# Organic carbon content controls the severity of water repellency and the critical moisture level across New Zealand pasture soils

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## ABSTRACT

Organic matter can render soil hydrophobic and cause soil water repellency (SWR) which has large implications for agriculture. Consequences such as fingered flow, uneven wetting patterns, and increased overland flow reduce irrigation efficiency and plant nutrient availability. The phenomenon of SWR is a transient soil property depending, inter alia, on soil water content ($w$). Soil can exhibit SWR from oven-dry $w$ until the critical $w$ where it again becomes fully wettable ($w_{NON}$). The total SWR can be obtained from the nonlinear SWR-$w$ relationship as the integrated trapezoidal area under the SWR-$w$ curve ($SWR_{AREA}$). We analyzed 78 soil samples, representing five dominant soil orders in the South Island of New Zealand. The soils had a large range in clay (0.000–0.520 kg kg$^{-1}$) and organic carbon (OC) content (0.021–0.217 kg kg$^{-1}$). The degree of SWR was measured on soils at air-dry conditions ($SWR_{AD}$) and after heat-pretreatment at 60 ($SWR_{60}$) and 105°C ($SWR_{105}$). Further, SWR was measured in small $w$ increments above air-dry $w$ until $w_{NON}$ was reached. The SWR-$w$ curves were either unimodal or bimodal, or no SWR occurred. $SWR_{AREA}$ ranged from 0.16 to 26.82 mN m$^{-1}$ kg kg$^{-1}$. Among the five soil orders tested, the Podzols exhibited the highest severity in SWR, whereas the Semiarid soils were the least hydrophobic soils. In conclusion, OC was the main factor for controlling the severity of SWR. Though, pH also had minor effects on SWR. Further, an upper limit critical water content was derived from the simple relationship between the $w_{NON}$ and OC, which could be applied to improve irrigation practices of pastoral soils. However, there is a need for further testing on different soils and land uses.

## 1. Introduction

Soil water repellency (SWR) is a transient soil property, which can severely alter soil functions. Certain species of plants, fungi and microorganisms create hydrophobic material that can cover soil particles and aggregates partly or completely with a hydrophobic skin (Bisdom et al., 1993; Capriel et al., 1990; Giovannini et al., 1983). The hydrophobic material decreases the surface free energy of the soil and renders the soil resistant towards wetting (Doerr et al., 2000).

It is well-documented that SWR can increase overland flow and surface erosion (Leighton-Boyce et al., 2007; Osborn et al., 1964), reduce the infiltration rate (Leighton-Boyce et al., 2007; Müller et al.,

2010), induce finger flow (de Jonge et al., 2009; Dekker and Ritsema, 1995), and decrease the filtering capacity for nutrients and chemicals (de Jonge et al., 2009; Dekker and Ritsema, 1995; Müller et al., 2014b). Some indirect consequences hereof are reduced crop productivity (Müller et al., 2014a; Müller et al., 2010; Roy and McGill, 2002) and a higher risk of groundwater contamination (de Jonge et al., 2009; Dekker and Ritsema, 1995).

SWR is a widespread phenomenon across New Zealand. For example, Deurer et al. (2011) found SWR to occur in ten soil orders under pastoral production across the North Island of New Zealand. This has economic consequences, since a large part of New Zealand's agriculture relies on pasture production (Müller et al., 2010).

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The occurrence and severity of SWR depend on fluctuating factors such as soil water content ($w$) (de Jonge et al., 1999; de Jonge et al., 2007; Kawamoto et al., 2007; King, 1981), temperature (de Jonge et al., 1999; Graber et al., 2009; King, 1981), pH (Diehl et al., 2010), and ambient relative humidity (Doerr et al., 2002; Roy and McGill, 2002). For example, variations in $w$ can affect the orientation of amphiphilic molecules in organic matter. Amphiphilic molecules are composed of a hydrophobic hydrocarbon chain with a polar hydrophilic functional group at the end. In wet conditions, the hydrophilic end is exposed from the grain surface, but as the soil dries, the hydrophilic end turns inwards, thus exposing the non-polar end, rendering the soil water-repellent (Graber et al., 2009; Roy and McGill, 2000).

The relation between the severity of SWR and $w$ is non-linear, and the shape of the SWR-$w$ curve varies between soils (de Jonge et al., 1999; Regalado et al., 2008). The SWR-$w$ curve is either unimodal or bimodal. Soils characterized by zero peaks are hydrophilic (de Jonge et al., 1999). For unimodal curves, the severity of SWR increases from dry conditions until it reaches a maximum level either before wilting point, around wilting point, between wilting point and field capacity or close to field capacity (Karunarathna et al., 2010b; Kawamoto et al., 2007; King, 1981; Regalado et al., 2008; Wijewardana et al., 2016). After reaching a maximum level, the severity of SWR decreases until a critical soil water content ($w_{NON}$) at which the soil becomes hydrophilic (Dekker et al., 2001; Dekker and Ritsema, 1994). For bimodal SWR-$w$ curves, there is a local maximum around oven-dry conditions, after which the severity of SWR decreases or even reaches hydrophilic conditions. Then, the severity of SWR increases towards a second peak with increasing $w$ and follows the pattern of the unimodal curve (de Jonge et al., 1999; Regalado et al., 2008).

The molarity of an ethanol droplet (MED) test (King, 1981; Roy and McGill, 2002) and the water droplet penetration time (WDPT) (King, 1981) are two of the most commonly used methods to measure SWR. The MED test is used to measure the degree of SWR, whereas the WDPT test is used to measure the persistence of SWR. In some studies SWR was measured at several discrete points across the entire range of $w$ for which the soil is hydrophobic, in other studies only single points of the SWR-$w$ curve were measured. Single point measurements often include measurements on field-fresh samples (Dekker and Ritsema, 1994) and/or measurements on samples after pretreatment at 60 °C ($SWR_{60}$), since heat pretreatment increases the severity of SWR (de Jonge et al., 1999). Deurer et al. (2011) found the $SWR_{60}$ to be positively correlated with organic carbon (OC) content for New Zealand soil samples with OC contents between 0.038 and 0.406 kg kg$^{-1}$. The pH (range from 4 to 6) was not correlated to SWR for either SWR of field-fresh samples or $SWR_{60}$. For a homogeneous Danish sandy field it was found that the $SWR_{60}$ and $SWR_{105}$ (SWR after heat-pretreatment at 105 °C) were weakly positively correlated with OC content (range from 0.014 to 0.025 kg kg$^{-1}$), positively correlated with fine sand content (range from 0.024 to 0.073 kg kg$^{-1}$) and negatively correlated with clay content (range from 0.037 to 0.052 kg kg$^{-1}$) (Knadel et al., 2016). Another study on Danish soils with a higher variability in soil properties found the $SWR_{105}$ to correlate positively with total sand content (range from 0.575 to 0.954 kg kg$^{-1}$) and negatively with total silt content (range from 0.015 to 0.540 kg kg$^{-1}$), whereas there was no significant relationship with clay, OC or pH (de Jonge et al., 1999). These references support that both soil texture and OC influence the severity of SWR after heat pretreatment, but other soil properties influencing SWR have also been reported in the literature.

