all placed on the vacuum box which was especially prepared for this experiment. The box was connected to pressure, and the water was slowly poured into the cylinders. Depending on how long the water was pending on the soil, pressure was applied stronger or weaker or not at all. Usually gley soil would not let the water leach through easily, so here pressure had to be applied in order to perform the experiment in a tolerable amount of time.

After the whole water leached through and no more drops could be spotted, the box was opened, and the leachate was filtered through 0.45µm. The plastic containers that were labeled accordingly were then closed once they were filled with about 20ml of filtered leachate and set aside, to be taken to the lab once all the experiments were done and all the leachates were collected. As only 10 cylinders of soil could be used at a time, after leaching these soils were taken out of the cylinder, cut in half as to keep half of the soil of each leaching procedure to put in the freezer and leave it for possible future investigations. The other half of the leached soil was sieved through a 2mm sieve, put in the oven for 48 hours at a temperature of 65°C, and taken out again to equilibrate for 24 hours at room temperature. Then, as has been described at 3.4, a WDPT and a MED test was done for each soil. After this was finished, the next replicates were taken from the soil blocks and the same procedure was performed over again. This continued until five replicates of each soil had been treated with cold water, and four had been treated with hot water. Once the gley soil, the brown soil and the organic soil were finished, the next experiment was started using the next greater amount of water to leach through.

After 400ml, the same procedure was done using 800ml. As according to the MED and WDPT tests, the hydrophobicity of the soils did not show an obvious change, a much greater amount of water was used for experiment four, this time using 1600ml. After Experiment Four was completely done, 2400ml of water was used for the last experiment.

Once all the experiments were done, the plastic containers which until then were stored at room temperature, with the filtered leachates were taken to the Landcare Research lab to get analyzed with the DOC analyzer as described in section 3.5. The soils that have been used for MED and WDPT tests were dried again and each put back into labeled plastic bags to be stored for possible future use.

3.8 Statistical Data Analysis

Data was analyzed by setting up correlations between the different data sets, such as the times of the water droplets, the contact angles and the dissolved organic carbon content found in the leachates. To get a clear picture and to evaluate whether the data collected does actually show a change, the ANOVA Test was used. With this test the significance of the correlation could be evaluated. If there was significance, the Tukey Kramer Test, which will be explained in more detail below, was then used to find out exactly which data was the significant one, and which data did not show a significant change.

An ANOVA (Analysis of Variance) test was used to discuss whether the data shows statistically significant differences somewhere in the data as a whole, without specifying where exactly these differences are. It can show that at least one group is different from another group, however cannot directly show which groups are different. If the differences between the groups are substantially greater than the differences within the groups the p-value is very low. In that case an additional test needs to be done to find out the precise differences. The p-value can be found in the ANOVA test results table in Appendix E and in Chapter 4.5. The smaller the p-value, the stronger are the differences between the means of the different leachate groups (0ml, 400ml, 800ml, 1600ml and 2400ml). The Tukey Kramer test (a multiple comparison test), which pinpoints just where the real differences lie, is performed only if the p-value falls below 0.05 (Science, (n.d.)).

In the Tukey Kramer test the means of every treatment are compared to the means of every other treatment. In this way it identifies where the differences of two means are greater than the standard value. The formula used is known as Tukey Kramer Formula and goes as follows: $Qcrit*\sqrt{((MSE/2*(1/n_1+1/n_2))}$. Finally the result compares whether there is a significant difference between certain means, which is indicated by the abbreviation “Sig” or if there is no significant change, which is indicated by the abbreviation “NS” (see chapters 4.3 and 4.5). Looking at the result tables of the Tukey Kramer Test an exact analysis can be performed.

Most of the data that has been collected in this thesis is presented in the Appendices at the end of this paper and the final data after calculation can be found in this chapter.

4. Results and discussion

All results of the lab experiments, which were the main experiments of this paper, can be found in Appendix D. This is to give an overview of everything that needed to be done in order to be able to make an analysis in Chapter 5 and reach a conclusion. The tables of Appendix D show a very basic presentation of the data, using different colour shades to show positive, negative or no changes. Trend lines are used to show whether there seems to be an increase or a decrease in contact angle which indicate a change of hydrophobicity. In Table 42 “All results of WDPT and MED” the colour green is used to show a positive change in the soil after leaching, yellow indicates no change and red indicates a negative change, meaning the soil becomes more hydrophobic after leaching.

4.1 Soil Property Results (Appendix A)

The table below shows the general soil properties such as soil pH, water content before and after winter, the soil bulk density, the particle density and the pore volume which was used as a measure for the water that needs to be applied on the soils.

Table 2 General Soil Properties

Soil Type	Soil pH	Water content before winter [g/g]	Water content after winter [g/g]	Soil bulk density ρB [g/cm³]	Particle density ρS [g/cm³]	Porosity of soil = 1-(ρB/ρS)	Pore Volume [ml]
Gley	5.94	1.19	0.91	0.50	1.97	0.77	193.39
Organic	5.32	0.76	0.90	0.32	2.19	0.84	210.33
Brown	5.94	0.74	1.29	0.43	2.21	0.81	202.56

In the table above, the results of the general soil property calculations can be found. The exact calculations to each result can be followed in Appendix A.

Looking at the pH, gley and brown soil have about the same pH of 5.94 whereas the organic soil measures a more acid pH of 5.34. The comparatively low pH could be identified as one of the reasons for the high degree of hydrophobicity of the organic soil, as low pH impedes microorganisms from decomposing organic matter and hence, the hydrophobic substances cannot be decomposed as quickly.

According to the data on soil density, gley soil has the highest density of the three soils with a value of 0.50 g/cm³, brown soil with 0.43 g/cm³, and the organic soil with only 0.32 g/cm³. The bulk density indicates the level of compaction and porosity of the soil as it takes into account the pore space in the soil. The density calculated for these soils is very low compared to recently cultivated soils that have soil bulk densities which range from 0.9 to 1.2 g/cm³ (McLaren & Cameron, 1996). As the soil was taken from Taranaki region, and soils that derive from volcanic ash have lower bulk densities, the values seem to be plausible. Also the fact that there are a greater amount of organic compounds in these soils (Deurer et al., 2011), as they are very water repellent, reduces the bulk density.

The particle densities of the soils used range from 1.97 g/cm³ of the organic soil to 2.21 g/cm³ of the brown soil. These are still relatively low values as usually for mineral soils the particle density is assumed to be around 2.67 g/cm³, however, as organic matter has a particle density of around 1.3 g/cm³ (McLaren & Cameron, 1996), these soils are also expected to have lower densities, since they have a higher content of organic material.

In addition to the general soil properties, gravimetric water content of the soils before 2011/04/28 and after winter 2011/08/28 was also calculated for the field experiments. The exact calculations for these data can be found in Appendix A, Table 23 and Table 24. Brown and organic soils have about the same water content at an average of 0.74 g/g and 0.76 g/g respectively, while gley soil has a relatively high water content of 1.19 g/g. This however changes after the soil receives more moisture during winter which leaves the organic soil by the end of winter with 0.9 g/g and the brown soil with an even higher gravimetric water content at 1.29 g/g. However, for reasons that are pointed out in the “Analysis of results“, the gley soil unexpectedly reduced its water content to 0.91 g/g during the winter.

4.2 Trial Procedure (Appendix B)

Table 3 Change of Molarity of Ethanol used to infiltrate into the soil within 10sec

Molarity of Ethanol	Gley1	Gley2	Gley3	Organic1	Organic2	Organic3	Brown1	Brown2	Brown3
0.171									
0.342									
0.513									
0.684									
0.855									
1.026									
1.368									
1.71									
2.052									
2.393									
2.735									
3.077									
3.419									
3.932									
4.445									
4.958									
5.471									
5.981									

	results without wash
	results after wash
	Both

The table above shows the trial procedure. Appointing the yellow filled out results as the degree of hydrophobicity *before* any leaching was done, and the light blue ones *after* the final leaching, also indicating positive changes. Dark blue means in this case that there was no change. This table was set up to merely show in the simplest and fastest way that there is change between before and after leaching without having to do any further contact angle calculations, since when the Molarity of Ethanol decreases, so does the hydrophobicity. Assuming that in this case, lime just helped to quicken the effect, it was not used in the main experiment, as the research question is only trying to find a correlation between water percolation to change hydrophobicity and dissolved organic carbon leaching from the soil without any chemical input.

4.3 Field Experiments

(The collected data that provide the basis of the results that are stated in this section, refer to the tables in Appendix C)

It is hardly possible to get a valid result from the field data analysis, as the samples were taken during random times. The first one was taken at the beginning of January 2010 by M. Deurer which was right in the middle of summer. Then another one was taken at the beginning of April 2011 and yet another at the end of April 2011 which can both be considered as the end of summer/fall. The final sampling was taken after winter, in the end of August 2011. Data before and after winter were mainly compared.

An ANOVA test was performed in order to find out whether the differences are significant as such, that there is an obvious change in hydrophobicity after the precipitation during winter increased to 6.9mm/day at the organic soil field sites (Table 7), and to 6.4mm/day at the gley soil field sites (Table 8). As a result it turns out that the brown soil data results cannot be used for further analysis, as the resulting p-value from the ANOVA test is, with a value of 0.41, far above the threshold value of 0.05 resulting in insignificant differences between the data.

The organic soil on the other hand does show significant changes between the Summer 2009/2010 (Start Jan-10)) and the end of August 2011 (End Aug-11), as well as between the beginning of April 2011 (Start Apr-11) and end of August 2011 (End Aug-11) and between the end of April 2011 (End Apr-11) and the end of August 2011 (End Aug-11) (see Table 4). The first three samples have in common that they were all taken in or after summer. Therefore, the results have shown that after winter the hydrophobicity of organic soil did go down significantly compared to the time during and after summer. However, this only applies to the contact angles and when looking at the final result after winter, and after a prolonged wet period, the contact angle only went down to 101.72 compared to the 103 during summer 2010. This result (Figure 22), however, still shows a very high hydrophobicity and when looking at the water droplet penetration time, all treatments can be categorized as “extreme persistent”, not showing any change at all at any of the different times of the year.

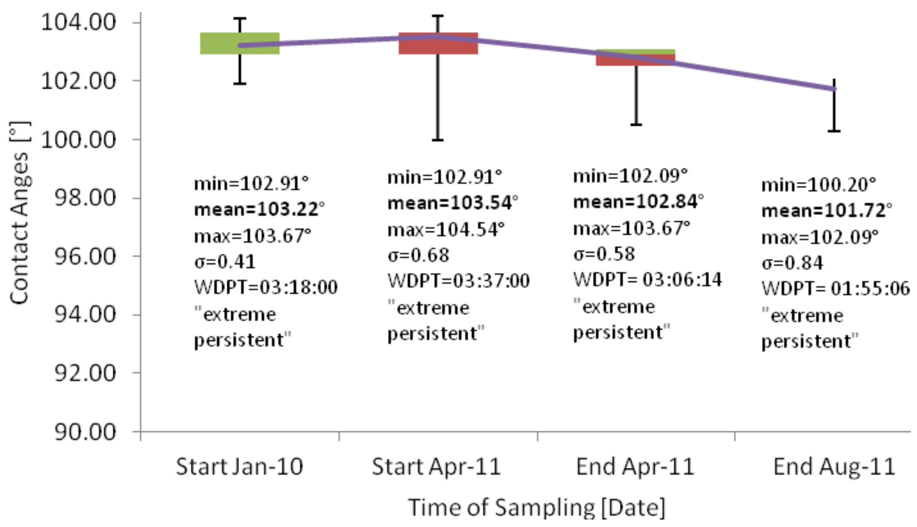

Figure 22 ANOVA: Field Experiment Organic Soil

p-value=0.0016

Table 4 ANOVA - Tukey Kramer Test: Field Experiment Organic Soil

	Start Jan-10	Start Apr-11	End Apr-11	End Aug-11
Start Jan-10				
Start Apr-11	NS			
End Apr-11	NS	NS		
End Aug-11	**Sig**	**Sig**	**Sig**	

As according to the ANOVA results for the gley soil, the p-value is also below 0.05, significant differences were also detected. The Tukey Kramer Test finds significant differences between the first and third as well as the first and the fourth sampling taking period (Table 5). This can be due to the fact that the first was taken at the hottest time of year, and therefore the hydrophobicity was the highest during that time. However, the differences of the WDPT-test results only lie within severely persistent and strongly persistent (Figure 23).

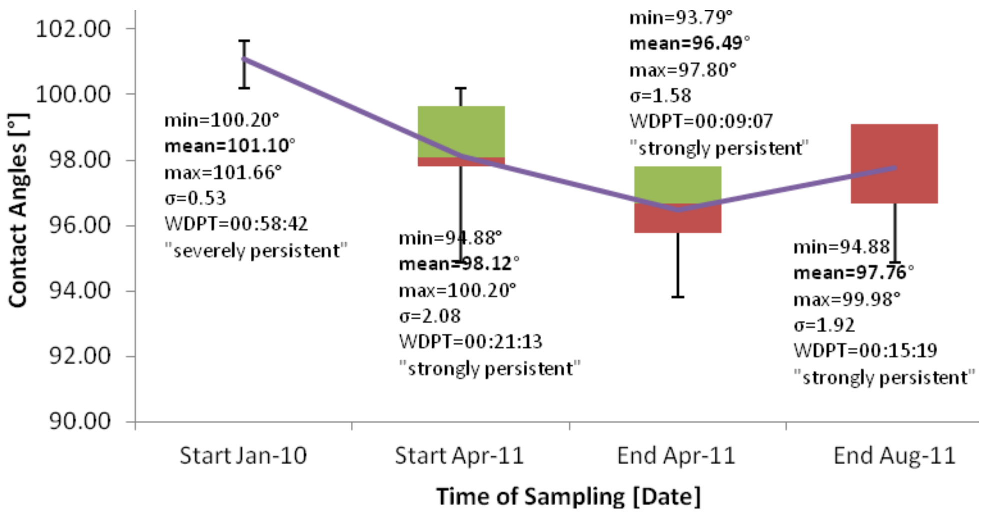

Figure 23 ANOVA: Field Experiment Gley Soil

p-value=0.0015

Table 5 ANOVA - Tukey Kramer Test: Field Experiments Gley Soil

	Start Jan-10	Start Apr-11	End Apr-11	End Aug-11
Start Jan-10				
Start Apr-11	NS			
End Apr-11	**Sig**	NS		
End Aug-11	**Sig**	NS	NS	

According to the ANOVA results of the brown soil, no significant difference of the data could be found, as the p-value was calculated to 0.4, which is much higher than 0.05. Therefore the Tukey Kramer Test did not need to be performed here. The WDPT went from extremely persistent to severely persistent, which is a decrease, but not a significant one (Figure 24).

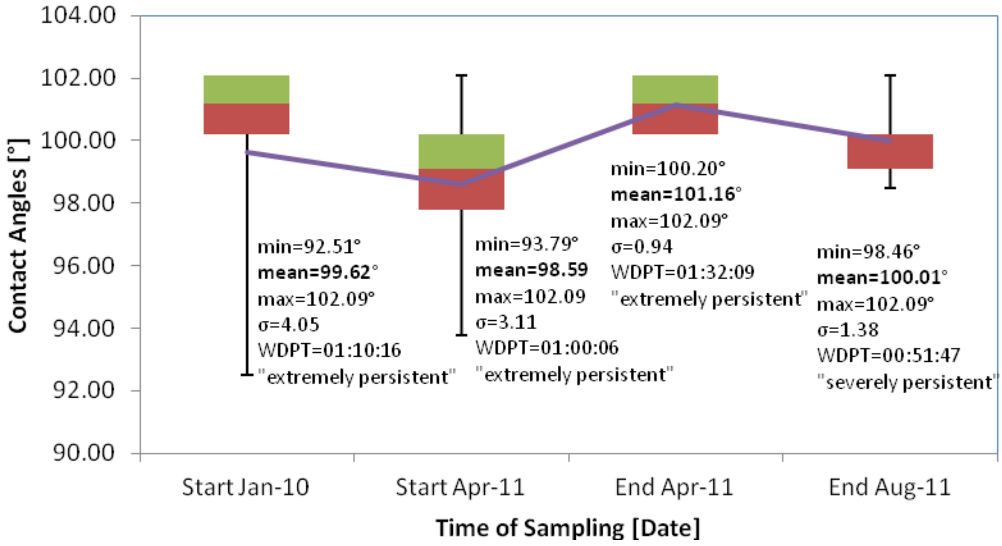

Figure 24 ANOVA: Field Experiment Brow Soil

p-value=0.4076

The carbon contents of the soils that were used for the experiment are listed in Table 6, for the exact values of which the averages were calculated see Table 29 of Appendix C. To make sure that the carbon content did not change over the time periods of sampling taking, one done by M. Deurer in 2010 and the second done for this present study in 2011, the carbon contents were taken again and recorded (see Table 32 of Appendix C). The carbon contents stayed about the same, so the initial soils that have been compared can be said to have the same initial state. These data can be taken for further analysis to find out whether carbon content of the soil does reduce, when the DOC in the leachate increases after infiltration, which however is not part of this study.

Table 6 Average Carbon Contents of Soils

	C% 2010	C% 2011
Gley Soil	10.36	10.48
Organic Soil	21.92	20.50
Brown Soil	10.28	10.06

Data of precipitation during the times of field experiment sampling taking are presented in the following three tables. These results were taken from the NIWA data collection for daily precipitation. According to the website of the National Institute of Water and Atmospheric Research (NIWA) the average rainfall per day for these areas was around 5mm/day, ranging between 4.88mm/day of the brown soil to 5.32 mm/day of the gley soil. From the time between the third sampling taking in April 2011 and the third in August 2011 it was expected that due to the increase in rainfall during winter, the hydrophobicity would be reduced or even eliminated. The average rainfall per day during this period for all three soils ranges between 6 and 7mm/day which is slightly higher than the average daily precipitation per year (Table 7, Table 8, Table 9). As the results of the hydrophobicity test have not exactly shown an obvious change in hydrophobicity, the precipitation data here can be seen as general information in terms of completeness of the field experiment not to prove any correlation between hydrophobicity and precipitation. Through the following tables it can be seen, however, that the precipitation during winter is generally slightly higher than during summer or the rest of the year.

Table 7 Precipitation Data Organic Soil

Precipitation between the sampling takings

Timeperiod between sampling		Precipitation [mm/day]	Soil Moisture [mm/day]	Average Rainfall per Year [mm/day]
1.1.2010 -	31.3.2011	4.51	-45.13	
1.4.2011 -	24.4.2011	4.89	-12.33	
25.4.2011 -	28.8.2011	6.89	3.66	5.21

Table 8 Precipitation Data Gley Soil

Precipitation between the sampling takings

Timeperiod between sampling		Precipitation [mm/day]	Soil Moisture [mm/day]	Average Rainfall per Year [mm/day]
1.1.2010 -	31.3.2011	4.59	-44.53	
1.4.2011 -	24.4.2011	4.89	-11.63	
25.4.2011 -	28.8.2011	7.02	3.52	5.34

Table 9 Precipitation Data Brown Soil

Precipitation between the sampling takings

Timeperiod between sampling		Precipitation mm/day	Soil Moisture mm/day	Average Rainfall per Year [mm/day]
1.1.2010 -	31.3.2011	4.20	-48.27	
1.4.2011 -	24.4.2011	5.50	-17.54	
25.4.2011 -	28.8.2011	6.43	3.06	4.88

4.4 Results of Contact Angels and Water Droplet Penetration Time Test of Lab Experiments (Appendix D)

All the direct results for each soil and replicate of WDPT test as well as the according MED concentrations that took the droplets less than 10 seconds to enter the soils are listed in Table 42 of Appendix D. Every single test that was performed in the main experiment is listed here. This shows for example that per replicate used in a cylinder, there were five WDPT tests done. In some cases there was not one obvious result for the MED, instead two that both seemed to work were used and both recorded in the table. The four columns on the right of this table use colours to indicate whether there is a positive change (=green) indicating decrease in the hydrophobicity, no change (=yellow) where the hydrophobicity stays the same or a negative change (=red) indicating increase in the hydrophobicity of the sample. The columns are divided into a comparison of first and second treatment, second and third treatment and so on, whereas the last column includes the entire treatment for that particular replicate and shows whether hydrophobicity did or did not change from 0ml treatment to 2400ml treatment.