However, single point measurements are not sufficient to describe the severity of SWR from dry to wet conditions. Despite variations in the curve shape and the number of peaks, there are some parameters that can be derived from the entire SWR-$w$ curve starting from dry to wet conditions. These parameters can be used to measure SWR more accurately. The trapezoidal integrated area underneath the SWR-$w$ curve ($SWR_{AREA}$) describes the total SWR of soils. The $SWR_{AREA}$ parameter integrates the degree of SWR across the entire range of $w$ for

which the soil is water repellent, and the $w_{NON}$ parameter has important practical applicability since it gives the water content above which SWR can be avoided. Both $SWR_{AREA}$ and $w_{NON}$ are linearly (de Jonge et al., 2007; de Jonge et al., 2009; Kawamoto et al., 2007; Regalado and Ritter, 2005; Regalado et al., 2008) and non-linearly (Karunarathna et al., 2010a; Wijewardana et al., 2016) correlated with OC. The majority of the literature on SWR focuses on the effect of OC on the severity of SWR, but negative correlations between $SWR_{AREA}$ and pH have also been shown (range from 4.1 to 7.3) (de Jonge et al., 1999). The ratio between $SWR_{AREA}$ and $w_{NON}$ has further been suggested as 'Integrative Repellency Dynamic Index' (Regalado and Ritter, 2005; Regalado et al., 2008) to characterize the average SWR of a soil across the range of $w$ for which the soil is hydrophobic.

Throughout the literature, it is obvious that OC is one of the most important soil properties controlling the severity of SWR. However, it is not obvious how other soil constituents affect the severity of SWR across different soil types. Further, deriving $w_{NON}$ from basic soil properties could be advantageous for obtaining the $w$ above which the soil is hydrophilic. Thus, this paper aims at examining:

i) Basic relationships between SWR and soil water content ($w$) from oven-dry to wet conditions for soils sampled across the entire South Island of New Zealand.
ii) How basic soil properties (texture, OC, and pH) control the severity of SWR ($SWR_{60}$, $SWR_{105}$, $SWR_{AREA}$, and 'Integrative Repellency Dynamic Index' (IRDI)) and critical soil water content ($w_{NON}$).
iii) Potential differences in the $SWR_{60}$, $SWR_{105}$, $SWR_{AREA}$, $w_{NON}$, and IRDI between the five soil orders.
iv) If the $w_{NON}$ can be obtained from basic soil properties as a support for irrigation practices. Hereunder, if an upper limit critical water content can be predicted across New Zealand pastoral soils to avoid dry, water repellency-inducing soil conditions.

## 2. Materials and methods

### 2.1. Design of survey on soil water repellency

Our study comprised 26 unirrigated pastoral sites in New Zealand's South Island. The soil orders that cover most of the South Island and are closely related to agricultural production according to the Fundamental Soil Layers (FSL; scale 1:50,000, http://lris.scinfo.org.nz/layer/79-fsl-new-zealand-soil-classification) and the Land Cover Database II (Ministry for the Environment, 2004) were included in the survey. These included the soil orders Brown (B), Pallic (P), Podzol (Z) and Recent (R) (New Zealand Soil Classification (NZSC) Scheme; (Hewitt, 2010)). They were complemented with sites of the soil order Semiarid (S), which is particularly dominant in the region Otago. According to the classification of the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006) Brown, Pallic, Podzol, Recent and Semiarid Soils correspond to Cambisols, Luvisols, Podzols, Fluvisols and Arenosols.

We stratified the sampling within the selected five soil orders by 'Annual Summer Rainfall'. The data layer was available through NIWA (NZMG projection, 500 m resolution). The data are based on the 30-year period 1971–2000. The spatial data layer was reclassified into three vectorized summer rainfall classes: L ≤ 150 mm (low), M = 150–350 mm (medium) and H ≥ 350 mm (high). Next, to ensure accessibility of the sampling sites we selected only polygons intersected by State Highways (New Zealand Transport Association, http://koordinates.com/layer/1331-nz-state-highway-centrelines-sept-2011/). Only polygons with high producing pasture as specified in Land Cover Database II (Ministry for the Environment, 2004) were considered. The intersection of the data layers was performed in ArcGIS (ArcEditor Vers. 9.2, ESRI). Based on the area and northing of the resulting polygons, target polygons were selected with the aim to maximize latitudinal spread for each selected soil order. In the high and low rainfall areas,
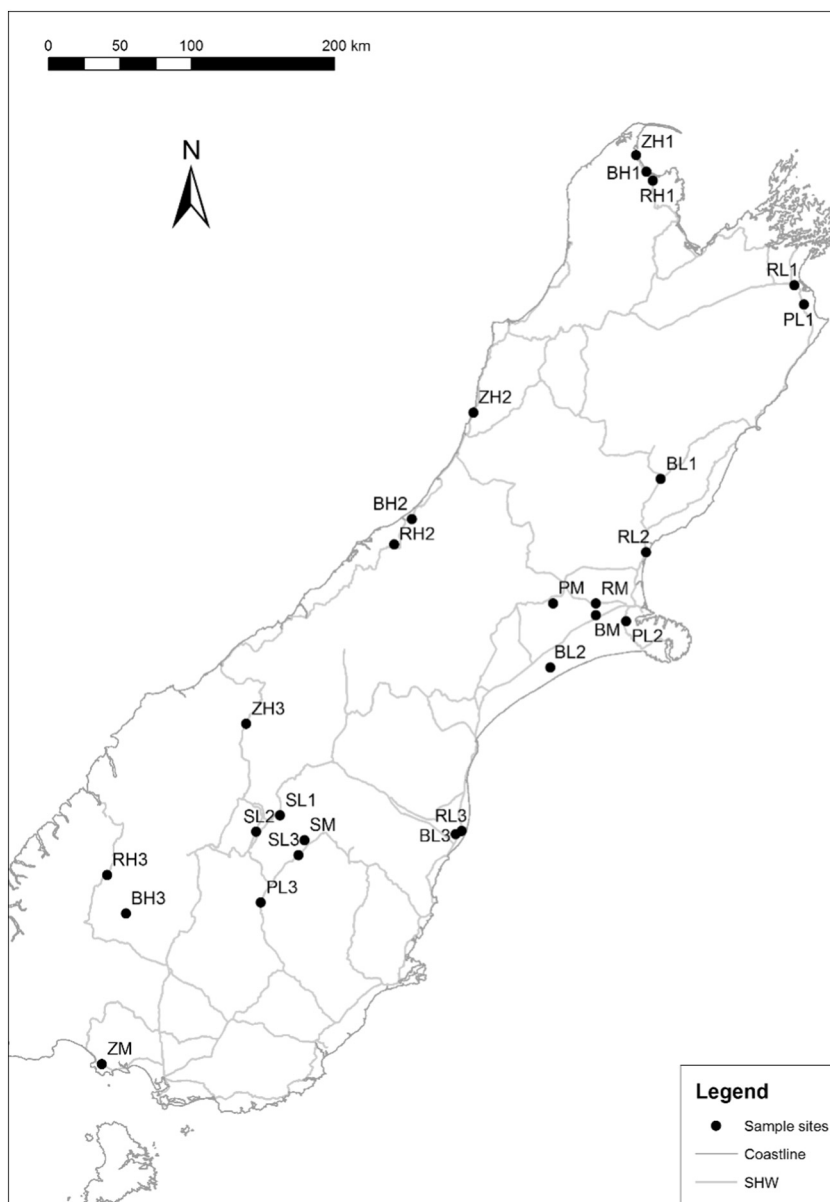
**Fig. 1.** Location of the 26 sampling sites distributed across the South Island of New Zealand. The samples represent five soil orders (Brown (B), Pallic (P), Podzol (Z), Recent (R), and Semiarid (S) according to the New Zealand Soil Classification Scheme. Three replicates were collected at each site. SHW, state highway network.

replicates were selected to represent the northernmost, the southernmost and the central polygon. In the medium summer rainfall areas, one target polygon was selected as central as possible to those selected in the high and low rainfall areas. The final sampling site within each selected polygon was randomly chosen from four to five reasonably easily accessible sites on farms, where we received sampling permission. We transferred centroids for each selected property and polygons for each selected target polygon to an outdoor GPS (Garmin Dakota 20) and the same centroids to an automotive GPS (Garmin nuvi 1390). The final selected sites cover most regions with the exception of Nelson (Statistics NZ, http://koordinates.com/#/layer/197-nz-regional-councils-2008-yearly-pattern/), topographical and farming situations of pastoral land use in the South Island (Fig. 1).

### 2.2. Soil sampling and analysis

The sampling was conducted between 5 and 17 January 2012. At each of the 26 sites, three bulk soil samples (approximately 2000 cm$^3$; depth 0 to 50 mm) were taken along a transect, each sample

approximately 10 m apart. All samples were stored at 4 °C until analysis. The thatch layer of the soil samples (~10 mm) was cut off and discarded. A subsample of the remaining mineral soil was sieved to 2 mm. The gravimetric soil water content and pH (in 1 M KCL) were measured using standard methodology (Blakemore et al., 1987). The pH meter was a Hanna HI 9812. Total OC contents were analyzed by the Dumas method for %C using a Leco TruMac instrument (Blakemore et al., 1987).

### 2.3. Soil water repellency measurements

Prior to the SWR measurements the soil samples were pretreated to reach different $w$ below and above air-dried conditions. This included oven-drying air-dried samples at 105 °C, followed by subsequent cooling in a desiccator, and oven-drying at 60 °C, followed by equilibration at 20 °C for a minimum of 48 hours. We reached $w$ above air-dried conditions by pipetting tap water onto air-dried soil to reach predetermined soil-specific $w$. The intended increments in $w$ above air-dried conditions were soil-specific between 0.015 to 0.10 kg kg$^{-1}$.
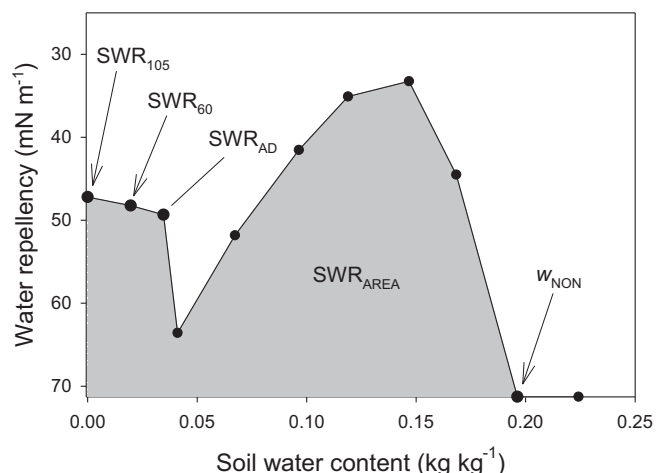
**Fig. 2.** Soil water repellency (SWR) as a function of soil-water content and the derived parameters. $SWR_{105}$ and $SWR_{60}$ are SWR determined after heat pre-treatments at 105 °C and 60 °C, respectively. The $SWR_{AD}$ is determined at air-dried conditions. Finally, $w_{NON}$ is the critical soil-water content at which the soil turns hydrophilic, and the grey area represents the total degree of SWR, which is the trapezoidal integrated area under the curve. The y-axis has been reversed, starting from zero SWR (71.72 mN m$^{-1}$) and increasing to higher SWR (25 mN m$^{-1}$).

Then, the soil was mixed and left to equilibrate for a minimum of two weeks before SWR measurements.