According to this table, it is obvious that the brown soil seems to be very consistent with the results, as all the treatments show a positive change for the soils' hydrophobicity. However, looking at gley and organic soil, the results are not that obvious. Looking at the gley soil, there is still a majority of improvement of the soil in terms of hydrophobicity, as there are eight positive results, four samples that stayed the same and only one negative result, however, the conclusion needs to be analyzed further, as was done in Appendix E using the ANOVA Test. Also the organic soil shows similar uncertainties as the gley soil treatments, as here the results were made up of eight positive impacts, two samples that stayed the same, and four samples actually increased their water repellency.

In the following three figures, the average values of the different soil for hot water as well as for cold water were used to show the trendlines how contact angles change over the amount of water used for the treatment. For detail information on the calculations, see Appendix D Table 39, Table 40 and Table 41.

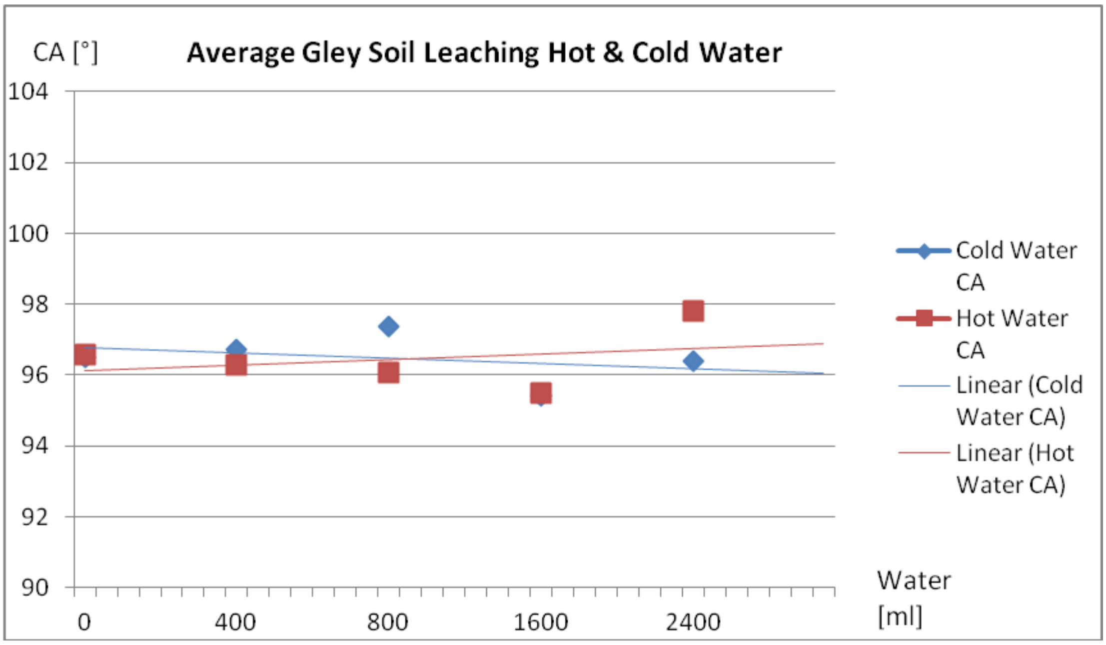

Figure 25 Average Gley Soil Leaching Hot & Cold Water

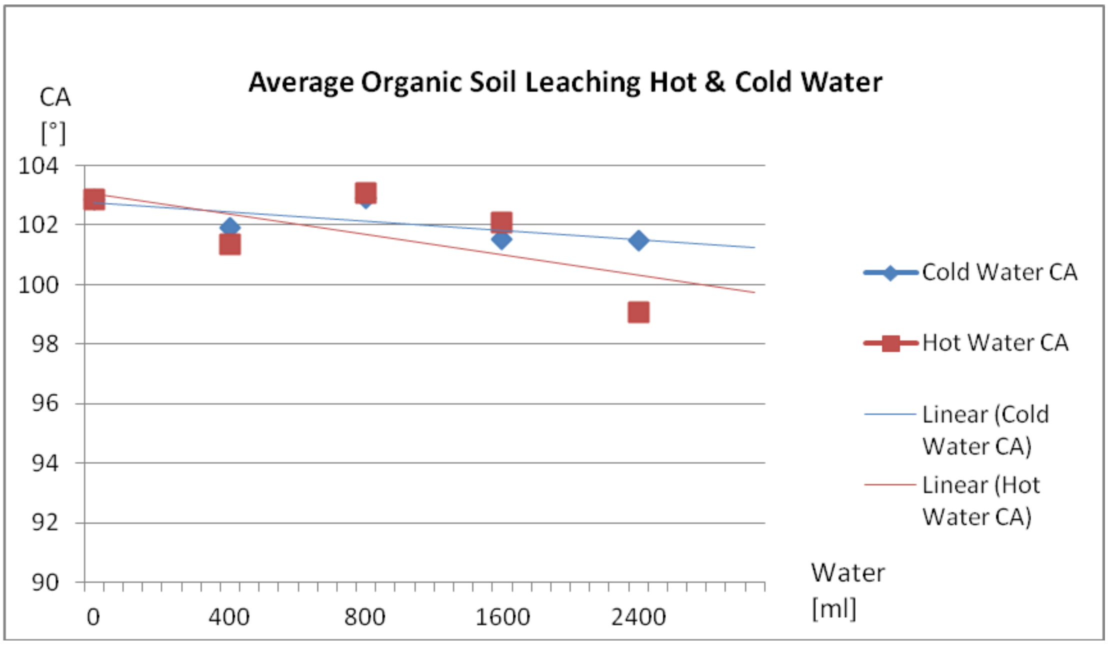

Figure 26 Average Organic Soil Leaching Hot & Cold Water

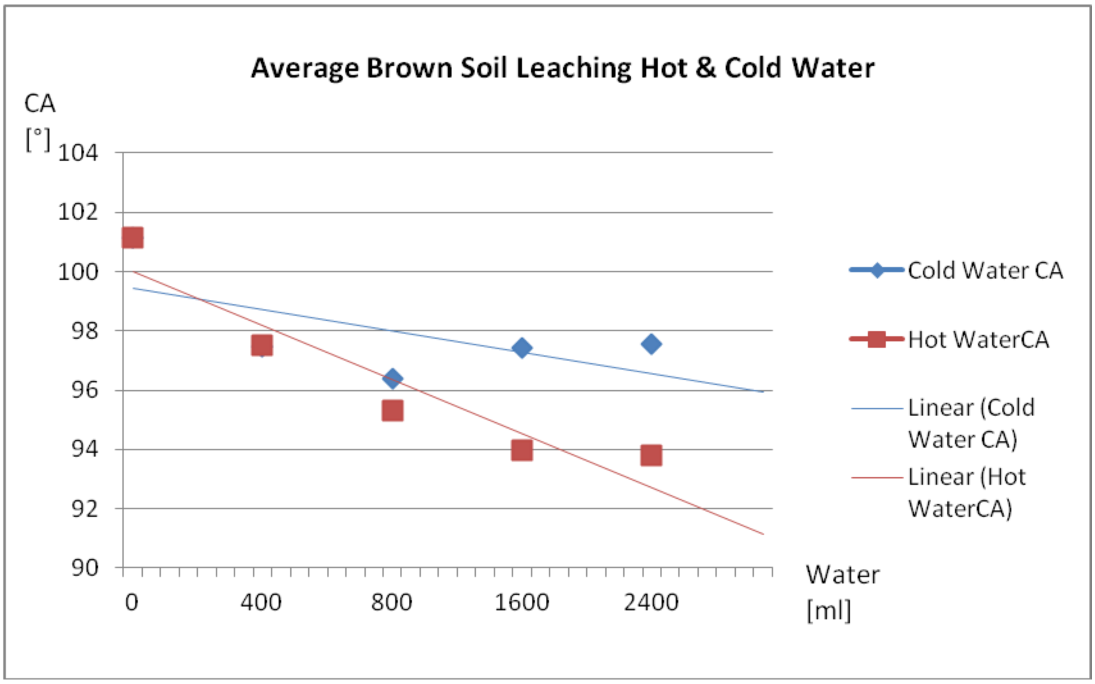

Figure 27 Average Brown Soil Leaching Hot & Cold Water

The points in the graphs indicate the averages of the calculated contact angles in the tables, which indicate the severity/degree of hydrophobicity in the soil, as described in section 3.4. For each table the averages were calculated, put in the diagram and a trend line was constructed by Excel to show, whether according to the averages, there is an increasing or decreasing trend in the soil hydrophobicity. The red graphs indicate the hot water application and the blue indicates the cold water application. As it was interesting to find out whether hot and cold water applications have a different effect on the hydrophobicity, both graphs were placed on the same diagram so a comparison could be made. According to these diagrams, there seems to be a very slight decrease in contact angle for organic soil (Figure 26) and a very obvious decrease in the brown soil (Figure 27). In the gley soil (Figure 25), however, there actually seems to be an increase in contact angle, which indicates an increase in hydrophobicity, when using hot water and only a slight decrease when using cold water. As these are only the trend lines, and only averages are used of which the particular values vary vastly from one another, the results here cannot be taken as final indications. They need to be analyzed further using the ANOVA test; as was done in Appendix E and of which the main results can be found in the next chapter.

Correlation of MED and WDPT

The correlation between the WDPT and the MED test is shown in Figure 28. This graph shows clearly that as the contact angle increases so does the water droplet penetration time following a very steady slope. A similar graph has already been presented by Deurer et al in one of his studies in 2011 in hydrophobic soils of the North Island of New Zealand, and is just presented once again to emphasize his findings. It can also be seen as verification for the results concluded in this study.

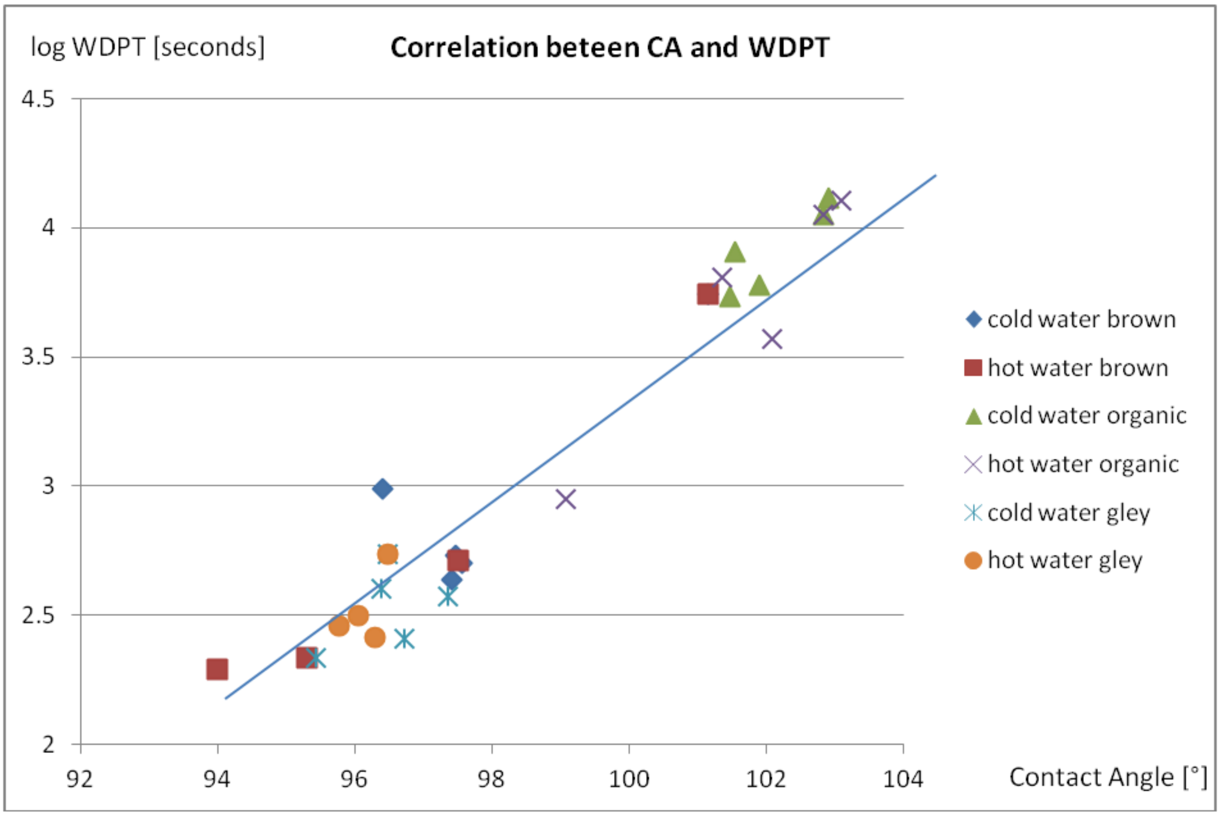

Figure 28 Correlation between MED & WDPT

4.5 Results of ANOVA Test for MED (Appendix E)

According to the ANOVA test done for contact angles for each of the 6 different experiments (2 organic soils hot and cold water leaching, 2 gley soils hot and cold water leaching and 2 brown soils hot and cold water leaching), only the brown soil and the organic soil show results that can be evaluated further.

The results found from gley soil cannot be used for future analysis as the means of the treatments do not show a significant difference that would suggest the treatment with water does affect the hydrophobicity of the soil. The Tukey Kramer Test was not applied here as the p-value is much greater than 0.05, with p=0.3779 for the cold water application on gley soils and p=0.6754 for hot water application on gley soils. The graphs for hot water and cold water applications can be found in the figures below (Figure 29, Figure 30).

4.5.1 Gley Soil ANOVA Results

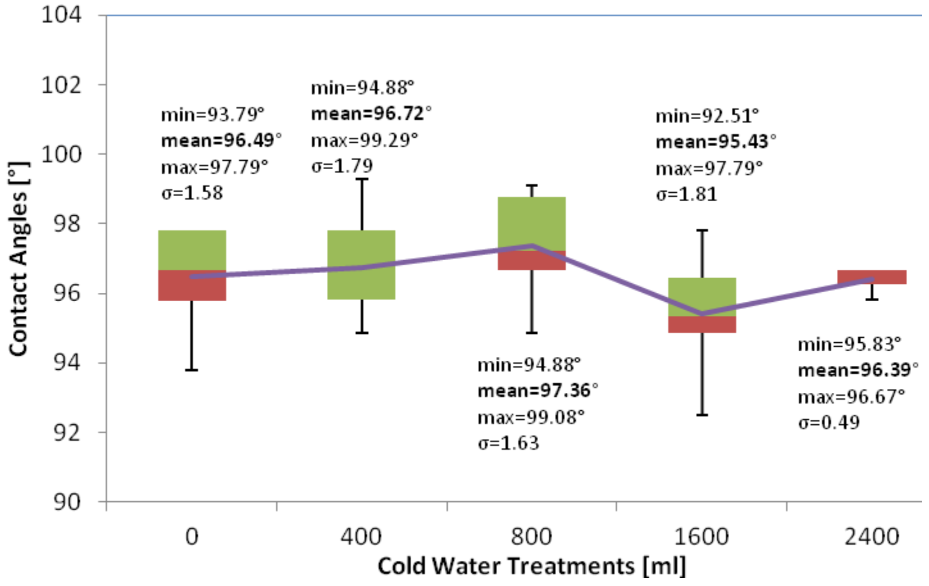

Figure 29 ANOVA: Cold water treatment Gley Soil - CA vs Treatments

p-value=0.3779

The above graph shows the average contact angles for the cold water treatment and the means, minimum and maximum values as well as the standard deviation. For more detailed information of calculations, see Appendix E Table 48 and Table 47.

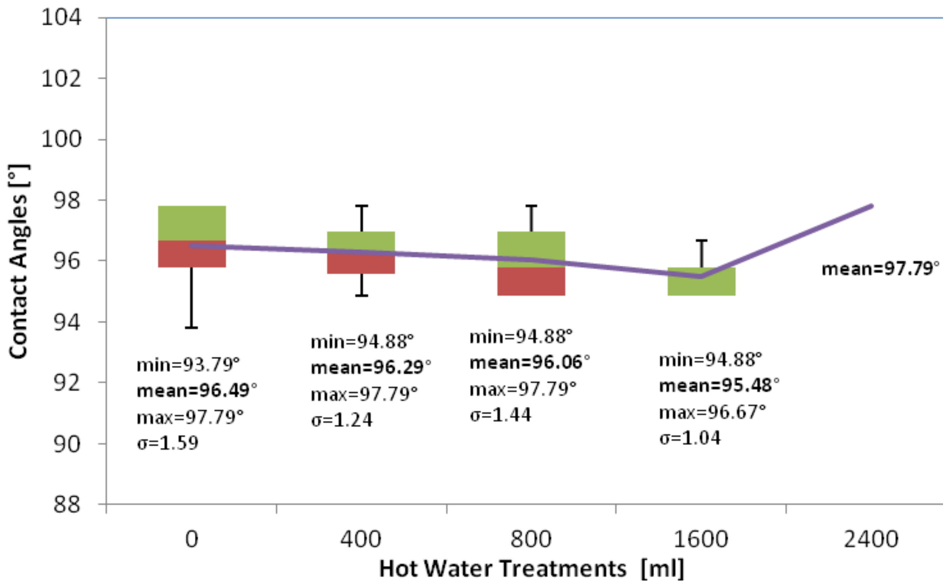

Figure 30 ANOVA: Hot water treatment Gley Soil - CA vs Treatments

p=0.6754

Figure 30 shows the average contact angles for the hot water treatment and the means, minimum and maximum values as well as the standard deviation. For more detailed information of calculations, see Appendix E Table 49 and Table 50.

4.5.2 Organic Soil ANOVA Results

As a comparison, following the next figures (Figure 31 and Figure 32) the p-value of organic soils resulted in 0.009 for cold water application and 0.0131 for hot water respectively. The ANOVA test was performed in order to find out whether the means of the different leachings are in fact significantly different from one another.
As in the following four experiments the p-value was lower than 0.05 and Fcrit<F, a Tukey Kramer Test was performed for each of them. These were both treatments of the organic soil and both treatments of the brown soil.

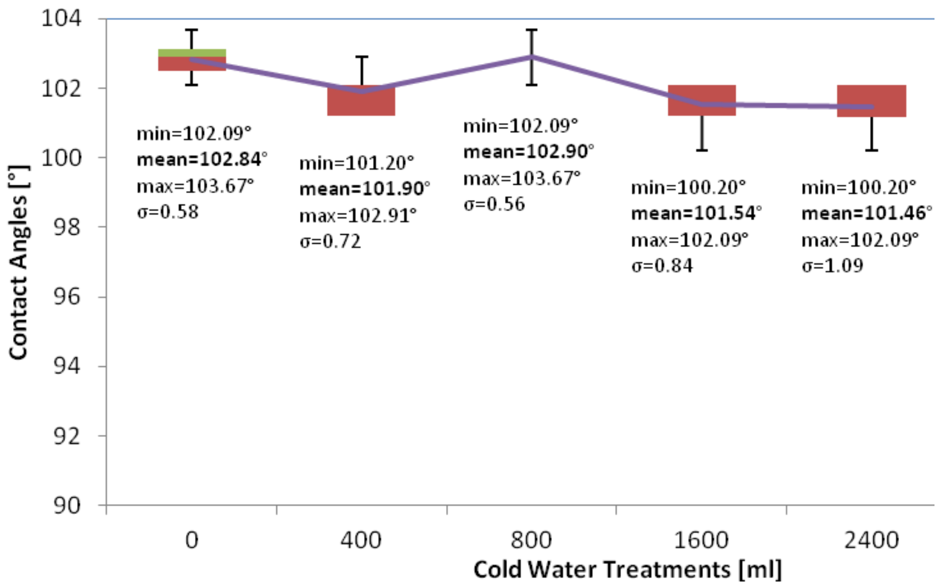

Figure 31 ANOVA: Cold water treatment Organic Soil - CA vs Treatments

p-value=0.009024

Figure 31 shows the average contact angles for the cold water treatment and the means, minimum and maximum values as well as the standard deviation of the organic soil. For more detailed information of calculations, see Appendix E (Table 43 and Table 44). As the p-value is smaller than 0.05, a Tukey Kramer test was done to find out which treatments show significantly different results from each other. Table 10 below shows the results.

Table 10 ANOVA - Tukey Kramer Test: Cold Water Treatment Organic Soil

Cold Water [ml] (Organic)	0	400	800	1600	2400
0					
400	NS				
800	NS	NS			
1600	**Sig**	NS	**Sig**		
2400	NS	NS	NS	NS	

As shown in the table above, the organic soil leaching with cold water had significant differences between the means of the first treatment (no leaching) to the 4th treatment (1600ml leaching) and the 4th treatment with the 3rd treatment (800ml leaching).

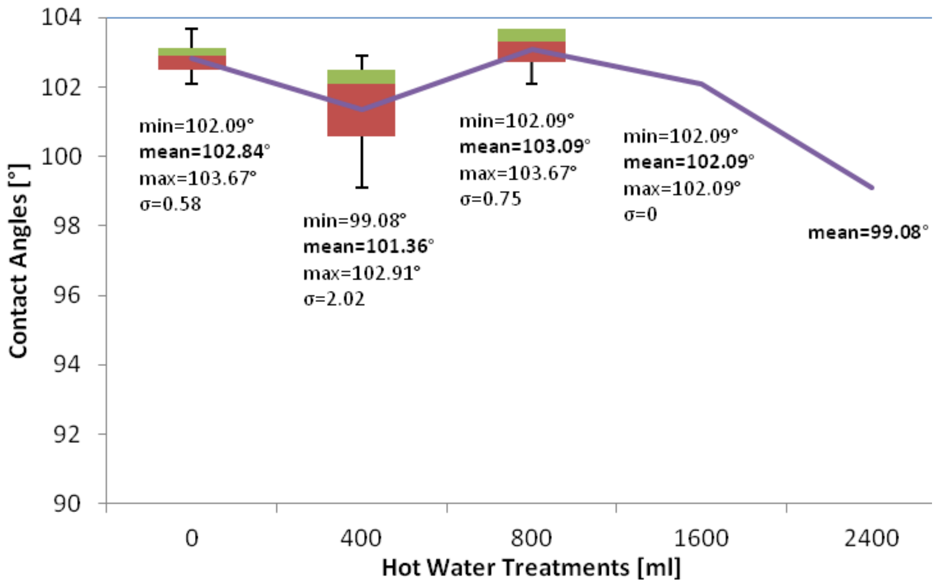

Figure 32 ANOVA: Hot water treatment Organic Soil - CA vs Treatments

p-value=0.013107

Figure 32 shows the average contact angles for the cold water treatment and the means, minimum and maximum values as well as the standard deviation of the organic soil. For more detailed information of calculations see Appendix E (Table 45, Table 46). As the p-value is smaller than 0.05, a Tukey Kramer test was done to find out which treatments show significantly different results from each other. Table 11 shows the results.

Table 11 ANOVA: Tukey Kramer Test - Hot Water Treatment Organic Soil

Hot Water [ml] (Organic)	0	400	800	1600	2400
0					
400	NS				
800	NS	NS			
1600	NS	NS	NS		
2400	**Sig**	NS	**Sig**	NS	

For the hot water leaching of organic soil the Tukey Kramer Test showed significant differences between the 1st (no leaching) and the 5th (2400ml leaching) as well as the 3rd (800ml leaching) and the 5th treatment.

4.5.3 Brown Soil ANOVA Results

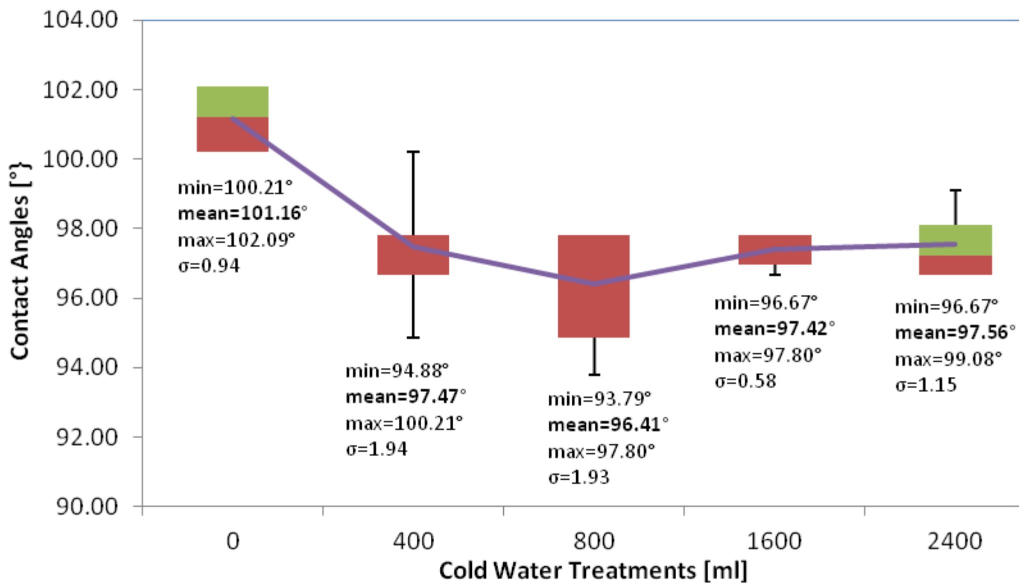

Figure 33 ANOVA: Cold water treatment Brown Soil - CA vs Treatments

p-value=3.6x10^{-5}

Figure 33 shows the average contact angles for the cold water treatment and the means, minimum and maximum values as well as the standard deviation of the brown soil. For more detailed information of calculations, see Appendix E (Table 52).
According to the p-value which is much below 0.05, and therefore gives reference to the significance of the difference between the data sets, the following table shows the significant differences.

Table 12 ANOVA: Tukey Kramer Test- Cold Water Treatment Brown Soil

Cold Water [ml] (Brown)	0	400	800	1600	2400
0					
400	Sig				
800	Sig	NS			
1600	Sig	NS	NS		
2400	Sig	NS	NS	NS	

For the Tukey Kramer Test of the brown soil cold water treatment, the final results show that there is a significant difference in means (therefore an obvious difference in hydrophobicity) between the 1st treatment (no leaching) with each of the consequent ones, however, there is no significant change between the treatments 400ml, 800ml, 1600ml and 2400ml.

As for the brown soil where hot water was applied (Table 13), again there were significant differences between the initial soil and the soils that were treated with hot water, no matter how much water was applied. Here another significant change between the results of the leaching of 1600ml and the ones of 800ml were found in the hot water leaching.

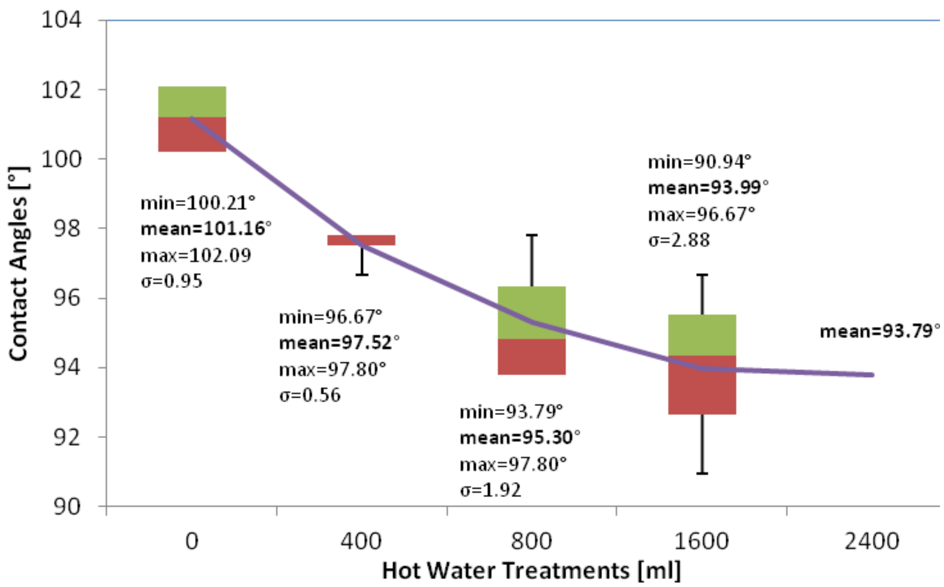

Figure 34 ANOVA: Hot water treatment Brown Soil - CA vs Treatments

p-value=8.14x10^{-6}

Figure 34 shows the average contact angles for the hot water treatment and the means, minimum and maximum values as well as the standard deviation of the brown soil. For more detailed information of calculations, see Appendix E (Table 53 and Table 54).

The graph shows the result which in the initial state of this paper was expected to be the result for all of the soils. According to the p-value which is much below 0.05 and therefore gives reference to the significance of the difference between the data sets, the following table shows where these significant differences lie.

Table 13 ANOVA: Tukey Kramer Test - Hot Water Treatment Brown Soil

Hot Water [ml] (Brown)	**0**	**400**	**800**	**1600**	**2400**
0					
400	**Sig**				
800	**Sig**	NS			
1600	**Sig**	**Sig**	NS		
2400	**Sig**	NS	NS	NS	

4.6 Results of WDPT & CA vs DOC increase

(The collected data that provide the basis of the results that are stated in this section, refer to the tables in Appendix F)

At the final stage of data collection, the WDPT data and the MED data were correlated with the DOC that was filtered from the leachate and then analyzed separately in the Landcare lab of Massey University. Here, not only the mg/l of DOC was used, but the total amount of DOC that the soil lost by draining with water. This is to show that as the soils DOC content decreases (which is the obvious conclusion if DOC is found in the leachate), the hydrophobicity of the soil also decreases and in the case of brown soil, using hot water leachate, the soil even seems to be becoming hydrophilic.

4.6.1 Gley Soil WDPT & CA vs DOC Results

The following two graphs (Figure 35, Figure 36) show the relationship of WDPT and CA with the DOC in gley soils. The graphs do not show any obvious correlation. Even though the trend line of the cold water treatment in gley soil seems to have a tendency to decrease hydrophobicity as the DOC found in the leachate increases, however in such a remote way that no definite conclusion can be drawn from it. The graphs of the hot water leachate in gley, however, show opposite results with the contact angle increasing as DOC increases and the WDPT decreasing as the DOC increases. These results comply with the results of the ANOVA test earlier in 4.5.1, where it was statistically analyzed that the hydrophobicity does not change in a significant way.

Table 14 GLEY SOIL cold water leaching: DOC vs WDPT vs CA

Gley Soil Cold DOC vs WDPT & CA		
Total DOC [mg]	WDPT [sec]	CA [°]
0.00	547	96.49
1.73	255	96.72
4.53	375	97.36
8.40	216	95.43
8.00	401	96.39

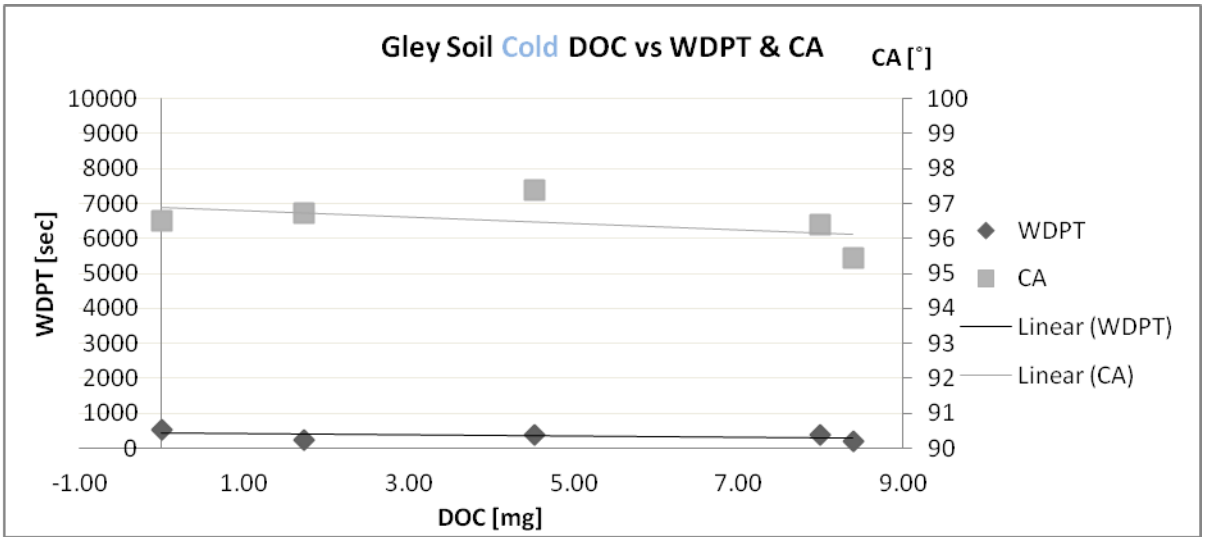

Figure 35 Gley Soil cold water leaching: Decrease of WDPT&CA as DOC increases

When hot water is used for leaching, the results show an increase in DOC that is leached out, however still not great enough to actually decrease hydrophobicity. The calculated results are presented in the following Table 15 and graphically displayed in Figure 36.

Table 15 GLEY SOIL hot water leaching: DOC vs WDPT vs CA

Gley Soil Hot DOC vs WDPT & CA		
Total DOC [mg]	WDPT [sec]	CA [°]
0.00	547	96.49
8.53	258	96.29
17.87	314	96.06
48.53	288	95.78
64.80	12	97.79

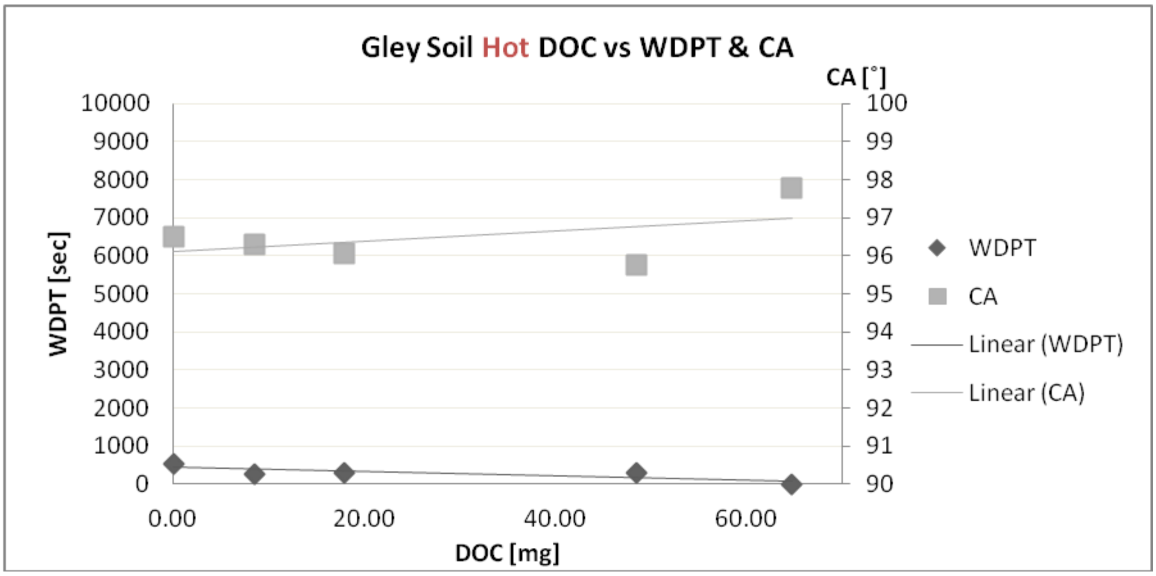

Figure 36 Gley Soil hot water leaching: Decrease of WDPT&CA as DOC increases

4.6.2 Organic Soil WDPT & CA vs DOC Results

The following two graphs show the relationship between DOC vs. WDPT and DOC vs. CA for **organic soil** that was leached with cold water (Figure 37) and hot water (Figure 38) respectively.

The calculated values are presented in the Table 16.

Table 16 ORGANIC SOIL cold water leaching: DOC vs WDPT vs CA

Organic Soil Cold DOC vs WDPT & CA		
Total DOC [mg]	WDPT [sec]	CA [°]
0.00	11174	102.84
2.53	6011	101.90
4.00	13054	102.90
11.60	8064	101.54
10.40	5439	101.46

The graph below shows the decrease of hydrophobicity with the slow increase of dissolved organic carbon in the leachate. Even though organic soil has very high carbon contents originally, the dissolved organic carbon amount that leached out was not much greater than the one of gley soil. However, when looking at the hot water leaching of organic soil in Figure 38 the quantity that has leached out is much smaller than that of hot water leaching.