The degree of SWR was measured using the MED test (de Jonge et al., 1999; de Jonge et al., 2007; Kawamoto et al., 2007; King, 1981; Roy and McGill, 2002). Ethanol and deionized water solutions were prepared to reach ethanol concentrations between 0.01 m$^3$ m$^{-3}$ and 0.80 m$^3$ m$^{-3}$ with concentration increments of 0.01 m$^3$ m$^{-3}$. The highest concentration of an aqueous ethanol droplet (60 μL) which remained on the soil surface for at least 5 s was determined. Then ethanol solution concentrations were converted to surface tensions (Roy and McGill, 2000; Roy and McGill, 2002). Immediately after SWR measurements, the actual gravimetric $w$ was measured. The SWR measurements were plotted as a function of $w$ (Fig. 2). The total SWR of each sample was calculated as the trapezoidal integrated area under this SWR-$w$ curve ($SWR_{AREA}$). The $w_{NON}$ was determined as the $w$ at which the soil turned hydrophilic (Fig. 2). Soil samples which were hydrophilic (six samples from two locations) were excluded from further analysis.

Further, the average SWR function (Regalado and Ritter, 2005) was calculated for $w$ from 0.00 kg kg$^{-1}$ to $w_{NON}$:

$$IRDI = \frac{SWR_{AREA}}{w_{NON}} \tag{1}$$

This parameter allows comparing SWR of samples by characterizing the SWR-$w$ curves with a single value.

### 2.4. Statistical analyses

We applied a Kruskal-Wallis One Way Analysis of Variance on Ranks to compare differences in OC contents, $SWR_{60}$, $SWR_{AREA}$, $w_{NON}$, and IRDI between the soil orders at a confidence level of 95 %. This test is applicable for data, which are not normally distributed, and thus this test was appropriate for our data set.

Soil properties (OC, clay, silt, sand, and pH) were correlated to functional SWR parameters ($SWR_{AREA}$ and $w_{NON}$) using forward multiple linear regression (MLR) on water repellent soil samples. Soil properties which contributed significantly ($p < 0.05$) to explain the variation in $SWR_{AREA}$ and $w_{NON}$ were included in the final MLR expression. The accuracy was determined using the coefficient of determination ($R^2$) and the root mean square error (RMSE). The MLR and

**Table 1**

Soil characteristics: Clay ($< 0.002$ mm), silt (0.002–0.050 mm), sand and organic carbon (OC) contents, pH, SWR after drying the samples at 60 °C ($SWR_{60}$) and 105 °C ($SWR_{105}$), the total degree of soil water repellency ($SWR_{AREA}$), the critical soil-water content ($w_{NON}$) and the integrative repellency dynamic index (IRDI) of the 72 hydrophobic soil samples.

| | n | Brown | Pallic | Podzol | Recent | Semiarid | All |
|---|---|---|---|---|---|---|---|
| | | 21 | 12 | 12 | 18 | 9 | 72 |
| Clay | Mean | 0.081 | 0.060 | 0.093 | 0.080 | 0.128 | 0.085 |
| kg kg$^{-1}$ | Min | 0.012 | 0.007 | 0.002 | 0.037 | 0.000 | 0.000 |
| | Max | 0.443 | 0.223 | 0.328 | 0.210 | 0.520 | 0.520 |
| | Sd | 0.125 | 0.061 | 0.091 | 0.039 | 0.170 | 0.101 |
| Silt | Mean | 0.579 | 0.734 | 0.621 | 0.672 | 0.477 | 0.622 |
| kg kg$^{-1}$ | Min | 0.064 | 0.400 | 0.505 | 0.425 | 0.253 | 0.064 |
| | Max | 0.954 | 0.896 | 0.803 | 0.885 | 0.745 | 0.954 |
| | Sd | 0.240 | 0.161 | 0.094 | 0.133 | 0.200 | 0.191 |
| Sand | Mean | 0.340 | 0.206 | 0.287 | 0.248 | 0.395 | 0.292 |
| kg kg$^{-1}$ | Min | 0.020 | 0.086 | 0.092 | 0.067 | 0.022 | 0.020 |
| | Max | 0.923 | 0.535 | 0.486 | 0.476 | 0.747 | 0.923 |
| | Sd | 0.273 | 0.139 | 0.132 | 0.131 | 0.313 | 0.214 |
| OC | Mean | 0.063 | 0.038 | 0.095 | 0.042 | 0.041 | 0.056 |
| kg kg$^{-1}$ | Min | 0.037 | 0.024 | 0.048 | 0.021 | 0.025 | 0.021 |
| | Max | 0.096 | 0.055 | 0.217 | 0.068 | 0.061 | 0.217 |
| | Sd | 0.019 | 0.007 | 0.047 | 0.012 | 0.013 | 0.030 |
| pH | Mean | 5.3 | 5.5 | 5.4 | 5.2 | 5.6 | 5.4 |
| | Min | 4.6 | 4.8 | 4.5 | 4.5 | 5.0 | 4.5 |
| | Max | 6.3 | 6.2 | 5.8 | 5.6 | 6.0 | 6.3 |
| | Sd | 0.5 | 0.5 | 0.5 | 0.3 | 0.4 | 0.4 |
| $SWR_{60}$[a] | Mean | 57.46 | 61.25 | 50.62 | 56.53 | 63.62 | 57.49 |
| mN m$^{-1}$ | Min | 40.88 | 47.21 | 39.65 | 41.54 | 46.26 | 39.65 |
| | Max | 71.27 | 71.27 | 63.58 | 71.27 | 71.27 | 71.27 |
| | Sd | 9.24 | 8.57 | 8.19 | 9.54 | 11.52 | 9.90 |
| $SWR_{105}$ | Mean | 57.01 | 59.01 | 45.95 | 54.52 | 62.62 | 55.58 |
| mN m$^{-1}$ | Min | 42.95 | 42.95 | 37.45 | 42.23 | 43.71 | 37.45 |
| | Max | 71.27 | 71.27 | 58.55 | 71.27 | 71.27 | 71.27 |
| | Sd | 8.01 | 11.31 | 6.16 | 9.32 | 12.06 | 10.29 |
| $SWR_{AREA}$[b] | Mean | 6.33 | 3.39 | 9.36 | 4.91 | 2.99 | 5.57 |
| mN m$^{-1}$ kg kg$^{-1}$ | Min | 3.46 | 0.82 | 6.56 | 0.93 | 0.16 | 0.16 |
| | Max | 12.55 | 7.48 | 26.82 | 8.48 | 9.17 | 26.82 |
| | Sd | 2.32 | 2.23 | 5.63 | 2.22 | 2.98 | 3.70 |
| $w_{NON}$ | Mean | 0.26 | 0.18 | 0.35 | 0.20 | 0.16 | 0.23 |
| kg kg$^{-1}$ | Min | 0.13 | 0.07 | 0.23 | 0.07 | 0.11 | 0.07 |
| | Max | 0.51 | 0.26 | 0.78 | 0.31 | 0.29 | 0.78 |
| | Sd | 0.10 | 0.07 | 0.14 | 0.07 | 0.06 | 0.11 |
| IRDI[c] | Mean | 24.65 | 17.80 | 26.08 | 24.62 | 15.38 | 22.58 |
| mN m$^{-1}$ | Min | 14.63 | 8.02 | 21.56 | 13.10 | 1.52 | 1.52 |
| | Max | 31.26 | 29.22 | 34.19 | 35.01 | 31.28 | 35.01 |
| | Sd | 4.35 | 6.03 | 3.95 | 6.25 | 11.33 | 7.21 |