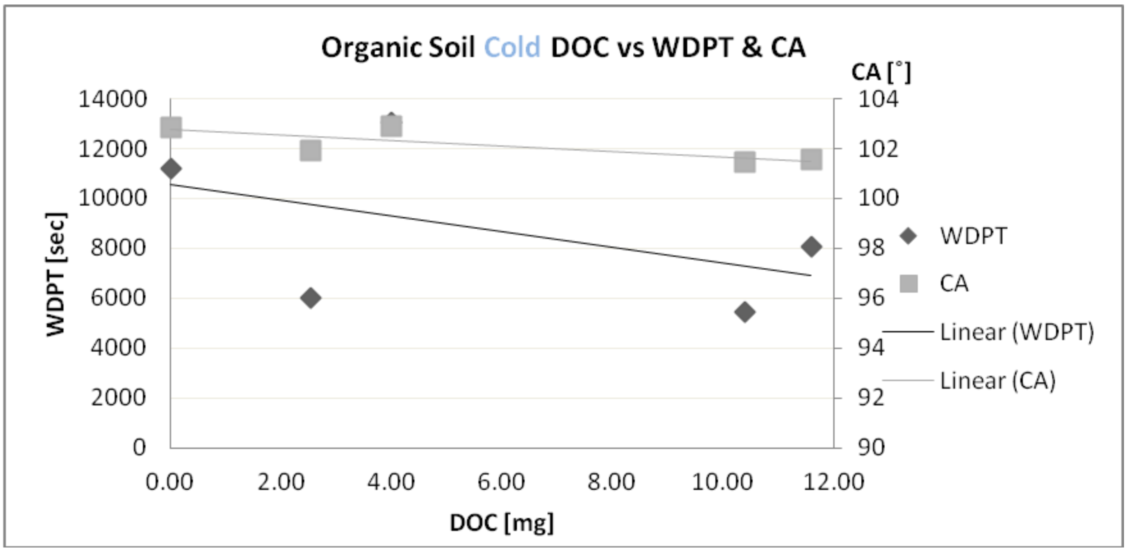

Figure 37 Organic Soil cold water leaching: Decrease of WDPT&CA as DOC increases

The following table presents the results of hot water application on the organic soil replicates. The quantity of dissolved organic carbon is up to 17 times as high as when cold water is used. The hydrophobicity decreases according to the WDPT test by a great amount whereas the contact angles do not show these obvious results. If during the statistical data analysis the

WDPT data had been taken instead of the CA, the results would probably have shown much more significant differences than they did in the analysis done for this study.

Table 17 ORGANIC SOIL hot water leaching: DOC vs WDPT vs CA

Organic Soil Hot DOC vs WDPT & CA		
Total DOC [mg]	WDPT [sec]	CA [°]
0.00	11174	102.84
18.53	6390	101.36
38.13	12803	103.09
122.67	3711	102.09
170.40	892	99.08

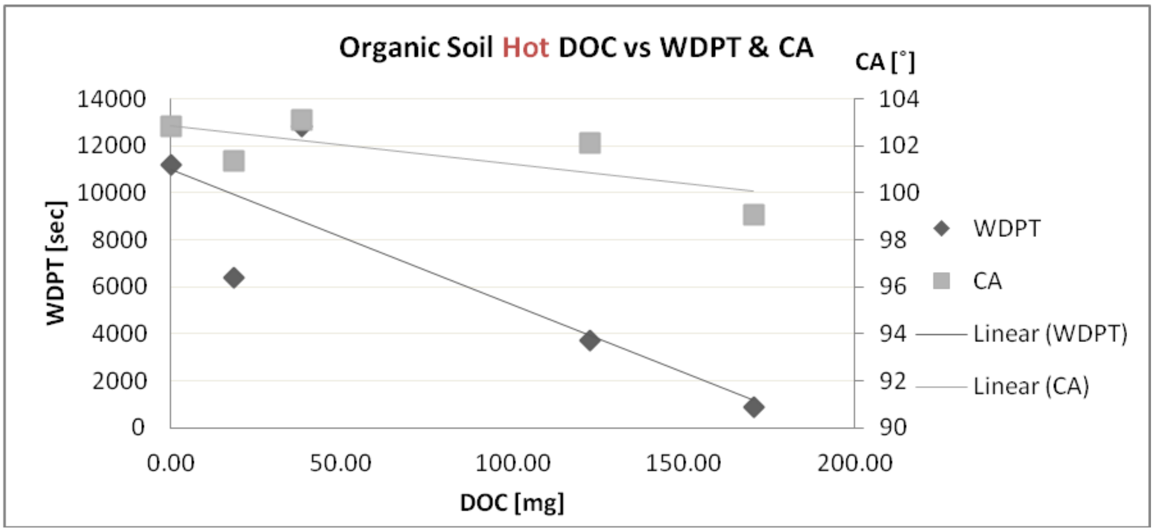

Figure 38 Organic Soil hot water leaching: Decrease of WDPT&CA as DOC increases

4.6.3 Brown Soil WDPT & CA vs DOC Results

Looking at each result separately, the first graph of brown soil cold water leaching (Figure 39) shows the relationship between the water droplet penetration time and the dissolved organic carbon found in the leachate, as well as the relationship between the contact angles, which stand for the severity of hydrophobicity in the soil. Here it can be seen that both graphs show a decrease as DOC increases, with WDPT having a steeper curve than the curve of the CA. The curve itself is only the trend line placed in between the points of measure, and each point is only the average of all the measures taken for each treatment. When looking at the points and the line they would make if they were connected, the graph resulting from it would be an exponential graph. This form was expected to result at the initial state of data collection. The first leaching shows the greatest drop of hydrophobicity resulting in an exponential decrease. To show this even more clearly refer to the following chapter 4.6.4 where the combined results are displayed.

Table 18 BROWN SOIL cold water leaching: DOC vs WDPT vs CA

Brown Soil Cold DOC vs WDPT & CA		
Total DOC [mg]	WDPT [sec]	CA [°]
0.00	5529	101.16
2.10	541	97.47
5.87	976	96.41
13.20	436	97.42
13.60	501	97.56

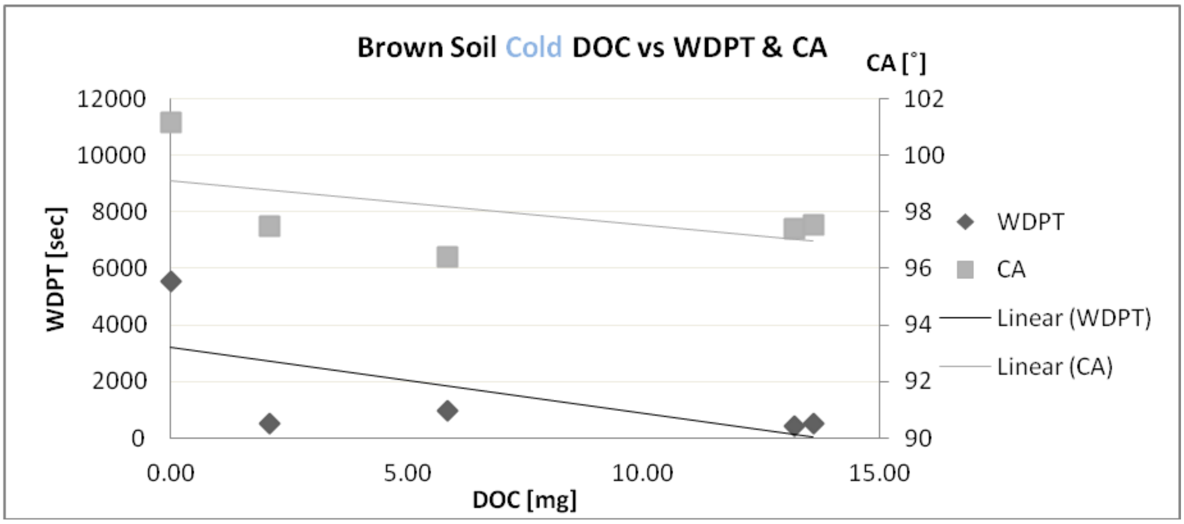

Figure 39 Brown Soil cold water leaching: Decrease of WDPT&CA as DOC increases

As the results of the previous cold water leaching, the following table shows the calculated values of DOC, WDPT and CA of the brown soil hot water leaching. There is a strong decrease from the first to the second soil application following a slow decrease. The DOC leached here using hot water are about nine times as high as those in the previous treatment.

Table 19 BROWN SOIL hot water leaching: DOC vs WDPT vs CA

Brown Soil Hot DOC vs WDPT & CA		
Total DOC [mg]	WDPT [sec]	CA [°]
0.00	5529	101.16
13.73	515	97.51
42.67	215	95.30
117.87	196	93.99
97.20	35	93.79

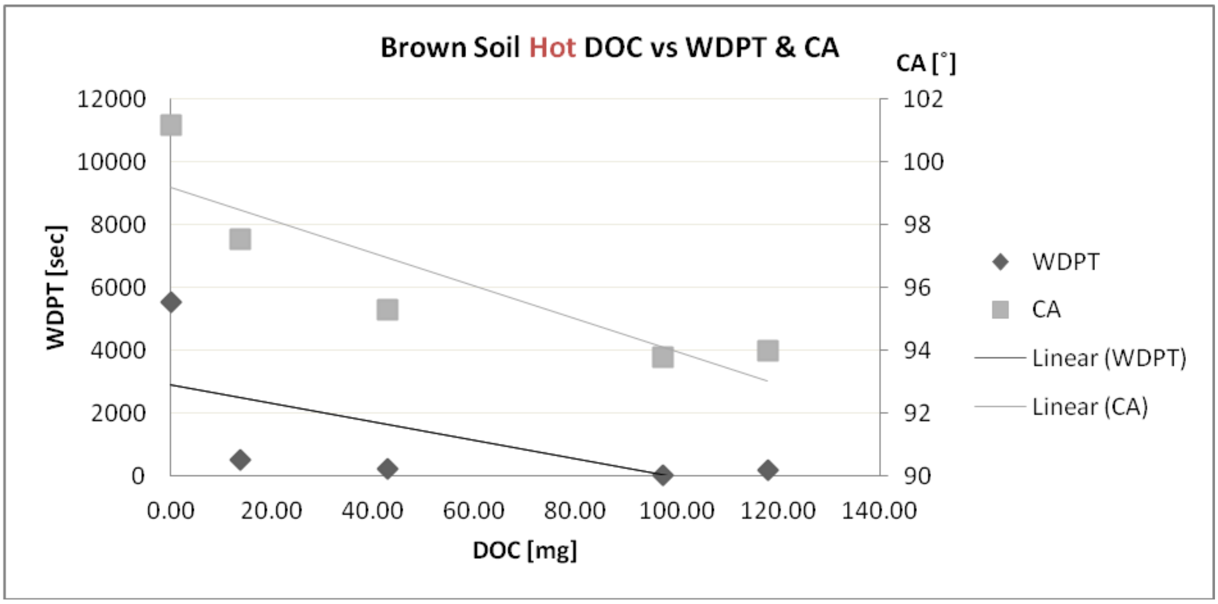

Figure 40 Brown Soil hot water leaching: Decrease of WDPT&CA as DOC increases

The graphs that resulted from the treatment of brown soil show much more obvious results. This data can be used for further analysis. Again, when connecting the exact points there is an obvious and steep decrease in WDPT and in the contact angle after the first leaching with 400ml. After the next leaching the decrease becomes less obvious, but still continues till the final application. As 90° is the threshold for a soil to be considered hydrophobic, as well as for the WDPT it can be said to be around 10sec, the graphs do show a tendency to become hydrophilic if the experiment was continued with more hot water.

4.6.4 Combined results (hot&cold) of WDPT & CA vs DOC

The following graphs were added to show a combination of hot and cold water leachate of organic and the brown soil, as these are the soils where the results for water application did make a significant difference according to chapter 4.5 and according to the DOC vs WDPT and contact angle.

Table 20 shows the combined data of the previous section including the quantity of water used for each treatment.

Table 20 BROWN SOIL: hot and cold water treatment - DOC vs WDPT vs CA

Brown soil cold and hot water treatment: DOC vs WDPT & CA			
Treatment water [ml]	Total DOC [mg]	WDPT [sec]	CA [°]
0	0.00	5529	101.16
400	2.10	541	97.47
800	5.87	976	96.41
1600	13.20	436	97.42
2400	13.60	501	97.56
400	13.73	515	97.52
800	42.67	215	95.30
1600	117.87	196	93.99
2400	97.20	35	93.79

When drawing an adjusting the graph to all the data combined, an exponential decreasing graph is the result. This result was initially expected, and will be explained in the data analysis in the following section.

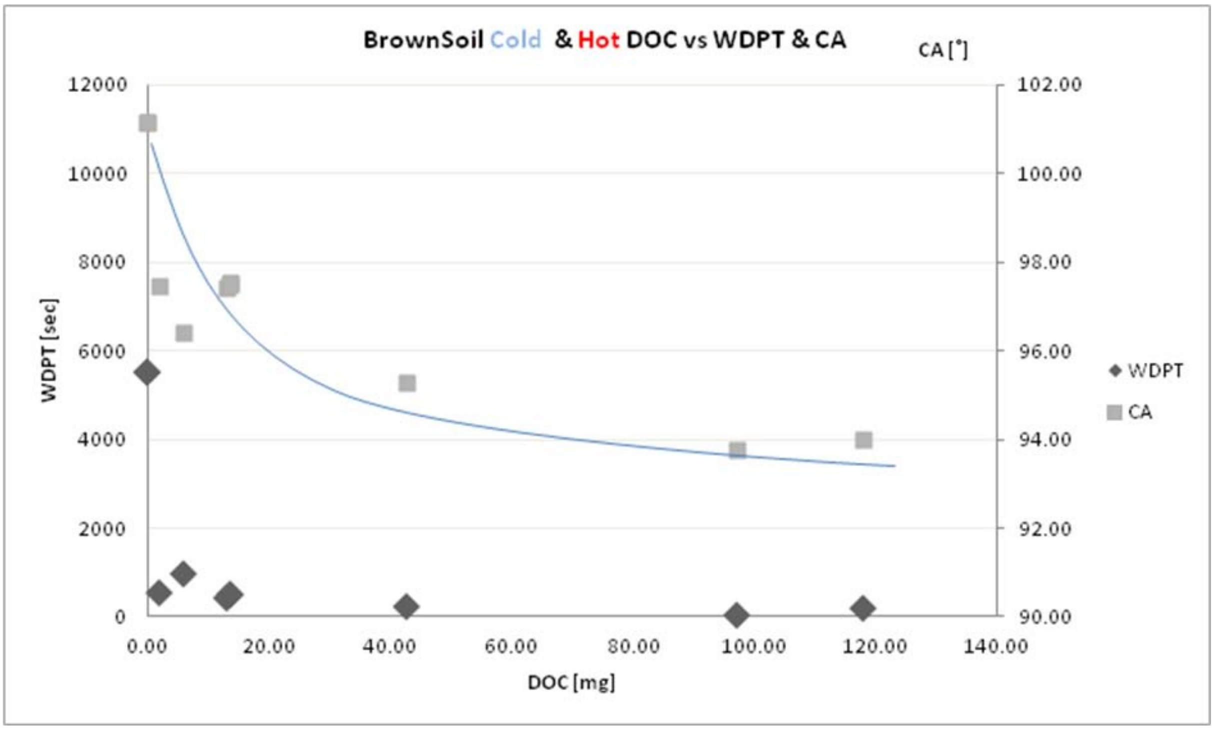

Figure 41 BROWN SOIL: hot and cold water treatment - DOC vs WDPT vs CA

Table 21 shows the combined results of the previous section for organic soils. Here, similar to the combined results of the brown soil, the DOC leached using hot water is much greater than using cold water. However, the results of change in hydrophobicity are not as obvious as before, as the contact angles do not show such an obvious decrease, contrary to the penetration times.

Table 21 ORGANIC SOIL: hot and cold water treatment - DOC vs WDPT vs CA

Organic soil cold and hot water treatment: DOC vs WDPT & CA			
Treatment water in ml	Total DOC in mg	WDPT	CA
0	0.00	11174	102.8431
400	2.53	6011	101.8995
800	4.00	13054	102.9016
1600	11.60	8064	101.5369
2400	10.40	5439	101.4642
400	18.53	6390	101.3642
800	38.13	12803	103.0876
1600	122.67	3711	102.094
2400	170.40	892	99.08437

The graph resulting from the organic soil combined data can be found below, however, as there does not seem to be a clear graph resulting (exponential or linear) only the points of data are presented, with interpretations left open for discussion. Analysis for these results can be found in the next section.

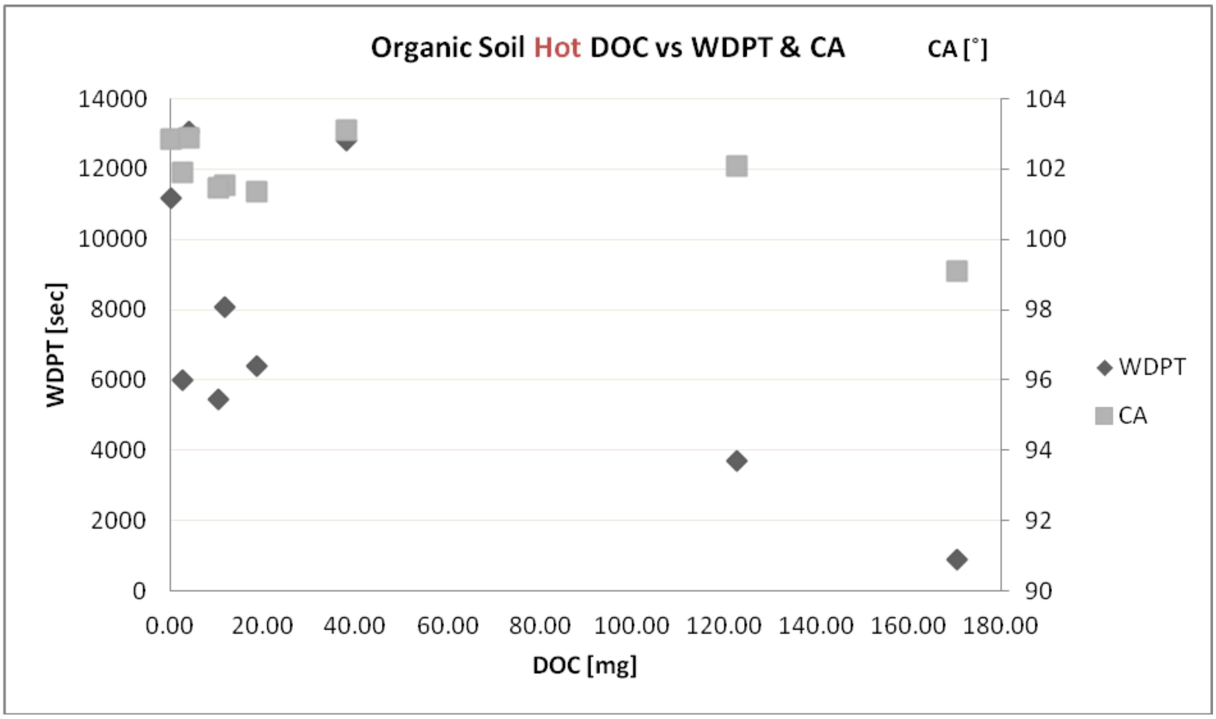

Figure 42 ORGANIC SOIL: hot and cold water treatment - DOC vs WDPT vs CA

5. Analysis of results

5.1 Field Experiment

When comparing the water content of the soils before and after winter, there was an obvious increase in water content for the brown soil and also a bit of an increase for the organic soil. As only the water contents in “End Apr-11” and “End Aug-11” were taken, only these data can actually be compared with the statistical analysis of ANOVA of chapter 4.3. As there were no significant differences in hydrophobicity, neither for brown soil nor for gley soil at these two dates, the hydrophobicity change cannot be correlated with the water content or precipitation. Only the organic soil showed significant differences for these data, and the increase in water content might be part of the reason. However, as there was no correlation between the other soils and the increase/decrease in water content, it can be concluded that the water content does not seem to be a major factor concerning hydrophobicity. The field samples have been taken too randomly to make an analysis possible. As this was only marginally important for the present thesis, the main focus lies on the lab experiments which were done according to a set method and timeframe.

5.2 Lab Experiment

As the results in 4.6 present, it is evident that when applying the WDPT and the MED for defining water repellency, the hydrophobicity does decrease in most cases. The most obvious results and changes can be found in brown soils, however. The reason might be that it only takes a very thin layer of carbon compounds to line up around the soil particles to make the soil hydrophobic. As the carbon quantity of brown soil is much less than that of the organic soils, and the bulk density is less than that of gley soils, the amount of water used for these experiments seems to have been sufficient to leach out most of the DOC that was assumed to be the main factor making the brown soil hydrophobic. In one case using hot water leaching, the soil actually changed to be hydrophilic again. However, the amount of water used for the experiments was not sufficient to change the very hydrophobic organic soil into a hydrophilic soil. The amount of carbon in these soils is initially about 22% compared to the 10% of brown soil and gley soil.

According to the hydrophobicity results of **gley soils**, no significant differences were detected, therefore the data results cannot be correlated with the DOC content in the leachate. Gley soil initially had a lower degree of hydrophobicity compared to the other soils. Possibly due to the higher compactness of gley soils (bulk density is 0.5), the carbon compounds directly surrounding the soil particles were rearranged rather than leached. The amount of DOC leached was less than for the other two soils, however, compared to the brown soil there was not a great difference. As the soil is more compact it seems that only other carbon compounds, not the ones surrounding the soil particles forming the hydrophobic layer, were leached. This compactness could also be observed when filling up the soil cylinders with water. It took a greater amount of time for the water to be drained through the soil as the pores were too tight together.

Figure 28 shows the correlation of WDPT and CA, therefore if WDPT decreases, CA should also decrease. The values for the contact angles of Figure 36 do not have the same tendency as the WDPT values, which might be an indication for a mistake made during lab experiments. As according to the ANOVA results, where only the contact angles were analyzed, gley soil in general does not show significant changes between water treatments. Therefore, gley soil cannot be used to indicate the relationship between DOC and hydrophobicity. In addition, the results of summed up DOC do not seem to make any sense, as for the leaching of 2400ml the amount of DOC found in the leachate was less with only 8mg than the total amount of DOC found in 1600ml with 8.4mg. Therefore, when looking at the graphs of WDPT and CA vs. DOC in chapter 4.6.1, it can only be emphasized once again, that the experiments performed in this study, were not suitable for finding a change of hydrophobicity for gley soils.

The ANOVA results of **brown soil** show the greatest change in hydrophobicity after water is applied for the first time. The Tukey Kramer calculation finds a significant difference of means between the first treatment and each of the subsequent ones. Looking at the graph, a very steep drop in hydrophobicity can be found right after the first leaching and then only very slight changes can be detected for the next four treatments. Before the experiment took place, it was expected that the highest quantity of hydrophobic substances actually does exit the soil once the soil gets wet up for the first time, and that the remaining hydrophobic substances need a much greater effort to disappear. This agrees with a study done recently, where it was found that the first leaching event had the greatest effect on WDPT, reducing the time by already 95% (Hardie et al., 2011).

Also, concluding from the final graph in chapter 4.6.4, where the brown soil hot and cold water treatment is correlated with the dissolved organic carbon, the degree of hydrophobicity, as well as the persistence of hydrophobicity decrease suddenly after the first water application. With additional water, the decreasing of water repellency continues, however at a much slower rate. This again agrees with previous findings in the field, that when soil is completely dried out after summer, the degree of hydrophobicity seems to be very high and as the winter progresses, and the soil is moist, it can take up water much easier, making the soil sometimes even hydrophilic again. This conclusion however, could not be reached in this present study, as field research was not the main focus of this study, and much more field data would have needed to be collected in order to draw a valid conclusion.

In hydrophobic soils, soil particles are coated with 'hydrophobic waxy skins' which in general are made up of amphiphilic molecules which have a hydrophobic (non-polar) and a hydrophilic (polar) end. In wet soils they are arranged in a way that they attach themselves to the soil particles on their hydrophobic side, leaving the hydrophilic side exposed to the water that attracts the soil. Once the soil dries out however, they turn 180° such that the hydrophilic end is faced towards the capillary moisture that is held tight around the soil particle, leaving the non-polar end, which has no affinity to water, exposed. This non-polar end repels the water so that a water droplet can stay on its surface just like it could stay on wax (Slay, 2007). For this reason the first rewetting of the soil makes the greatest impact on the soil in terms of the change in hydrophobicity. As DOC represents all types of organic carbons that are dissolved, these include the substances that represent these "waxy skins". Lipids, waxes and resins represent the more difficult breakdown of soil organic matter that are the main components of these hydrophobic soil coatings (Slay, 2007) and are part of the solutions that are expected to leach out as DOC when water is applied on the surface.

It is expected that the cold water treatment for brown soils would eventually show the same results as the hot water treatment, making the soil hydrophilic after much more of DOC is leached out using a higher quantity of water. Even though in the case of hot water treatment the soil did not become completely hydrophilic after all. It did show a tendency of the graph coming closer and closer to the contact angle of 90 however, where it is said that the soil changes from being hydrophobic to hydrophilic.

Whether the results really give a conclusion about the relationship of DOC with the hydrophobicity of the soil is still a question that needs to be analyzed in the future. According to the results of the graphs in chapters 4.6.3 and 4.6.4 there seems to be a clear relationship in the case of brown soil. However, the other soils still need to be analyzed maybe also by introducing new and more accurate methods to measure soil water repellency, as discussed in Chapter 5.3 neither of the WDPT and the MED tests are flawless.

The reason why **organic soil** does not show such an obvious reduction in hydrophobicity is most likely due to the fact that organic soil has a huge amount of carbon in its initial state with carbon contents of 20-22%. It would therefore take a much greater amount of water to leach out the carbon that makes the soil hydrophobic. For this reason, brown soil shows much better results for this analysis, as the same amount of water was used for each soil overlooking the fact, that different amounts of carbon content in the initial soils would have needed different amount of water applications.

According to a recent study it was found that the critical contact angle, above which the SWR is at least moderately persistent, is at 93.8°. Above this angle, it is more likely that SWR leads to economic and environmental impacts under pastoral land-use (Deurer et al., 2011). When comparing the data of this study, the initial soils after soil sampling are all above this contact angle, which means the negative impacts on the agricultural industry are inevitable. After treatments, only the brown soil using hot water application actually drops just below this contact angle, with an average of 93.78°. This means, that the treatment with water alone, even when looking at the brown soil, is not a good method to get rid of hydrophobicity. Similar results were found in a recent study in Australia, where it turned out that the magnitude of rainfall did contribute to reduction of severity and stability of water repellence, however not alone. There were other factors involved such as root activity, duration of saturation, leaching, rainfall intensity or microbial activity (Hardie et al, 2011).

5.3 Problems and Improvements for procedure

The methods used for this experiment, even though easy to handle, might not be the most accurate methods (however the only known method at this point in time) to find out the severity of hydrophobicity. The water droplet penetration test is criticized for its inconsistency. This is mainly because, if a soil is hydrophobic, it does not mean that at each single spot of the soil surface the WDPT would be equal. If only five droplets are placed, the values can vary vastly from one another. Research on a bigger scale is needed to find methods that indicate better results. Also, the WDPT is very time consuming, and is therefore not a good method if data is needed quickly.

Changes in original properties of the three phases (solid, liquid and gas) are excluded when using the MED calculation during the solid liquid contact (Berg, 1993; (Roy&McGill, 2002)). Soil surfaces have such heterogeneous distribution of chemical groups that very specific interactions can take place. Even in soils with water repellency some polar, polarized or H-bonding groups can be found that have a strong affinity to water. There could be faster evaporation of ethanol than of water across the liquid/gas interface or dissolution of soil components and preferential sorption of ethanol across the solid/liquid interface. The contact time for MED test is limited to 10seconds as it is accepted that system composition does not change significantly during this time (Roy&McGill, 2002).

When soils are sieved, to limit the range of pore size diameters, even though the soil surface chemistry is hardly changed, soil aggregates could be broken down. This might increase the ration of hydrophilic to hydrophobic area if the interior of the aggregates is more hydrophilic. In this case, as the soils were sieved in a moist state after water application, just a slight percentage of soil passed through the sieve easily, and the rest needed to be crushed in order to make passing through the sieve easier. This could have effected abrasion and dilution that might have altered the soils chemistry. However, as water repellent soils are usually characterized by poor structure, these errors should be very small.

If ethanol solutions are stored for a long time, they may change in composition as a result of microbial growth, ethanol decomposition, and volatilization. As the ethanol solutions were already prepared before April 2011, and the same solutions were used for all the experiments, which took place over a three months period, this could have had a negative effect on the test solutions. Usually ethanol solutions that are stored in the fridge should be replaced every month (Roy&McGill, 2002), however, due to the limited time, the same solutions were used for all the experiments.

The water droplet penetration test might have had slight errors when recording some of the infiltration times. Due to the amount of time that is needed for one single droplet to enter the soil, all the soils that were stored at a time in the oven, were used at the same time for the WDPT test. Five droplets were placed on each petri-dish with soil and all of the drops were recorded simultaneously. The time was recorded, without stopping the stopwatch, and as it is not possible to look at all the drops at the same time, the noted times might have an error to up to a few minutes. This, however, does not affect the definition of the persistency of the SWR, as according to the WDPT the times are not analyzed according to seconds or minutes, but rather as specific timeframes with certain levels of persistency. To improve the method used, it would be wise to take undisturbed soil cylinders directly from the field.

Due to plant route channels or possible earthworm activity, but also the interface between the flat wall of the cylinder and the soil, preferential flow occurred on various soil replicates. This last issue was tried to be avoided by creating a fringe on the sidewalls, to cover the gap between soil and wall. This did lead the water directly through the soil avoiding the sidewalls, however, preferential flow through pore channels could not be avoided. To avoid this problem, every leachate for each replicate could have been noted down and analyzed for preferential flow. Then these data could have been compared to each other and analyzed in detail. This, however, was not done in detail, as the time was limited and the research was focused more on collecting as much data as possible in order to perform correlation of data.

Some of the water that was leaking through the soil did not reach the beaker underneath, but leaked directly into the vacuum box. This could affect the DOC concentration, as it is possible that a higher concentration of DOC mg/L might have leaked and was then not available for analysis. This might have affected the data results. During lab experiments it was recorded where this kind of leaking occurred. However, as there were only very few replicates where this was the case, the effects this error might have had on the results was discarded in this thesis.

6. Conclusion

Soil hydrophobicity is a complex phenomenon that has caused many scientists all over the world to ponder over how it occurs, where it comes from, and what can be done against it. This thesis has yet again found that the answer to the question is not of simple character. The Field data analysis has not shown an answer to this problem. As the main focus on this paper was set on the lab experiments, creating data on changes of hydrophobicity in three different types of soils compared to the increase in dissolved organic carbon in the leachates, it turned out that only the brown soil, which is of very light nature and at its initial state the carbon content is not very high, showed the results that were hypothesized in the beginning of this paper. As the soil gets wet up for the first time, most of the dissolved organic carbon that seems to be the reason for hydrophocicity gets leached out of the soil. The subsequent water treatment does decrease the hydrophobicity further, however not as after the first treatment. The relationship between hydrophobicity and DOC is therefore in mathematical terms a decreasing exponential function. It is not just the quantity of DOC within the soil, to make the soil hydrophilic but rather a combination of soil compactness, initial carbon content of the soil and quantity of water applied.

The method of water treatment without applying any other chemicals or treatments does not seem to be a sufficient method to reduce hydrophobicity in the field. As the amount of water that would be needed to reduce hydrophobicity is much greater than seems to be economically plausible. Also, using irrigation for the field would probably encourage overland flow more than it would actually enter the soil. Further research is definitely needed to find better solutions for the problem of hydrophobicity.

7. Bibliography

Aslam, T., Deurer, M., Mueller, K., Clothier, B., Northcott, G., & Ghani, A. (2009). Does an increase in soil organic carbon improve the filtering capacity of aggregated soils for organic pesticides? - A case study. *GEODERMA, A Global Journal of Soil Science* , pp. 187-193.

Council, T. R. (2004). *Taranaki Regional Council*. Retrieved January 8, 2012, from http://www.trc.govt.nz/assets/taranaki/publications/publications/cdem/group-plan/taranaki.pdf

Deurer, M. & Bachmann, J. (2007). Modelling Water Movement in Heterogenous Water-Repellent Soil: A Conceptual Numerical Simulation. *Vadose Zone Journal* , pp. 446-457.

Deurer, M. & Mueller, K. (2010). Workshop: Towards a better understanding of the causes, effects and remediation of soil hydrophobicity. Palmerston North and Ruakura: Plant & Food Research.

Deurer, M., Mueller, K., Dijssel, C. v., Mason, K., & Clothier, J. C. (2011). *Survey of soil water repellency in New Zealand.* The New Zealand Institute for Plant & Food Research Ltd.: Palmerston North.

Deurer, M., Müller, K., van den Dijssel, C., Mason, K., Carter, J., & Clothier, B. (2011). Is soil water repellency a function of soil order and proness to drought? A survey of soils under pasture in the North Island of New Zealand. *European Journal of Soil Science* .

Doerr, S. (2007, Summer). Fear of Water. *Planet Earth* , pp. 18-19.

Doerr, S. H., Shakesby, R. A., & MacDonald, L. H. (2009). Soil Water Repellency: A Key Factor in Post-Fire Erosion? In A. &. Cerda, *Restoration Strategies after Forest Fires.* Wales.

Doerr, S., Ritsema, C., Dekker, L., Scott, D., & Carter, D. (2007, July 30). Water repellence of soils: new insights and emerging research needs. *Hydrological Processes; Volume 21, Issue 17* , pp. 23-28.

Ghani, A., Dexter, M., & Perrot, K. W. (2002). Hot-water carnon is an integrated indicator of soil quality. *Wold Congress of Social Science.* Thailand.

Ghani, A., Dexter, M., & Perrott, K. W. (2003, March 17). Hot-water extractable carbon in soils: a sensitive measurement. *Soil Biology & Biochemistry 35* , pp. 1231-1243.

Goolge. (n.d.). *Google Maps*. Retrieved September 2011, from http://maps.google.com

Hallett, P. D. (2007). An Introduction to Soil Water Repellency. *Proceedings of the 8th International Symposium on Adjuvants for Agrochemicals (ISAA2007).* Columbus, Ohio, USA: International Society for Agrochemical Adjuvants (ISAA).

Hardie, M. A., Cotching, W. E., Doyle, R. B., & Lisson, S. (2011, August 30). Influence of climate water content and leaching on seasonal variations in potential water repellence. *Hydrological Processes*

Jeyakumar, P., & Deurer, M. (2011, November). A newsletter about water in the soil-plant-atmosphere system. *WISPAS* .

Klute, A. e. (1986). *Methods of Soil analysis Part 1.* Soil Science Society of America.

Landcare, R. (1996-2012). *Landcare Research, Manaaki Whenua*. Retrieved January 7, 2012, from http://www.landcareresearch.co.nz/services/laboratories/eclab/eclabmethods_waters.asp

Landcare, R. (2011). *New Zealand Soil Portal*. Retrieved December 13, 2011, from http://soils.landcareresearch.co.nz/contents/SoilNames_NZSoilClassification_SoilFormation.aspx?currentPage=SoilNames_NZSoilClassification_SoilFormation&menuItem=SoilNames

Lewthwaite, E. (n.d.). *NIWA Tauhoro Nukurangi*. Retrieved September 9, 2011, from New Zealand's climate archive, past and present: http://www.niwa.co.nz/our-science/ei/environmental-information-update/environmental-information-update-01-april-2011/niwaas-national-climate-database-a-the-robust-archive-of-new-zealandas-climate-past-and-present

Deurer, M., J. B. (2007). Modelling Water Movement in Heterogenous Water-Repellent Soil: A Conceptual Numerical Simulation. *Vadose Zone Journal* , pp. 446-457.

McLaren, R., & Cameron, K. (1996). *Soil Science.* Melbourne: Oxford University Press.

Molloy, L. (1998). *Soils in the New Zealand Landscape the living mantle.* Wellington: Mallinson Rendel Publishers Ltd.

Mueller, K., Deurer, M. (2010). *Environmental and economic consequences of soil water repellency.* Retrieved February 9, 2012, from NZ Grassland Association: http://www.grassland.org.nz/publications/nzgrassland_publication_45.pdf

Mueller, K., & Deurer, M. (2011, August 10). Review of the remediation strategies for soil water repellency. *Agrculture, Ecosystems and Environment 144* , pp. 208-221.

Mueller, K., Deurer, M., Slay, M., Aslam, T., & Carter, J. a. (n.d.). *www.grassland.org.nz/publications/nzgrassland_publication_45.pdf.* Retrieved August 27, 2011, from Environmental and economic consequences of soil water repellency under pasture.

Münziger, A., & Rodriguez, J. S. (1999). *Water Repellent Soils*. Retrieved February 9, 2012, from DEVELOPMENT OF AMELIORATION STRATEGIES TO REDUCE ENVIRONMENTAL DETERIORATION AND AGRICULTURAL PRODUCTION LOSSES IN WATER REPELLENT REGIONS: http://www.water-repellency.alterra.nl/

Roy, J. L., & McGill, W. B. (2002, February). Assessing soil water repellency using the Molarity of Ethanol Droplet (MED) Test. *Soils Issues Vol. 167* , pp. 83-97.

Roy, J. L., & McGill, W. B. (2002). Assessing Soil Water Repellency using the Molarity of Ethanol Droplet (MED) Test. *Soil Science* , 83-97.

Science, C. (n.d.). *www.cbgs.k12.va.us.* Retrieved from How to run statistical Tests in Excelhttp: http://www.cbgs.k12.va.us/cbgs-document/research/Statistical%20Tests%20in%20Excel.pdf

Slay, M. (2007). *'Soil Water Repellency', its cause and possible amelioration strategies for hydrophobic soils at Maraetotara, Hawke's Bay.* Hasiting, New Zealand: Meat and Wool New Zealand.

Swansea, U. (2009). *Soil Hydrophobicity Research*. Retrieved December 1, 2011, from http://geography.swan.ac.uk/hydrophobicity/soil_hydrophobicity.htm

WRB, I. W. (2006). *World reference base for soil resources.* Rome: Food and Agriculture Organization of the United Nations.

Zhang, B., Peng, X., Zhao, Q., & Hallet, P. (2004, December). Eluviation of dissolved organic carbon under wetting and drying and its influence on water infiltration in degraded soils restored with vegetation. *European Journal of Soil Science* , pp. 725-737.