a: $SWR_{60}$ and $SWR_{105}$ are in the unit of surface tension, which has an inverse relationship to the degree of soil water repellency. As surface tension decreases, the degree of soil water repellency increases. Zero water repellency is 71.27 mN m$^{-1}$.

b: $SWR_{AREA}$ is the trapezoidal integrated area underneath the SWR versus water content curve.

c: IRDI is the average SWR of a sample, and it is calculated as the ratio between $SWR_{AREA}$ and $w_{NON}$.

the Kruskal-Wallis One Way Analysis of Variance on Ranks were performed with SigmaPlot 11.00.

We applied the Akaike information criterion (AIC) to evaluate the accuracy of the SWR and $w_{NON}$ correlations with soil properties. The AIC penalizes an increasing number of input variables:

$$AIC = n \left[ \ln(2\pi) + \ln\left( \frac{\sum_{i=1}^{n} (d_i^2)}{n-k} \right) + 1 \right] + k \tag{2}$$

where k represents the number of input variables, n represents the number of samples and $d_i$ represents the residual value between the measured value and the value obtained from the model. The best model has the lowest AIC value.
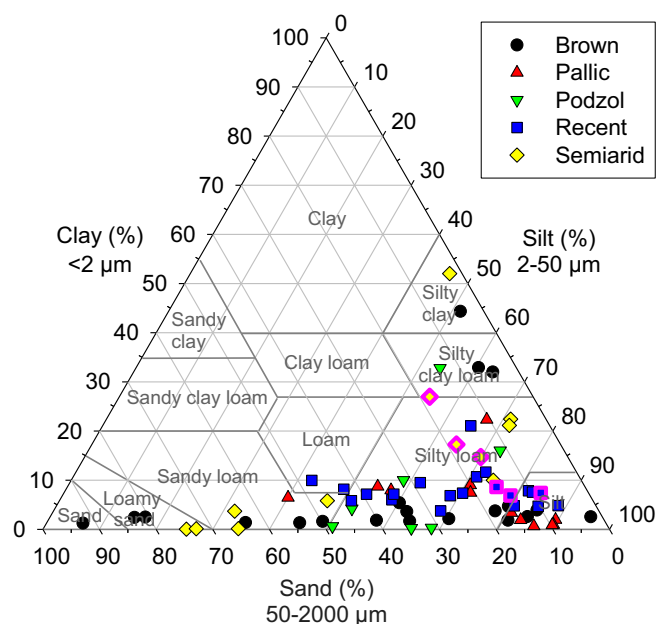
**Fig. 3.** Distribution of the 78 soil samples across the USDA soil textural triangle. Samples highlighted with pink edges denote hydrophilic soil samples.

## 3. Results and discussion

### 3.1. Soil texture and organic carbon

The soil samples had clay contents between 0.000 and 0.520 kg kg$^{-1}$ (Table 1) and represented a wide range in texture. The soils represented sand to silty loam classes of the USDA textural classification (Fig. 3). Especially the Brown soils had a wide distribution in texture, and covered seven classes. The Pallic soils covered three classes between sandy loam to silt, while the Podzols covered two classes from silty loam to silty clay loam. The Recent soils were distributed across three classes from loam to silt, and the Semiarid soils were equally wide in their textural distribution, covering five classes from loamy sand to silty clay. The OC contents ranged from 0.021 and 0.217 kg kg$^{-1}$ (Table 1) with the Podzols having the highest OC contents.

3.2 Soil water repellency versus water content curves

Soil water repellency was measured in discrete soil-specific intervals in the $w$ between oven-dried conditions and $w_{NON}$. The $w_{NON}$ was higher than air-dried conditions for all hydrophobic samples. The soil samples were characterized as hydrophobic if they were water repellent across one or several $w$, whereas the samples were characterized as hydrophilic if they did not exhibit hydrophobicity at any $w$. Among the 78 samples, 72 of the samples were hydrophobic (92%). The six hydrophilic samples represented the sites RL1 (clay: 0.069–0.086, silt: 0.757–0.842, sand: 0.084–0.157 and OC: 0.036–0.040 kg kg$^{-1}$) and SL3 (clay: 0.147–0.270, silt: 0.548–0.699, sand: 0.154–0.184 and OC: 0.037–0.057 kg kg$^{-1}$), and they were located in the northern and southern end of the South Island, respectively (Fig. 1). Deurer et al. (2011) conducted a survey across the North Island of New Zealand for soils under pasture representing ten soil orders and found 98% of the soils to be potentially water repellent. This emphasizes that SWR is an important phenomenon for soils under pasture across entire New Zealand.

The SWR-$w$ curves for the individual sites are shown in Fig. 4, sorted according to increasing OC content. The soils were hydrophilic (e.g., Fig. 4f) or were characterized by unimodal or bimodal SWR-$w$ curves. Soil with unimodal curves were either hydrophilic or hydrophobic at oven-dry $w$, but ultimately became more water repellent at intermediate $w$ exceeding air-dried conditions (e.g., Fig. 4b) or they were

already water repellent at oven-dry $w$ (e.g., Fig. 4e). All soils, which had bimodal curves, were water repellent at oven-dry $w$. Further, for the bimodal curves the degree of SWR either decreased to a local minimum with increasing $w$, still retaining some degree of SWR (e.g., Fig. 4s), or the degree of SWR decreased to become temporarily hydrophilic (e.g., Fig. 4p). The wide representation of different curve shapes in this study represents vastly the SWR-$w$ curve varieties found in previous studies (de Jonge et al., 1999; de Jonge et al., 2007; Kawamoto et al., 2007; Regalado et al., 2008).

It was common for all soils exhibiting bimodal behavior that the global maximum was located in the second peak. Thus, it is necessary to measure the whole SWR-$w$ curve to derive the highest degree of SWR that a soil can exhibit. de Jonge et al. (1999) similarly found the second peak to reach a higher level of SWR than the first peak, whereas bimodal SWR-$w$ curves in the study of Regalado et al. (2008) had the global maximum in either the first or second peak. Among the three replicates collected at each site, the number of peaks was not always consistent (e.g., Fig. 4m). Further, for some of the three replicates within specific locations exhibiting bimodal behavior, it was not consistent whether the SWR-$w$ curves decreased to wettable conditions or remained water repellent at the local minima at intermediate $w$ (e.g., Fig. 4u). Although the soils were sampled as replicates at each site, there were considerable spatial variations in texture and OC content within some sites. For example, the highest difference in OC within one site was 0.106 kg kg$^{-1}$ for ZH1-1 (Fig. 4ab), for which sample 1 had 0.217 kg kg$^{-1}$ OC and sample 2 had 0.111 kg kg$^{-1}$ OC. The differences in OC content between these samples affected the SWR$_{AREA}$, which was 26.82 mN m$^{-1}$ kg kg$^{-1}$ and 8.11 mN m$^{-1}$ kg kg$^{-1}$ for sample 1 and 2, respectively. Among the individual soil orders, all Podzols were characterized by a bimodal behavior, indicating a consistent local maximum in the degree of SWR after heating pretreatment. Chemical bonding between OC and minerals might cause the increase in SWR after heating (DeBano, 2003). There was no trend for whether the curves were hydrophilic, unimodal or bimodal within the remaining soil orders.

Some soils, e.g., site BL2 reached a relatively high maximum level of SWR despite high clay contents between 0.32 and 0.44 kg kg$^{-1}$. Clay has a large surface area compared to sand, and dispersible clay addition is sometimes used as a remediation technique for SWR in sandy soils (Cann, 2003). However, clay rich soils might still be susceptible to severe degrees of SWR. Studies have found soils to exhibit SWR despite high clay contents up to 34% (Wijewardana et al., 2016) and 60% (Dekker and Ritsema, 1996a). Hydrophobic (Giovannini et al., 1983) and aliphatic fractions of organic matter (Capriel et al., 1990) can increase aggregate stability presumably because of hydrophobic coatings around the aggregates, which might explain the high degree of SWR in these clay-rich soils. Some clay-rich soils even exhibit fingerlike or preferential wetting patterns (Dekker and Ritsema, 1995; Dekker and Ritsema, 1996a; Dekker and Ritsema, 1996b).

### 3.2. Effect of soil orders on soil water repellency

Among the five soil orders, the severity of SWR in terms of the parameters SWR$_{AREA}$, $w_{NON}$, and IRDI decreased in the following identical sequence: Podzols > Brown > Recent > Pallic > Semiarid (Table 1, Fig. 5c–d). With regards to SWR$_{60}$ the Podzols were significantly ($p < 0.05$) higher in SWR than the Semiarid soils (Fig. 5b). Further, the Podzols had a significantly ($p < 0.05$) higher SWR$_{AREA}$ and $w_{NON}$ than the Recent, Pallic and Semiarid soils (Fig. 5c and d). The differences within the remaining soil orders for the SWR$_{60}$, SWR$_{AREA}$, and $w_{NON}$ were not significant. Deurer et al. (2011) examined the degree and persistence of SWR across ten soil orders in the North Island of New Zealand. They similarly found the Podzols to exhibit the highest degree and persistence of SWR after heat pretreatment of 65 °C. With regards to IRDI, there where no significant differences within any soil orders.

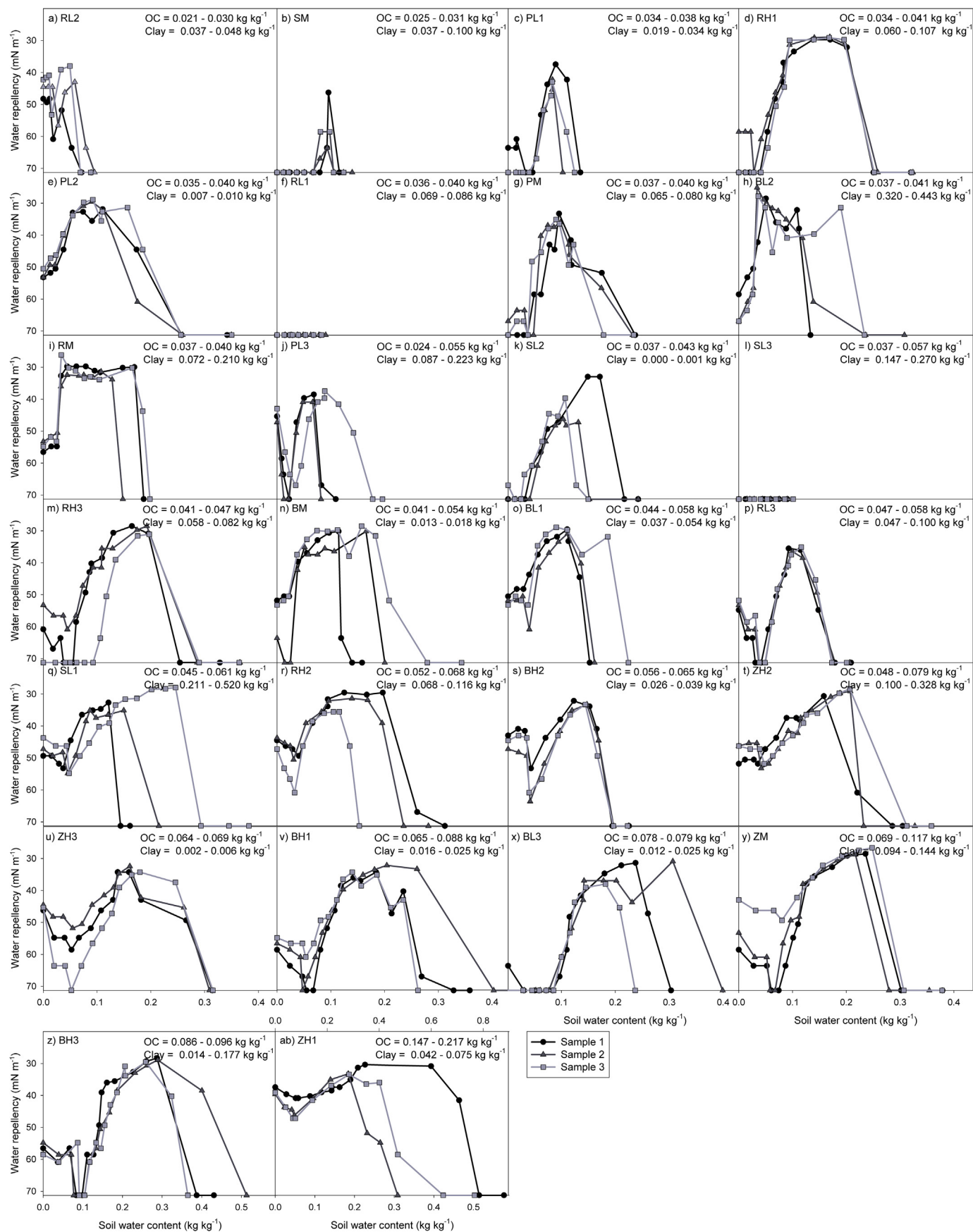As is evident from Fig. 5a–d, the relationship between OC content,