Appendix A - Soil Property Calculations

pH results

Table 22: Results of the pH analysis

Soil	pH	Average pH of Soils
B#6	5.76	
B#7	6.11	**5.94**
G#7	5.86	
G#3	6.01	**5.94**
O#4	5.3	
O#6	5.34	**5.32**

Gravimetric water content before and after winter

Water content after Summer

Table 23 Water Content before winter 2011

Soils	Gravimetric water content m_w/m_s	Standard- deviation	Average gravimetric water content of soils [g/g]
O#1	0.78		
O#2	0.79		
O#3	0.72	0.04	**0.76**
G#1	1.34		
G#2	1.02		
G#3	1.22	0.16	**1.19**
B#1	0.83		
B#2	0.73		
B#3	0.67	0.08	**0.74**

Average precipitation per day in the previous 4 months of April, 28, 2011 (December 27, 2010 – April 27, 2011) for:

Organic Soil = 4.91 mm/day

Gley Soil = 5.04 mm/day

Brown Soil = 4.54 mm/day

Water content after Winter

Table 24 Water Contents after winter 2011

Soils	Gravimetric water content m_w/m_s	Standard deviation	Average gravimetric water content of soils [g/g]
O#4	0.91		
O#1	0.91		
O#5	0.84		
O#3	0.94	0.04	**0.90**
G#3	0.73		
G#1	0.94		
G#4	0.84		
G#5	0.90		
G#2	1.12	0.15	**0.91**
B#2	1.23		
B#3	1.27		
B#1	1.39		
B#4	1.30		
B#5	1.27	0.06	**1.29**

Average precipitation per day between the soil sampling 2 and 3, in the previous 4 months of August 28, 2011 (April 28, 2011 – August 28, 2011) for:

Organic Soil = 8.65 mm/day

Gley Soil = 8.84 mm/day

Brown Soil = 7.91 mm/day

Bulk Density

Table 25 Bulk Density of Soils

Soil Bulk Density			
Soil	**Weight of dry soil [g]**	**Volume of soil [cm^3]**	**ρB [g/cm^3]**
Gley soil	49.49	98.175	0.50
Organic soil	31.48	98.175	0.32
Brown soil	42.01	98.175	0.43

Particle Density

Table 26 Particle Density of soils

Particle Density ρS						
Soil	**Weight of Flask with 100ml of Water**	**Weight of Flask + soil + water filled to 100ml**	**Volume of Soil (Vs) [ml]**	***Mass of soil [g]***	**ρS [g/ml] = ms/Vs**	**Average ρS**
B#1	157.95	171.27	11.68	25	2.14	
B#2	143.97	157.92	11.05	25	2.26	
B#3	157.41	171.11	11.3	25	2.21	**2.21**
G#1	144.2	157.8	11.4	25	2.19	
G#2	161.3	174.97	11.33	25	2.21	
G#3	147.07	160.5	11.57	25	2.16	**2.19**
O#1+O#2	155.58	168.03	12.55	25	1.99	
O#3	146.68	158.79	12.89	25	1.94	**1.97**

Porosity of soils and pore volume calculation

Table 27 Porosity and Pore Volume of Soils

Soil	**Particle Density ρS [g/cm^3]**	**Bulk Density [g/cm^3]**	**Porosity of soil = 1-(ρB/ρS)**	**Pore volume [ml]**	**Pore volume*4 used for first experiment [ml]**
Brown soil	2.21	0.43	0.81	218.03	872.13
Gley soil	2.19	0.50	0.77	208.17	832.67
Organic soil	1.97	0.32	0.84	226.40	905.61

Volume of Soil in ϕ8.3cm cylinder

=270.53 [cm^3]

Appendix B - Trial Procedure

Application for Lime ($Ca(OH)_2$)

Usually 750kg of $Ca(OH)_2$ are used on pastures per hectare

Core surface (diameter 80mm) = 0.083m

	A=πr^2	0.005026548	m2
One cylinder surface area is =		5.02655E-07	ha
	g of Ca(OH)2 per ha	g of Ca(OH)2 per cylinder	
	750000g	=0.376991118	g

0.38 g of $Ca(OH)_2$ was applied per cylinder

An additional 10ml water was applied per day for 3 days to make the process of $Ca(OH)_2$ infiltrating into the soil easier.

Table 28 Trial Procedure in Laboratory, Results of DOC leached out

	DOC [mg/L] *Leachate [L]			
Soil Type	DOC in Leachat 1	DOC in Leachat 2	DOC in Leachat 3	DOC in Leachat 4
B#1	4.31086			11.94597
B#2	5.11106			0
B#3	5.4304			29.31632
G#1	1.65264			1.4919
G#2	1.63488			2.88834
G#3	2.93272			2.69775
O#1	3.1658	7.13769	5.59767	12.20436
O#2	5.45844			7.82686
O#3	2.66779			2.7472

Table 29 Contact Angle Calculations before treatment (trial procedure)

Soils before treatment

Soiltype	>M	<M	Average	% Ethanol	Surface tension	CA	Contact Angles	Average contact angle
G#1	1.026	1.368	1.197	6.967	53.250	-0.136	97.800	
G#2	1.026	1.368	1.197	6.967	53.250	-0.136	97.800	
G#3	0.684	0.855	0.770	4.479	57.530	-0.102	95.828	**97.14**
O#1	3.077	3.419	3.248	18.904	41.562	-0.236	103.671	
O#2	3.419	3.932	3.676	21.392	39.969	-0.251	104.544	
O#3	3.419	3.932	3.676	21.392	39.969	-0.251	104.544	**104.25**
B#1	2.393	2.735	2.564	14.923	44.534	-0.210	102.094	
B#2	2.735	3.077	2.906	16.913	42.973	-0.224	102.914	
B#3	2.393	2.735	2.564	14.923	44.534	-0.210	102.094	**102.37**

Table 30 Contact Angle Calculations after hot water and lime application (trial procedure)

Soils after lime application and four pore volume washes with hot water (80°C)

Soiltype	>M	<M	Average	% Ethanol	Surface tension	CA	Contact Angles	Average contact angle
G#1	0.342	0.513	0.428	2.488	62.160	-0.066	93.790	
G#2	0.684	0.855	0.770	4.479	57.530	-0.102	95.828	
G#3	0.684	0.855	0.770	4.479	57.530	-0.102	95.828	**95.15**
O#1	1.71	2.052	1.881	10.948	48.254	-0.177	100.205	
O#2	1.71	2.052	1.881	10.948	48.254	-0.177	100.205	
O#3	1.71	2.052	1.881	10.948	48.254	-0.177	100.205	**100.21**
B#1	0.855	1.026	0.941	5.4738	55.667	-0.116	96.674	
B#2	1.710	2.052	1.881	10.948	48.255	-0.177	100.205	
B#3	2.052	2.393	2.223	12.935	46.277	-0.194	101.198	**99.36**

Appendix C - Field Experiments

Table 31 Results of Field Experiment WDPT & MED

Field Experiments over time. Comparing WDPT, CA of Brown, Gley and Organic soil at different times of the year

BROWN SOIL

Summer 2009/2010			Beginning April 2011			End April 2011 before winter			August 2011 after winter		
Sample #	**WDPT 0ml**	**CA 0ml**	**Sample #**	**WDPT 0ml**	**CA 0ml**	**Soil**	**WDPT 0ml**	**CA 0ml**	**Soil**	**WDPT 0ml**	**CA 0ml**
B#1	00:24:00	92.51	**B#1**	00:28:20	100.20	**B#1**	01:13:25	100.20	**B#1**	00:12:29	98.46
B#2	00:34:30	102.09	**B#2**	03:54:40	102.09	**B#2**	00:57:39	102.09	**B#2**	00:20:59	100.20
B#3	00:22:50	100.20	**B#3**	00:04:12	93.79	**B#3**	02:51:00	102.09	**B#3**	00:47:40	102.09
B#4	02:15:00	102.09	**B#4**	00:20:40	99.08	**B#4**	01:28:03	102.09	**B#4**	02:23:26	100.20
B#5	02:15:00	101.20	**B#5**	00:12:40	97.79	**B#5**	01:32:01	100.20	**B#5**	00:34:21	99.08
						B#6	00:58:47	101.20			
						B#7	01:44:06	100.20			
Average	**01:10:16**	**99.62**		**01:00:06**	**98.59**		**01:32:09**	**101.16**		**00:51:47**	**100.01**
	extremely persistent			extremely persistent			extremely persistent			severely persistent	

GLEY SOIL

Summer 2009/2010			Beginning April 2011			End April 2011 after summer			August 2011 after winter		
Sample #	**WDPT 0ml**	**CA 0ml**	**Sample #**	**WDPT 0ml**	**CA 0ml**	**Soil**	**WDPT 0ml**	**CA 0ml**	**Soil**	**WDPT 0ml**	**CA 0ml**
G#1	01:15:00	101.20	**G#1**	00:09:32	94.88	**G#1**	00:24:04	97.79	**G#1**	00:07:34	94.88
G#2	01:15:00	101.20	**G#2**	00:14:34	97.79	**G#2**	00:07:45	96.67	**G#2**	00:13:40	99.08
G#3	00:36:00	100.20	**G#3**	00:28:20	99.66	**G#3**	00:09:10	96.67	**G#3**	00:28:27	99.08
G#4	01:15:00	101.20	**G#4**	00:30:20	98.09	**G#4**	00:15:00	97.79	**G#4**	00:22:11	99.08
G#5	00:32:30	101.66	**G#5**	00:23:20	100.20	**G#5**	00:04:43	97.79	**G#5**	00:04:42	96.67
						G#6	00:01:26	94.88			
						G#7	00:01:41	93.79			
Average	**00:58:42**	**101.09**		**00:21:13**	**98.12**		**00:09:07**	**96.49**		**00:15:19**	**97.76**
	severely persistent			strongly persistent			strongly persistent			strongly persistent	

ORGANIC SOIL

Summer 2009/2010			Beginning April 2011			End April 2011 after summer			August 2011 after winter		
Sample #	**WDPT 0ml**	**CA 0ml**	**Sample #**	**WDPT 0ml**	**CA 0ml**	**Soil**	**WDPT 0ml**	**CA 0ml**	**Soil**	**WDPT 0ml**	**CA 0ml**
O#1	03:15:00	102.91	**O#1**	02:55:00	102.91	**O#1**	04:30:00	103.30	**O#1**	01:35:49	102.09
O#2	03:30:00	103.67	**O#2**	03:35:00	103.67	**O#2**	04:30:00	103.67	**O#2**	01:25:29	102.09
O#3	03:30:00	102.91	**O#3**	03:55:00	103.67	**O#3**	02:47:25	102.91	**O#3**	02:06:40	102.09
O#4	02:45:00	102.91	**O#4**	02:35:00	102.91	**O#4**	02:36:36	102.91	**O#4**	01:53:17	102.09
O#5	03:30:00	103.67	**O#5**	05:05:00	104.54	**O#5**	02:00:27	102.09	**O#5**	02:34:15	100.20
						O#6	03:27:05	102.91			
						O#7	01:52:07	102.09			
Average	**03:18:00**	**103.22**		**03:37:00**	**103.54**		**03:06:14**	**102.84**		**01:55:06**	**101.72**
	extreme persistent			extreme persistent			extreme persistent			extreme persistent	

Table 32 Carbon Contents in initial Soils

CARBON CONTENT Deurer 2010 & Holzinger 2011

GLEY SOIL	2010		2011
ID	C%	ID	C%
G#1	8.86	G#7	11.21
G#2	10.70	G#3	9.75
G#3	9.85		
G#4	11.30		
G#5	11.10		
Average	**10.36**		**10.48**

ORGANIC SOIL	2010		2011
ID	C%	ID	C%
O#1	21.8	O#4	20.10
O#2	23	O#6	20.89
O#3	22		
O#4	18.4		
O#5	24.4		
Average	**21.92**		**20.50**

BROWN SOIL	2010		2011
ID	C%	ID	C%
B#1	10.5	B#7	10.14
B#2	10.1	B#6	9.981
B#3	8.51		
B#4	12.1		
B#5	10.2		
Average	**10.28**		**10.06**

Organic soil

Anova Results

Table 33 ANOVA: Field Experiment- Raw Data - Organic Soil

ORGANIC SOIL FIELD EXPERIMENT

Replications\Time	Start Jan-10	Start Apr-11	End Apr-11	End Aug-11
O#1	102.91	102.91	103.30	102.09
O#2	103.67	103.67	103.67	102.09
O#3	102.91	103.67	102.91	102.09
O#4	102.91	102.91	102.91	102.09
O#5	103.67	104.54	102.09	100.20
O#6			102.91	
O#7			102.09	

Mean	103.22	103.54	102.84	101.72
Min	102.91	102.91	102.09	100.20
Q1	102.91	102.91	102.50	102.09
Q2/Median	102.91	103.67	102.91	102.09
Q3	103.67	103.67	103.11	102.09
Max	103.67	104.54	103.67	102.09
25%	102.91	102.91	102.50	102.09
50%	0.00	0.76	0.41	0.00
75%	0.76	0.00	0.19	0.00
Minimum	0.00	0.00	0.41	1.89
Maximum	0.00	0.87	0.56	0.00

Table 34 ANOVA: Results - Field Experiments Organic Soil

Anova: Einfaktorielle Varianzanalyse

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Start Jan-10	5	516.084993	103.216999	0.17190067
Start Apr-11	5	517.715098	103.54302	0.45656123
End Apr-11	7	719.901679	102.843097	0.33863944
End Aug-11	5	508.580568	101.716114	0.71398024

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9.49571632	3	3.16523877	7.6975597	0.00162754	3.1599076
Within Groups	7.4016052	18	0.41120029			
Total	16.8973215	21				

Gley soil

Anova Results

Table 35 ANOVA: Field Experiment- Raw Data - Gley Soil

GLEY SOIL FIELD EXPERIMENT

Replications\Time	Start Jan-10	Start Apr-11	End Apr-11	End Aug-11
G#1	101.20	94.88	97.79	94.88
G#2	101.20	97.79	96.67	99.08
G#3	100.20	99.66	96.67	99.08
G#4	101.20	98.09	97.79	99.08
G#5	101.66	100.20	97.79	96.67
G#6			94.88	
G#7			93.79	

Mean	101.09	98.12	96.49	97.76
Min	100.20	94.88	93.79	94.88
Q1	101.20	97.79	95.78	96.67
Q2/Median	101.20	98.09	96.67	99.08
Q3	101.20	99.66	97.79	99.08
Max	101.66	100.20	97.79	99.08
25%	101.20	97.79	95.78	96.67
50%	0.00	0.29	0.90	2.41
75%	0.00	1.58	1.12	0.00
Minimum	0.99	2.92	1.99	1.80
Maximum	0.46	0.54	0.00	0.00

Table 36 ANOVA: Results - Field Experiments Gley Soil

Anova: Einfaktorielle Varianzanalyse

SUMMARY				
Groups	*Count*	*Sum*	*Average*	*Variance*
Start Jan-10	5	505.4495	101.0899	0.28454
Start Apr-11	5	490.6249	98.12499	4.335373
End Apr-11	7	675.3999	96.4857	2.510544
End Aug-11	5	488.8053	97.76107	3.686578

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	63.32020446	3	21.10673	7.867618	0.001462	3.1599076
Within Groups	48.28923028	18	2.682735			
Total	111.6094347	21				

Brown soil

Anova Results

Table 37 ANOVA: Field Experiment- Raw Data - Brown Soil

BROWN SOIL FIELD EXPERIMENT

Replications\Time	Start Jan-10	Start Apr-11	End Apr-11	End Aug-11
B#1	92.51	100.20	100.20	98.46
B#2	102.09	102.09	102.09	100.20
B#3	100.20	93.79	102.09	102.09
B#4	102.09	99.08	102.09	100.20
B#5	101.20	97.79	100.20	99.08
B#6			101.20	
B#7			100.20	

Mean	99.62	98.59	101.16	100.01
Min	92.51	93.79	100.20	98.46
Q1	100.20	97.79	100.20	99.08
Q2/Median	101.20	99.08	101.20	100.20
Q3	102.09	100.20	102.09	100.20
Max	102.09	102.09	102.09	102.09
25%	100.20	97.79	100.20	99.08
50%	0.99	1.29	0.99	1.12
75%	0.90	1.12	0.90	0.00
Minimum	7.70	4.00	0.00	0.62
Maximum	0.00	1.89	0.00	1.89

Table 38 ANOVA: Results - Field Experiments Brown Soil

Anova: Einfaktorielle Varianzanalyse

SUMMARY				
Groups	*Count*	*Sum*	*Average*	*Variance*
Start Jan-10	5	498.094093	99.6188186	16.4221362
Start Apr-11	5	492.967303	98.5934607	9.70107179
End Apr-11	7	708.093445	101.156206	0.89281033
End Aug-11	5	500.051835	100.010367	1.91617867

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	19.947884	3	6.64929468	1.01849046	0.40765174	3.1599076
Within Groups	117.514409	18	6.52857825			
Total	137.462293	21				

Appendix D - Lab Experiment: WDPT & MED Test

Table 39 Gley Soil: Calculation of Contact Angles

Cold Water [ml]	Soiltype	Average M	% Ethanol	Surface tension	CA	CA 0ml	Average CA
	G#1	1.20	6.97	53.25	-0.14	97.79	
	G#2	0.94	5.47	55.67	-0.12	96.67	
	G#3	0.94	5.47	55.67	-0.12	96.67	
	G#4	1.20	6.97	53.25	-0.14	97.79	
	G#5	1.20	6.97	53.25	-0.14	97.79	
	G#6	0.60	3.48	59.66	-0.09	94.88	
0.00	G#7	0.43	2.49	62.16	-0.07	93.79	**96.49**
	G#1	0.77	4.48	57.53	-0.10	95.83	
	G#2	0.60	3.48	59.66	-0.09	94.88	
	G#3	1.60	9.30	50.12	-0.16	99.29	
	G#4						
	G#5	1.20	6.97	53.25	-0.14	97.79	
	G#6						
400.00	G#7	0.77	4.48	57.53	-0.10	95.83	**96.72**
	G#1	1.54	8.96	50.54	-0.16	99.08	
	G#2	0.94	5.47	55.67	-0.12	96.67	
	G#3						
	G#4	1.20	6.97	53.25	-0.14	97.79	
	G#5	1.54	8.96	50.54	-0.16	99.08	
	G#6	0.60	3.48	59.66	-0.09	94.88	
800.00	G#7	0.94	5.47	55.67	-0.12	96.67	**97.36**
	G#1	0.94	5.47	55.67	-0.12	96.67	
	G#2	0.26	1.49	65.17	-0.04	92.51	
	G#3						
	G#4	0.77	4.48	57.53	-0.10	95.83	
	G#5	0.60	3.48	59.66	-0.09	94.88	
	G#6	0.60	3.48	59.66	-0.09	94.88	
1600.00	G#7	1.20	6.97	53.25	-0.14	97.79	**95.43**
	G#1						
	G#2						
	G#3	0.94	5.47	55.67	-0.12	96.67	
	G#4	0.77	4.48	57.53	-0.10	95.83	
	G#5						
	G#6						
2400.00	G#7	0.94	5.47	55.67	-0.12	96.67	**96.39**

HOT Water [ml]	Soiltype	Average M	% Ethanol	Surface tension	CA	CA 0ml	Average CA
	G#1	1.20	6.97	53.25	-0.14	97.79	
	G#2	0.94	5.47	55.67	-0.12	96.67	
	G#3	0.94	5.47	55.67	-0.12	96.67	
	G#4	1.20	6.97	53.25	-0.14	97.79	
	G#5	1.20	6.97	53.25	-0.14	97.79	
	G#6	0.60	3.48	59.66	-0.09	94.88	
0.00	G#7	0.43	2.49	62.16	-0.07	93.79	**96.49**
	G#1	1.20	6.97	53.25	-0.14	97.79	
	G#2	0.60	3.48	59.66	-0.09	94.88	
	G#3	0.77	4.48	57.53	-0.10	95.83	
	G#4						
	G#5						
	G#6						
400.00	G#7	0.94	5.47	55.67	-0.12	96.67	**96.29**
	G#1						
	G#2	0.60	3.48	59.66	-0.09	94.88	
	G#3						
	G#4	1.20	6.97	53.25	-0.14	97.79	
	G#5						
	G#6	0.94	5.47	55.67	-0.12	96.67	
800.00	G#7	0.60	3.48	59.66	-0.09	94.88	**96.06**
	G#1	0.94	5.47	55.67	-0.12	96.67	
	G#2	0.60	3.48	59.66	-0.09	94.88	
	G#3						
	G#4						
	G#5						
	G#6	0.60	3.48	59.66	-0.09	94.88	
1600.00	G#7						**95.48**
	G#1						
	G#2						
	G#3						
	G#4						
	G#5						
	G#6						
2400.00	G#7	1.20	6.97	53.25	-0.14	97.79	**97.79**

Table 40 Organic Soil: Calculation of Contact Angles

Cold Water [ml]	Soiltype	Average M	% Ethanol	Surface tension	CA	CA 0ml	Average CA
	O#1	3.08	17.91	42.25	-0.23	103.30	
	O#2	3.25	18.90	41.56	-0.24	103.67	
	O#3	2.91	16.91	42.97	-0.22	102.91	
	O#4	2.91	16.91	42.97	-0.22	102.91	
	O#5	2.56	14.92	44.53	-0.21	102.09	
	O#6	2.91	16.91	42.97	-0.22	102.91	
0.00	O#7	2.56	14.92	44.53	-0.21	102.09	**102.84**
	O#1	2.56	14.92	44.53	-0.21	102.09	
	O#2						
	O#3	2.56	14.92	44.53	-0.21	102.09	
	O#4	2.22	12.94	46.28	-0.19	101.20	
	O#5	2.22	12.94	46.28	-0.19	101.20	
	O#6	2.91	16.91	42.97	-0.22	102.91	
400.00	O#7						**101.90**
	O#1	2.91	16.91	42.97	-0.22	102.91	
	O#2	2.91	16.91	42.97	-0.22	102.91	
	O#3	2.56	14.92	44.53	-0.21	102.09	
	O#4	2.91	16.91	42.97	-0.22	102.91	
	O#5	3.25	18.90	41.56	-0.24	103.67	
	O#6						
800.00	O#7						**102.90**
	O#1						
	O#2	2.56	14.92	44.53	-0.21	102.09	
	O#3	2.22	12.94	46.28	-0.19	101.20	
	O#4						
	O#5	2.56	14.92	44.53	-0.21	102.09	
	O#6	2.56	14.92	44.53	-0.21	102.09	
1600.00	O#7	1.88	10.95	48.25	-0.18	100.20	**101.54**
	O#1						
	O#2						
	O#3						
	O#4						
	O#5	2.56	14.92	44.53	-0.21	102.09	
	O#6	1.88	10.95	48.25	-0.18	100.20	
2400.00	O#7	2.56	14.92	44.53	-0.21	102.09	**101.46**

HOT Water [ml]	Soiltype	Average M	% Ethanol	Surface tension	CA	CA 0ml	Average CA
	O#1	3.08	17.91	42.25	-0.23	103.30	
	O#2	3.25	18.90	41.56	-0.24	103.67	
	O#3	2.91	16.91	42.97	-0.22	102.91	
	O#4	2.91	16.91	42.97	-0.22	102.91	
	O#5	2.56	14.92	44.53	-0.21	102.09	
	O#6	2.91	16.91	42.97	-0.22	102.91	
0.00	O#7	2.56	14.92	44.53	-0.21	102.09	**102.84**
	O#1	2.56	14.92	44.53	-0.21	102.09	
	O#2						
	O#3	2.91	16.91	42.97	-0.22	102.91	
	O#4	1.54	8.96	50.54	-0.16	99.08	
	O#5						
	O#6						
400.00	O#7						**101.36**
	O#1						
	O#2	2.91	16.91	42.97	-0.22	102.91	
	O#3	2.56	14.92	44.53	-0.21	102.09	
	O#4	3.25	18.90	41.56	-0.24	103.67	
	O#5	3.25	18.90	41.56	-0.24	103.67	
	O#6						
800.00	O#7						**103.09**
	O#1						
	O#2	2.56	14.92	44.53	-0.21	102.09	
	O#3	2.56	14.92	44.53	-0.21	102.09	
	O#4						
	O#5						
	O#6						
1600.00	O#7	2.56	14.92	44.53	-0.21	102.09	**102.09**
	O#1						
	O#2						
	O#3						
	O#4						
	O#5						
	O#6						
2400.00	O#7	1.54	8.96	50.54	-0.16	99.08	**99.08**

Table 41 Brown Soil: Calculation of Contact Angles

Cold Water [ml]	Soiltype	Average M	% Ethanol	Surface tension	CA	CA 0ml	Average CA
	B#1	1.88	10.95	48.25	-0.18	100.20	
	B#2	2.56	14.92	44.53	-0.21	102.09	
	B#3	2.56	14.92	44.53	-0.21	102.09	
	B#4	2.56	14.92	44.53	-0.21	102.09	
	B#5	1.88	10.95	48.25	-0.18	100.20	
	B#6	2.22	12.94	46.28	-0.19	101.20	
0.00	B#7	1.88	10.95	48.25	-0.18	100.20	**101.16**
	B#1	0.94	5.47	55.67	-0.12	96.67	
	B#2	0.60	3.48	59.66	-0.09	94.88	
	B#3						
	B#4	1.88	10.95	48.25	-0.18	100.20	
	B#5						
	B#6	1.20	6.97	53.25	-0.14	97.79	
400.00	B#7	1.20	6.97	53.25	-0.14	97.79	**97.47**
	B#1	1.20	6.97	53.25	-0.14	97.79	
	B#2	0.43	2.49	62.16	-0.07	93.79	
	B#3	0.60	3.48	59.66	-0.09	94.88	
	B#4						
	B#5	1.20	6.97	53.25	-0.14	97.79	
	B#6						
800.00	B#7	1.20	6.97	53.25	-0.14	97.79	**96.41**
	B#1						
	B#2	1.20	6.97	53.25	-0.14	97.79	
	B#3	0.94	5.47	55.67	-0.12	96.67	
	B#4	1.20	6.97	53.25	-0.14	97.79	
	B#5	1.20	6.97	53.25	-0.14	97.79	
	B#6	1.20	6.97	53.25	-0.14	97.79	
1600.00	B#7	0.94	5.47	55.67	-0.12	96.67	**97.42**
	B#1						
	B#2	0.94	5.47	55.67	-0.12	96.67	
	B#3						
	B#4	1.54	8.96	50.54	-0.16	99.08	
	B#5						
	B#6	1.20	6.97	53.25	-0.14	97.79	
2400.00	B#7	0.94	5.47	55.67	-0.12	96.67	**97.56**

HOT Water [ml]	Soiltype	Average M	% Ethanol	Surface tension	CA	CA 0ml	Average CA
	B#1	1.88	10.95	48.25	-0.18	100.20	
	B#2	2.56	14.92	44.53	-0.21	102.09	
	B#3	2.56	14.92	44.53	-0.21	102.09	
	B#4	2.56	14.92	44.53	-0.21	102.09	
	B#5	1.88	10.95	48.25	-0.18	100.20	
	B#6	2.22	12.94	46.28	-0.19	101.20	
0.00	B#7	1.88	10.95	48.25	-0.18	100.20	**101.16**
	B#1	1.20	6.97	53.25	-0.14	97.79	
	B#2						
	B#3						
	B#4	1.20	6.97	53.25	-0.14	97.79	
	B#5						
	B#6	0.94	5.47	55.67	-0.12	96.67	
400.00	B#7	1.20	6.97	53.25	-0.14	97.79	**97.51**
	B#1						
	B#2	0.43	2.49	62.16	-0.07	93.79	
	B#3	1.20	6.97	53.25	-0.14	97.79	
	B#4						
	B#5	0.77	4.48	57.53	-0.10	95.83	
	B#6						
800.00	B#7	0.43	2.49	62.16	-0.07	93.79	**95.30**
	B#1						
	B#2						
	B#3	0.94	5.47	55.67	-0.12	96.67	
	B#4						
	B#5						
	B#6	0.51	2.99	60.86	-0.08	94.35	
1600.00	B#7	0.09	0.50	68.95	-0.02	90.94	**93.99**
	B#1						
	B#2						
	B#3						
	B#4						
	B#5						
	B#6	0.43	2.49	62.16	-0.07	93.79	
2400.00	B#7	0.43	2.49	62.16	-0.07	93.79	**93.79**

Table 42 All results of WDPT and MED

SOILS	WDTP 0ml	MED 0ml	WDPT 400ml	MED 400ml	WDPT 800ml	MED 800ml	WDPT 1600ml	MED 1600ml	WDPT 2400ml	MED 2400ml	change from 0ml to 400ml	change from 400ml to 800ml	change from 800ml to 1600ml	change from 1600ml to 2400ml	comparing hot and cold method
O#1	>3hrs	3.077/3.419	1h-3hrs	2.393/2.745	>3hrs	2.735/3.077					BETTER	SAME			
	>3hrs	& 2.735/3.077	1h-3hrs		>3hrs										
	>3hrs		1h-3hrs		>3hrs										
	>3hrs		1h-3hrs		>3hrs										
	>3hrs		1h-3hrs		>3hrs										
															BETTER
O#1 HOT	>3hrs	3.077/3.419	30min-1h	2.393/2.755							BETTER				
	>3hrs	& 2.735/3.077	1h-3hrs												
	>3hrs		1h-3hrs												
	>3hrs		30min-1h												
	>3hrs		30min-1h												
															BETTER
O#2	>3hrs	3.077/3.419			>3hrs	2.735/3.077	1h-3hrs	2.393/2.735				BETTER	BETTER		
	>3hrs				>3hrs		1h-3hrs								
	>3hrs				>3hrs		1h-3hrs								
	>3hrs				>3hrs		1h-3hrs								
	>3hrs				>3hrs		1h-3hrs								
															BETTER
O#2 HOT	>3hrs	3.077/3.419			>3hrs	2.735/3.077	1h-3hrs	2.393/2.735				BETTER	BETTER		
	>3hrs				>3hrs		1h-3hrs								
	>3hrs				>3hrs		1h-3hrs								
	>3hrs				>3hrs		1h-3hrs								
	>3hrs				1h-3hrs		30min-1h								
															BETTER
O#3	1h-3hrs	2.735/3.077	1h-3hrs	2.393/2.735	30min-1h	2.393/2.735	1h-3hrs	2.052/2.393			BETTER	SAME	BETTER		
	1h-3hrs		>3hrs		1h-3hrs		1h-3hrs								
	>3hrs		1h-3hrs		30min-1h		1h-3hrs								
	1h-3hrs		>3hrs		30min-1h		1h-3hrs								
	>3hrs		1h-3hrs		>3hrs		1h-3hrs								
															BETTER
O#3 HOT	1h-3hrs	2.735/3.077	>3hrs	2.735/3.077	30min-1h	2.393/2.735	1h-3hrs	2.393/2.735			SAME	BETTER	SAME		
	1h-3hrs		>3hrs		30min-1h		30min-1h								
	>3hrs		>3hrs		30min-1h		30min-1h								
	1h-3hrs		>3hrs		30min-1h		1h-3hrs								
	>3hrs		>3hrs		30min-1h		30min-1h								
															WORSE
O#4	1h-3hrs	2.735/3.077	5-30min	2.052/2.393	>3hrs	2.735/3.077					BETTER	WORSE			
	>3hrs		5-30min		>3hrs										WORSE

	1h-3hrs		30min-1h		>3hrs										
	1h-3hrs		30min-1h		>3hrs										
	>3hrs		30min-1h		>3hrs										
O#4 HOT	1h-3hrs	2.735/3.077	5-30min	1.368/1.710	>3hrs	3.077/3.419					BETTER	WORSE			
	>3hrs		5-30min		>3hrs										
	1h-3hrs		5-30min		>3hrs										
	1h-3hrs		5-30min		>3hrs										
	>3hrs		5-30min		>3hrs										
															WORSE
O#5	1h-3hrs	2.393/2.735	1h-3hrs	2.052/2.393	>3hrs	3.077/3.419	>3hrs	2.393/2.734	1h-3hrs	2.393/2.735	BETTER	WORSE	BETTER		
	1h-3hrs		30min-1h		>3hrs		>3hrs		1h-3hrs						
	1h-3hrs		1h-3hrs		1h-3hrs		>3hrs		1h-3hrs						
	1h-3hrs		>3hrs		>3hrs		>3hrs		1h-3hrs						
	>3hrs		5-30min		>3hrs		>3hrs		1h-3hrs						
															SAME
O#5 HOT	1h-3hrs	2.393/2.735	30min-1h	2.735/3.077	>3hrs	3.077/3.419					WORSE	WORSE			
	1h-3hrs		30min-1h		>3hrs										
	1h-3hrs		30min-1h		>3hrs										
	1h-3hrs		30min-1h		>3hrs										
	>3hrs		1h-3hrs		>3hrs										
															WORSE
O#6	>3hrs	2.735/3.077	1h-3hrs	2.735/3.077			30min-1h	2.393/2.735	1h-3hrs	1.710/2.052	SAME		BETTER	BETTER	
	>3hrs		1h-3hrs				30min-1h		1h-3hrs						
	>3hrs		1h-3hrs				30min-1h		5-30min						
	1h-3hrs		>3hrs				30min-1h		5-30min						
	>3hrs		1h-3hrs				1h-3hrs		5-30min						
															BETTER
O#6 HOT	>3hrs	2.735/3.077													
	>3hrs														
	>3hrs														
	1h-3hrs														
	>3hrs														
O#7	1h-3hrs	2.393/2.735					30min-1h	1.710/2.052	1h-3hrs	2.393/2.735			BETTER	WORSE	
	1h-3hrs						30min-1h		1h-3hrs						
	1h-3hrs						1h-3hrs		1h-3hrs						
	1h-3hrs						1h-3hrs		1h-3hrs						
	1h-3hrs						30min-1h		1h-3hrs						
															SAME
O#7 HOT	1h-3hrs	2.393/2.735							5-30min	1.368/1.710				BETTER	
	1h-3hrs								5-30min						
	1h-3hrs								5-30min						
	1h-3hrs								5-30min						BETTER

	1h-3hrs								5-30min						
G#1	5-30min	1.026/**1.368**	0-5 min	0.684/0.855	5-30min	1.368/1.710	5-30min	0.855/1.026			BETTER	WORSE	BETTER		
	5-30min		0-5 min		0-5 min		0-5 min								
	5-30min		0-5 min		5-30min		0-5 min								
	30min-1h		0-5 min		0-5 min		5-30min								
	30min-1h		0-5 min		5-30min		5-30min								
															BETTER
G#1 HOT	5-30min	1.026/**1.368**	5-30min	1.026/1.368			0-5 min	0.855/1.026			SAME		BETTER		
	5-30min		5-30min				0-5 min								
	5-30min		5-30min				0-5 min								
	30min-1h		5-30min				5-30min								
	30min-1h		5-30min				5-30min								
															BETTER
G#2	5-30min	0.855/1.026	0-5 min	0.513/0.684	0-5 min	0.342/0.513	0-5 min	0.171/0.342			BETTER	BETTER	BETTER		
	5-30min		0-5 min		0-5 min		0-5 min								
	5-30min		0-5 min		0-5 min		0-5 min								
	0-5 min		0-5 min		0-5 min		0-5 min								
	5-30min		0-5 min		0-5 min		0-5 min								
															BETTER
G#2 HOT	5-30min	0.855/1.026	0-5 min	0.513/0.684	0-5 min	0.513/0.684	5-30min	0.513/0.684			BETTER	SAME	SAME		
	5-30min		0-5 min		0-5 min		5-30min								
	5-30min		5-30min		0-5 min		0-5 min								
	0-5 min		0-5 min		0-5 min		5-30min								
	5-30min		0-5 min		0-5 min		5-30min								
															BETTER
G#3	5-30min	0.855/1.026	5-30min	0.855/1.026					5-30min	0.855/1.026	SAME			SAME	
	5-30min		0-5 min						0-5 min						
	0-5 min		0-5 min						5-30min						
	5-30min		0-5 min						0-5 min						
	5-30min		0-5 min						5-30min						
															SAME
G#3 HOT	5-30min	0.855/1.026	0-5 min	0.684/0.855							BETTER				
	5-30min		0-5 min												
	0-5 min		0-5 min												
	5-30min		0-5 min												
	5-30min		5-30min												
															BETTER
G#4	5-30min	1.026/1.368			5-30min	1.026/1.368	0-5 min	0.684/0.855	5-30min	0.684/0.855		SAME	BETTER	SAME	
	5-30min				5-30min		0-5 min		5-30min						
	5-30min				5-30min		0-5 min		5-30min						
	5-30min				5-30min		0-5 min		5-30min						
	5-30min				5-30min		0-5 min		0-5 min						
															BETTER

G#4 HOT	5-30min	1.026/1.368			5-30min	1.026/1.368						SAME			
	5-30min				5-30min										
	5-30min				5-30min										
	5-30min				5-30min										
	5-30min				5-30min										
															SAME
G#5	0-5 min	1.026/1.368	5-30min	1.026/1.363	5-30min	1.368/1.710	0-5 min	0.513/0.684			SAME	WORSE	BETTER		
	5-30min		5-30min		5-30min		0-5 min								
	5-30min		5-30min		5-30min		0-5 min								
	0-5 min		5-30min		0-5 min		0-5 min								
	0-5 min		5-30min		0-5 min		0-5 min								
															BETTER
G#5 HOT	0-5 min	1.026/1.368													
	5-30min														
	5-30min														
	0-5 min														
	0-5 min														
G#6	0-5 min	0.513/0.683			0-5 min	0.513/0.684	0-5 min	0.513/0684				SAME	SAME		
	0-5 min				0-5 min		0-5 min								
	0-5 min				0-5 min		0-5 min								
	0-5 min				0-5 min		0-5 min								
	0-5 min				0-5 min		0-5 min								
															SAME
G#6 HOT	0-5 min	0.513/0.683			0-5 min	0.855/1.026	0-5 min	0.513/0.684				WORSE	BETTER		
	0-5 min				0-5 min		0-5 min								
	0-5 min				0-5 min		0-5 min								
	0-5 min				0-5 min		0-5 min								
	0-5 min				0-5 min		0-5 min								
															SAME
G#7	0-5 min	0.342/0.513	0-5 min	0.684/0.855	0-5 min	0.855/1.026	0-5 min	1.026/1.368	5-30min	0.855/1.026	WORSE	WORSE	WORSE	BETTER	
	0-5 min		0-5 min		0-5 min		5-30min		0-5 min						
	0-5 min		0-5 min		0-5 min		5-30min		0-5 min						
	0-5 min		0-5 min		0-5 min		5-30min		5-30min						
	0-5 min		0-5 min		0-5 min		5-30min		0-5 min						
															WORSE
G#7 HOT	0-5 min	0.342/0.513	0-5 min	0.855/1.026	0-5 min	0.513/0.684			0-5 min	1.026/1.368	WORSE	BETTER		WORSE	
	0-5 min		0-5 min		5-30min				0-5 min						
	0-5 min		0-5 min		0-5 min				0-5 min						
	0-5 min		0-5 min		5-30min				0-5 min						
	0-5 min		0-5 min		5-30min				0-5 min						
															BETTER
B#1	30min-1h	1.710/2.052	0-5 min	0.855/1.026	5-30min	1.024/1.368					BETTER	WORSE			
	1h-3hrs		5-30min		5-30min										BETTER