**Fig. 4.** Soil water repellency as a function of soil water content. At each of the 26 sites, three samples were collected. The figures are arranged according to increasing organic carbon (OC) content. The y-axis has been reversed, starting from zero water repellency (71.72 mN m$^{-1}$) going to higher water repellency (20 mN m$^{-1}$). The plot of site ZH1 has two x-axes: Sample 1 relates to the top axis, Samples 2 and 3 to the bottom axis.
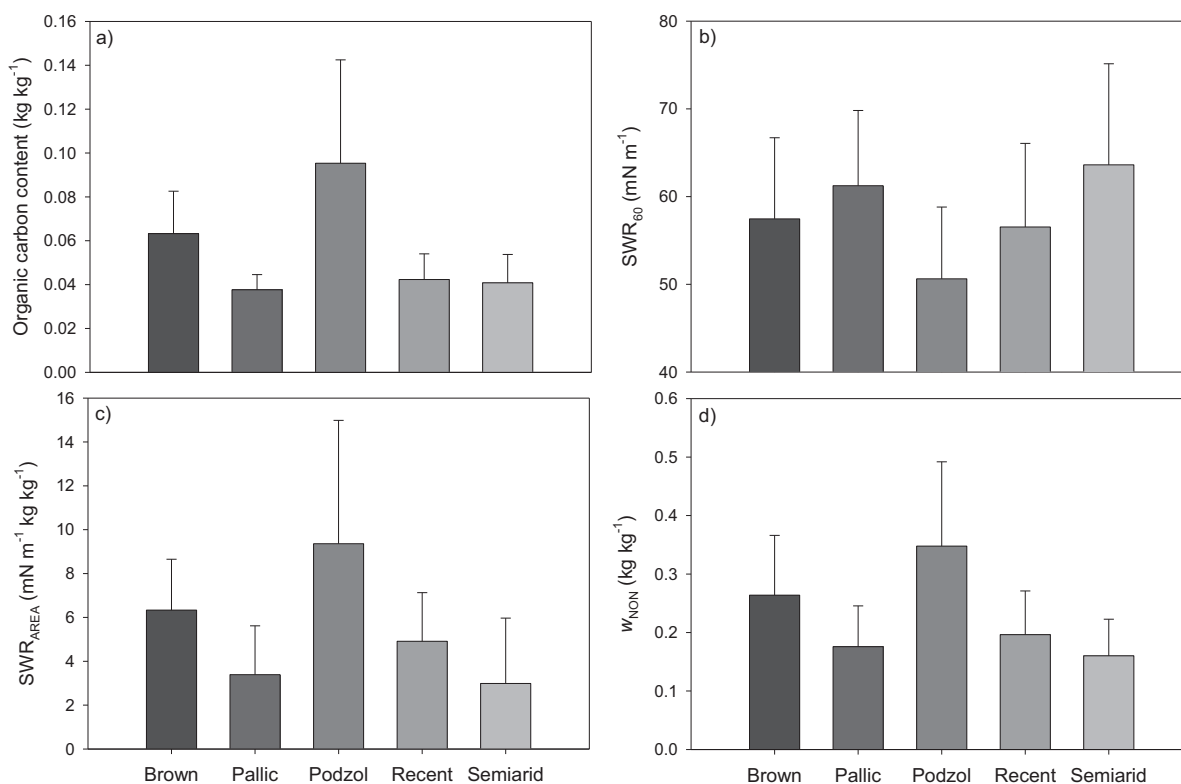
**Fig. 5.** a) Organic carbon content, b) soil water repellency after drying the samples at 60°C (SWR$_{60}$), c) total degree of soil water repellency (SWR$_{AREA}$), d) and the critical soil-water content ($w_{NON}$) of the five soil orders: Brown, Pallic, Podzol, Recent and Semiarid. The error bars represent the standard deviations. The SWR$_{60}$ is in the unit of surface tension, which has an inverse relationship to the degree of soil water repellency.

SWR$_{60}$, SWR$_{AREA}$, and $w_{NON}$ was strong, i. e., a relatively low or high OC content within a soil order was accompanied by a relatively low or high severity of SWR within that same soil order. The same trend was found for IRDI. The Podzols had a significantly ($p < 0.05$) higher OC content than the Recent, Pallic and Semiarid soils, which was the same trend as for the SWR$_{AREA}$ and $w_{NON}$ parameters. Thus, the high severity of SWR in the Podzols might be attributed to the relatively high OC content compared to the remaining soil orders.