	1h-3hrs		0-5 min		0-5 min										
	1h-3hrs		0-5 min		5-30min										
	1h-3hrs		0-5 min		0-5 min										
B#1 HOT	30min-1h	1.710/2.052	5-30min	1.026/1.368								BETTER			
	1h-3hrs		5-30min												
	1h-3hrs		5-30min												
	1h-3hrs		0-5 min												
	1h-3hrs		0-5 min												
															BETTER
B#2	30min-1h	2.393/2.735	0-5 min	0.513/0.684	0-5 min	0.342/0.513	5-30min	1.026/1.368	0-5 min	0.855/1.026	BETTER	BETTER	WORSE	BETTER	
	1h-3hrs		0-5 min		0-5 min		5-30min		5-30min						
	30min-1h		0-5 min		0-5 min		5-30min		0-5 min						
	30min-1h		0-5 min		0-5 min		5-30min		5-30min						
	30min-1h		0-5 min		0-5 min		5-30min		0-5 min						
															BETTER
B#2 HOT	30min-1h	2.393/2.735			0-5 min	0.342/0.513						BETTER			
	1h-3hrs				0-5 min										
	30min-1h				0-5 min										
	30min-1h				0-5 min										
	30min-1h				0-5 min										
															BETTER
B#3	>3hrs	2.393/2.735			0-5 min	0.513/0.684	0-5 min	0.855/1.026				BETTER	WORSE		
	1h-3hrs				0-5 min		0-5 min								
	1h-3hrs				0-5 min		0-5 min								
	>3hrs				0-5 min		0-5 min								
	1h-3hrs				0-5 min		0-5 min								
															BETTER
B#3 HOT	>3hrs	2.393/2.735			0-5 min	1.026/1.368	5-30min	0.855/1.026				BETTER	BETTER		
	1h-3hrs				0-5 min		5-30min								
	1h-3hrs				0-5 min		0-5 min								
	>3hrs				5-30min		0-5 min								
	1h-3hrs				0-5 min		5-30min								
															BETTER
B#4	1h-3hrs	2.393/2.735	5-30min	1.710/2.052			5-30min	1.026/1.368	5-30min	1.368/1.710	BETTER		BETTER	WORSE	
	1h-3hrs		5-30min				5-30min		5-30min						
	1h-3hrs		5-30min				5-30min		5-30min						
	1h-3hrs		5-30min				5-30min		5-30min						
	1h-3hrs		5-30min				5-30min		5-30min						
															BETTER
B#4 HOT	1h-3hrs	2.393/2.735	5-30min	1.026/1.368							BETTER				
	1h-3hrs		5-30min												
	1h-3hrs		5-30min												
	1h-3hrs		5-30min												BETTER

	1h-3hrs		5-30min												
B#5	1h-3hrs	1.710/2.052			1h-3hrs	1.026/1.368	0-5 min	1.026/1.368				BETTER	SAME		
	1h-3hrs				1h-3hrs		5-30min								
	1h-3hrs				1h-3hrs		5-30min								
	1h-3hrs				30min-1h		5-30min								
	1h-3hrs				1h-3hrs		0-5 min								
															BETTER
B#5 HOT	1h-3hrs	1.710/2.052			5-30min	0.684/0.858						BETTER			
	1h-3hrs				0-5 min										
	1h-3hrs				5-30min										
	1h-3hrs				5-30min										
	1h-3hrs				0-5 min										
															BETTER
B#6	30min-1h	2.052/2.393	0-5 min	1.026/1.368			5-30min	1.026/1.368	5-30min	1.026/1.368	BETTER		SAME	SAME	
	1h-3hrs		5-30min				0-5 min		5-30min						
	1h-3hrs		5-30min				5-30min		5-30min						
	30min-1h		0-5 min				5-30min		5-30min						
	30min-1h		5-30min				5-30min		5-30min						
															BETTER
B#6 HOT	30min-1h	2.052/2.393	0-5 min	0.855/1.026			0-5 min	0.342/**0.513**	0-5 min	0.342/0.513	BETTER		BETTER	SAME	
	1h-3hrs		0-5 min				0-5 min		0-5 min						
	1h-3hrs		0-5 min				0-5 min		0-5 min						
	30min-1h		0-5 min				0-5 min		0-5 min						
	30min-1h		5-30min				0-5 min		0-5 min						
															BETTER
B#7	1h-3hrs	1.026/1.368	5-30min	1.026/1.368	5-30min	1.026/1.368	0-5 min	0.855/1.026	5-30min	0.855/1.026	BETTER	SAME	BETTER	SAME	
	>3hrs	& 2.393/2.735	5-30min		5-30min		5-30min		5-30min						
	30min-1h		5-30min		5-30min		0-5 min		5-30min						
	1h-3hrs		5-30min		5-30min		5-30min		5-30min						
	30min-1h		5-30min		5-30min		0-5 min		5-30min						
															BETTER
B#7 HOT	1h-3hrs	1.026/1.368	5-30min	1.026/1.368	0-5 min	0.342/0.513	0-5 min	0.0/0.171	0-5 min	0.342/0.513	BETTER	BETTER	BETTER	WORSE	
	>3hrs	& 2.393/2.735	5-30min		0-5 min		0-5 min		0-5 min						
	30min-1h		5-30min		0-5 min		0-5 min		0-5 min						
	1h-3hrs		5-30min		0-5 min		0-5 min		0-5 min						
	30min-1h		5-30min		0-5 min		0-5 min		0-5 min						
															BETTER

Classification key for table above

0-10sec
10s-5 min
5-30min
30min-1h
1h-3hrs
>3hrs

- class 0 wettable/hydrophilic: 0-10sec
- class 1 slightly persistent: 10sec-5min
- class 2 strongly persistent: 5min-30min
- class 3 severely persistent: 30min-1hr
- class 4 extremely persistent: 1hr-3hrs
- class 5 extremely persistent: >3hrs

BETTER
SAME
WORSE

Appendix E - Anova Results of MED

5 treatments: 0ml water, 400ml water, 800ml water, 1600ml water and 2400ml water

7 replications (usually for each treatment about 5 were used)

Table 43 ANOVA: Raw Data - Cold Water Treatment Organic Soil

Organic Soil Cold Water Treatment

Replications\Treatments	0	400	800	1600	2400
O#1	103.30	102.09	102.91		
O#2	103.67		102.91	102.09	
O#3	102.91	102.09	102.09	101.20	
O#4	102.91	101.20	102.91		
O#5	102.09	101.20	103.67	102.09	102.09
O#6	102.91	102.91		102.09	100.20
O#7	102.09			100.20	102.09

Mean	102.84	101.90	102.90	101.54	101.46
Min	102.09	101.20	102.09	100.20	100.20
Q1	102.50	101.20	102.91	101.20	101.15
Q2/Median	102.91	102.09	102.91	102.09	102.09
Q3	103.11	102.09	102.91	102.09	102.09
Max	103.67	102.91	103.67	102.09	102.09

25%	102.50	101.20	102.91	101.20	101.15
50%	0.41	0.90	0.00	0.90	0.94
75%	0.19	0.00	0.00	0.00	0.00
Minimum	0.41	0.00	0.82	0.99	0.94
Maximum	0.56	0.82	0.76	0.00	0.00

Table 44 ANOVA: Results - Cold Water Treatment Organic Soil

Anova: Single Factor

SUMMARY				
Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	7	719.9017	102.8431	0.338639
Column 2	5	509.4976	101.8995	0.522575
Column 3	5	514.5078	102.9016	0.311238
Column 4	5	507.6843	101.5369	0.705299
Column 5	3	304.3926	101.4642	1.189967

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	9.591686	4	2.397922	4.537986	0.009024	2.866081
Within Groups	10.56822	20	0.528411			
Total	20.1599	24				

Table 45 ANOVA: Raw Data - Hot Water Treatment Organic Soil

Organic Soil Hot Treatment

Replications\Treatments	0	400	800	1600	2400
O#1	103.30	102.09			
O#2	103.67		102.91	102.09	
O#3	102.91	102.91	102.09	102.09	
O#4	102.91	99.08	103.67		
O#5	102.09		103.67		
O#6	102.91				
O#7	102.09			102.09	99.08

Mean	102.84	101.36	103.09	102.09	99.08
Min	102.09	99.08	102.09	102.09	99.08
Q1	102.50	100.59	102.71	102.09	99.08
Q2/Median	102.91	102.09	103.29	102.09	99.08
Q3	103.11	102.50	103.67	102.09	99.08
Max	103.67	102.91	103.67	102.09	99.08

25%	102.50	100.59	102.71	102.09	99.08
50%	0.41	1.50	0.58	0.00	0.00
75%	0.19	0.41	0.38	0.00	0.00
Minimum	0.41	1.50	0.62	0.00	0.00
Maximum	0.56	0.41	0.00	0.00	0.00

Table 46 ANOVA: Results - Hot Water Treatment Organic Soil

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	7	719.9017	102.8431	0.338639
Column 2	3	304.0926	101.3642	4.066381
Column 3	4	412.3506	103.0876	0.566147
Column 4	3	306.282	102.094	0
Column 5	1	99.08437	99.08437	#DIV/0!

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	17.63561	4	4.408903	4.831455	0.013107	3.179117
Within Groups	11.86304	13	0.912541			
Total	29.49865	17				

Table 47 ANOVA: Raw Data - Cold Water Treatment Gley Soil

Gley Soil Cold Treatment

Replications\Treatments	0	400	800	1600	2400
G#1	97.79	95.83	99.08	96.67	
G#2	96.67	94.88	96.67	92.51	
G#3	96.67	99.29			96.67
G#4	97.79		97.79	95.83	95.83
G#5	97.79	97.79	99.08	94.88	
G#6	94.88		94.88	94.88	
G#7	93.79	95.83	96.67	97.79	96.67

Mean	96.49	96.72	97.36	95.43	96.39
Min	93.79	94.88	94.88	92.51	95.83
Q1	95.78	95.83	96.67	94.88	96.25
Q2/Median	96.67	95.83	97.23	95.35	96.67
Q3	97.79	97.79	98.76	96.46	96.67
Max	97.79	99.29	99.08	97.79	96.67
25%	95.78	95.83	96.67	94.88	96.25
50%	0.90	0.00	0.56	0.48	0.42
75%	1.12	1.97	1.53	1.11	0.00
Minimum	1.99	0.95	1.80	2.37	0.42
Maximum	0.00	1.50	0.32	1.33	0.00

Table 48 ANOVA: Results - Cold Water Treatment Gley Soil

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	7	675.3999	96.4857	2.510544
Column 2	5	483.6193	96.72386	3.185533
Column 3	6	584.1897	97.36495	2.647262
Column 4	6	572.5625	95.42709	3.287511
Column 5	3	289.1765	96.39218	0.238464

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	11.67122	4	2.917805	1.10759	0.377941	2.816708
Within Groups	57.95619	22	2.634372			
Total	69.62741	26				

Table 49 ANOVA: Raw Data - Hot Water Treatment Gley Soil

Gley Soil Hot Treatment

Replications\Treatments	0	400	800	1600	2400
G#1	97.79	97.79		96.67	
G#2	96.67	94.88	94.88	94.88	
G#3	96.67	95.83			
G#4	97.79		97.79		
G#5	97.79				
G#6	94.88		96.67	94.88	
G#7	93.79	96.67	94.88		97.79

Mean	96.49	96.29	96.06	95.48	97.79
Min	93.79	94.88	94.88	94.88	97.79
Q1	95.78	95.59	94.88	94.88	97.79
Q2/Median	96.67	96.25	95.78	94.88	97.79
Q3	97.79	96.95	96.95	95.78	97.79
Max	97.79	97.79	97.79	96.67	97.79
25%	95.78	95.59	94.88	94.88	97.79
50%	0.90	0.66	0.90	0.00	0.00
75%	1.12	0.70	1.18	0.90	0.00
Minimum	1.99	0.71	0.00	0.00	0.00
Maximum	0.00	0.84	0.84	0.90	0.00

Table 50 ANOVA: Results - Hot Water Treatment Gley Soil

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	7	675.3999	96.4857	2.510544
Column 2	4	385.1751	96.29379	1.539314
Column 3	4	384.2249	96.05624	2.059898
Column 4	3	286.4303	95.47678	1.075215
Column 5	1	97.79461	97.79461	#DIV/0!

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4.722202	4	1.180551	0.590036	0.675377	3.11225
Within Groups	28.01133	14	2.000809			
Total	32.73353	18				

Table 51 ANOVA: Raw Data - Cold Water Treatment Brown Soil

Brown Soil Cold Water Treatment

Replications\Treatments	0	400	800	1600	2400
B#1	100.20	96.67	97.79		
B#2	102.09	94.88	93.79	97.79	96.67
B#3	102.09		94.88	96.67	
B#4	102.09	100.20		97.79	99.08
B#5	100.20		97.79	97.79	
B#6	101.20	97.79		97.79	97.79
B#7	100.20	97.79	97.79	96.67	96.67

Mean	101.16	97.47	96.41	97.42	97.56
Min	100.20	94.88	93.79	96.67	96.67
Q1	100.20	96.67	94.88	96.95	96.67
Q2/Median	101.20	97.79	97.79	97.79	97.23
Q3	102.09	97.79	97.79	97.79	98.12
Max	102.09	100.20	97.79	97.79	99.08
25%	100.20	96.67	94.88	96.95	96.67
50%	0.99	1.12	2.92	0.84	0.56
75%	0.90	0.00	0.00	0.00	0.88
Minimum	0.00	1.80	1.09	0.28	0.00
Maximum	0.00	2.41	0.00	0.00	0.97

Table 52 ANOVA: Results - Cold Water Treatment Brown Soil

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	7	708.0934	101.1562	0.8928103
Column 2	5	487.346	97.4692	3.7600004
Column 3	5	482.0517	96.41034	3.7409662
Column 4	6	584.5267	97.42111	0.3348023
Column 5	4	390.2272	97.5568	1.3160959

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	85.12723	4	21.28181	11.424235	3.59727E-05	2.816708
Within Groups	40.98303	22	1.862865			
Total	126.1103	26				

Table 53 ANOVA: Raw Data - Hot Water Treatment Brown Soil

Brown Soil Hot Water Treatment

Replications\Treatments	0	400	800	1600	2400
B#1	100.20	97.79			
B#2	102.09		93.79		
B#3	102.09		97.79	96.67	
B#4	102.09	97.79			
B#5	100.20		95.83		
B#6	101.20	96.67		94.35	93.79
B#7	100.20	97.79	93.79	90.94	93.79

Mean	101.16	97.51	95.30	93.99	93.79
Min	100.20	96.67	93.79	90.94	93.79
Q1	100.20	97.51	93.79	92.65	93.79
Q2/Median	101.20	97.79	94.81	94.35	93.79
Q3	102.09	97.79	96.32	95.51	93.79
Max	102.09	97.79	97.79	96.67	93.79
25%	100.20	97.51	93.79	92.65	93.79
50%	0.99	0.28	1.02	1.71	0.00
75%	0.90	0.00	1.51	1.16	0.00
Minimum	0.00	0.84	0.00	1.71	0.00
Maximum	0.00	0.00	1.47	1.16	0.00

Table 54 ANOVA: Results - Hot Water Treatment Brown Soil

Anova: Single Factor

SUMMARY				
Groups	*Count*	*Sum*	*Average*	*Variance*
Column 1	7	708.0934	101.1562	0.89281
Column 2	4	390.0579	97.51449	0.313877
Column 3	4	381.2024	95.3006	3.687974
Column 4	3	281.9702	93.99007	8.313176
Column 5	2	187.5795	93.78975	0

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	177.3559	4	44.33898	19.56778	8.13836E-06	3.055568
Within Groups	33.98877	15	2.265918			
Total	211.3447	19				

Appendix F - Change of WDPT & CA vs DOC increase

This shows the relationship between the DOC that has leached through the soil to the change in WDPT and the Contact Angle

Table 55 All Soils: WDPT vs CA vs DOC

ORGANIC	**COLD**					**HOT**				
Water [ml]	**WDPT [hh:mm:ss]**	**WDPT [sec]**	**CA [°]**	**AVERAGE DOC [mg/L] per wash**	**Total DOC [mg]**	**WDPT [hh:mm:ss]**	**WDPT [sec]**	**CA [°]**	**AVERAGE DOC [mg/L] per wash**	**Total DOC [mg]**
0	03:06:14	**11174**	102.84	0.00	0.00	03:06:14	**11174**	102.84	0.00	0.00
400	01:40:11	**6011**	101.90	6.33	2.53	01:46:30	**6390**	101.36	46.33	18.53
800	03:37:34	**13054**	102.90	5.00	4.00	03:33:23	**12803**	103.09	47.67	38.13
1600	02:14:24	**8064**	101.54	7.25	11.60	01:01:51	**3711**	102.09	76.67	122.67
2400	01:30:39	**5439**	101.46	4.33	10.40	00:14:52	**892**	99.08	71.00	170.40
GLEY	**COLD**					**HOT**				
Water [ml]	**WDPT [hh:mm:ss]**	**WDPT [sec]**	**CA [°]**	**AVERAGE DOC [mg/L] per wash**	**Total DOC [mg]**	**WDPT [hh:mm:ss]**	**WDPT [sec]**	**CA [°]**	**AVERAGE DOC [mg/L] per wash**	**Total DOC [mg]**
0	00:09:07	**547**	96.49	**0.00**	0.00	00:09:07	**547**	96.49	0.00	0.00
400	00:04:15	**255**	96.72	4.33	1.73	00:04:18	**258**	96.29	21.33	8.53
800	00:06:15	**375**	97.36	5.67	4.53	00:05:14	**314**	96.06	22.33	17.87
1600	00:03:36	**216**	95.43	5.25	8.40	00:06:08	**288**	95.78	30.33	48.53
2400	00:06:41	**401**	96.39	3.33	8.00	00:00:12	**12**	97.79	27.00	64.80
BROWN	**COLD**					**HOT**				
Water [ml]	**WDPT [hh:mm:ss]**	**WDPT [sec]**	**CA [°]**	**AVERAGE DOC [mg/L] per wash**	**Total DOC [mg]**	**WDPT [hh:mm:ss]**	**WDPT [sec]**	**CA [°]**	**AVERAGE DOC [mg/L] per wash**	**Total DOC [mg]**
0	01:32:09	5529	101.16	0.00	0.00	01:32:09	5529	101.16	0.00	0.00
400	00:09:01	541	97.47	5.25	2.10	00:08:35	515	97.51	34.33	13.73
800	00:16:16	976	96.41	7.33	5.87	00:03:14	215	95.30	53.33	42.67
1600	00:07:16	436	97.42	8.25	13.20	00:03:16	196	93.99	73.67	117.87
2400	00:08:21	501	97.56	5.67	13.60	00:00:35	35	93.79	40.50	97.20