### 3.3. Relations between soil water repellency and soil properties

The SWR$_{AREA}$ was strongly correlated with OC content (R = 0.82; $p < 0.001$) with an $R^2$ of 0.68 (Fig. 6a). Thus, a simple linear expression for SWR$_{AREA}$ utilizing only OC, resulted in an RMSE of

2.09 mN m$^{-1}$ kg kg$^{-1}$:

$$SWR_{AREA} = 100.6 \, OC - 0.088 \tag{3}$$

This high correlation is in consensus with other studies, which have found a similar positive and significant correlation between SWR$_{AREA}$ and OC (de Jonge et al., 1999; de Jonge et al., 2007; Kawamoto et al., 2007; Regalado and Ritter, 2005; Regalado et al., 2008). It has been suggested in an earlier study (de Jonge et al., 1999) that the effect of heat pretreatment on the degree of SWR might be depending on the type of OC rather than the total amount of OC present in a soil sample. Further, it is inconsistent in the literature whether the SWR after heat pretreatment exhibits a strong positive correlation (Deurer et al., 2011) a weak positive correlation (Knadel et al., 2016) or no correlation (de Jonge et al., 1999) with OC content. Thus, the results of this study
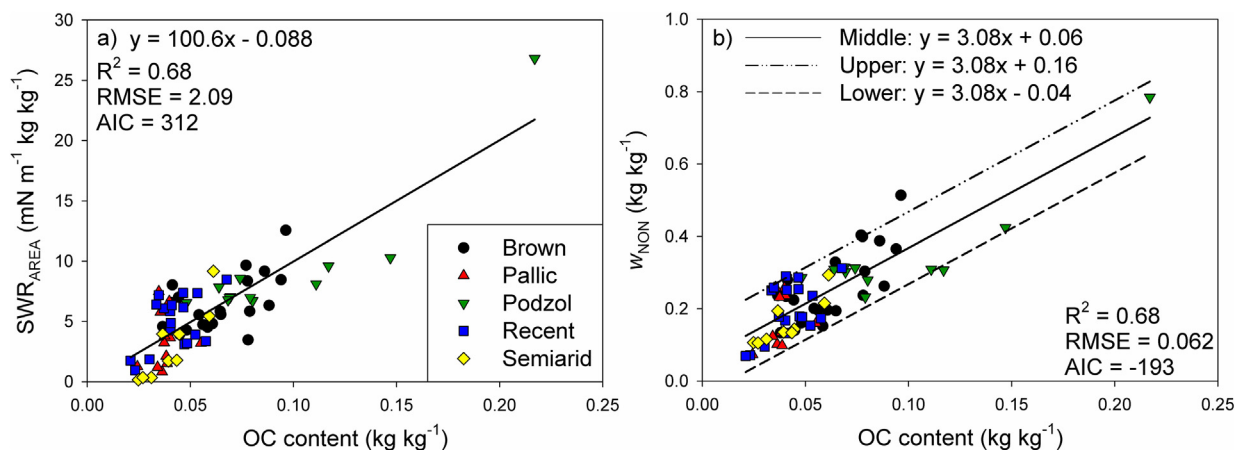


**Fig. 6.** a) The total degree of soil water repellency (SWR$_{AREA}$), and b) the critical soil-water content ($w_{NON}$) as a function of organic carbon (OC). An upper and lower limit represents the spread around the regression coefficient.

support the assumption that $SWR_{60}$ depends on the type rather than the total amount of OC, whereas the $SWR_{AREA}$ depends on the total amount of OC.

Similarly, the $w_{NON}$ was strongly positively correlated with OC (R = 0.83; p < 0.001) with an $R^2$ of 0.68. This parameter could also be described by a linear expression with OC as explanatory variable, resulting in an RMSE of 0.062 kg kg$^{-1}$:

$$w_{NON} = 3.08 \text{ OC} + 0.16 \tag{4}$$

The $w_{NON}$ delineates an important threshold above which the onset of SWR can be avoided. Thus, for practical purposes, we added an upper and lower limit to Fig. 6b, to represent the spread around the regression line. The upper limit is applicable for SWR remediation purposes since we integrated a 0.1 kg kg$^{-1}$ safety margin above which $w$ in the field should be kept to avoid SWR. The Semiarid soils and Podzols tended to be located below the middle regression line the $w_{NON}$ versus OC plot (Fig. 6b) and thus may not need the same extent of irrigation compared to the four other soil orders to avoid the onset of water repellent conditions. For now, however, the overall behavior of the five soil orders appears sufficiently similar to use the overall irrigation support model for avoiding water repellency given in Eq. (4). In perspective, when more comprehensive data for each soil order is available, it could be advantageous to develop soil-order specific models for $w_{NON}$ as a function of OC.

Sample 1 from location ZH1-1 exhibited the most extreme $SWR_{AREA}$ and $w_{NON}$ (Fig. 6a and b). Excluding this sample from the analysis, we repeated the correlation analysis for OC with all four SWR parameters. The $R^2$ and the RMSE for $SWR_{AREA}$ changed to 0.48 and 1.95 mN m$^{-1}$ kg kg$^{-1}$, respectively, while the $R^2$ and RMSE for $w_{NON}$ changed to 0.53 and 0.063 kg kg$^{-1}$, respectively. The clay content or pH of the soils did not show significant correlation with any of the SWR parameters included in this study ($SWR_{105}$, $SWR_{60}$, $SWR_{AD}$, $SWR_{AREA}$, and $w_{NON}$) (Table 2). Deurer et al. (2011) examined New Zealand soils with a similar range in pH between 4 and 6. They similarly found no relationship of soil pH with the degree or persistence of SWR. In contrast to our study, de Jonge et al. (1999) found $SWR_{AREA}$ to be negatively correlated with pH in the range between 4.1 and 7.3. In this present study, the silt content was weakly and positively correlated with $SWR_{60}$ (R = 0.36; p < 0.01) and $SWR_{105}$ (R = 0.31; p < 0.01), and sand content was weakly and negatively correlated with $SWR_{60}$ (R = −0.40; p < 0.001) but neither silt nor sand was correlated with $SWR_{AREA}$ or $w_{NON}$. The positive correlation between IRDI and OC was very low (R = 0.35; p < 0.01). Thus, in our study OC was a much more important soil property for describing $SWR_{AREA}$ or $w_{NON}$ than IRDI.

Based on a forward MLR, OC (p < 0.001) and pH (p = 0.002) contributed significantly to explain 72% of the variation in $SWR_{AREA}$ (RMSE = 1.94 mN m$^{-1}$ kg kg$^{-1}$) (Fig. 7a):

$$SWR_{AREA} = 104.191 \text{ OC} - 1.737 \text{ pH} + 9.012 \tag{5}$$

Including pH as explanatory variable had a minor effect on $SWR_{AREA}$, since the addition of this variable increased the degree to which we could explain the variation in $SWR_{AREA}$ (AIC = 304) compared to utilizing only OC in a linear regression analysis (AIC = 312).

Concerning $w_{NON}$, based on a forward MLR, OC (p < 0.001) and pH (p = 0.039) similarly contributed significantly to explain 70% of the variation (RMSE = 0.061 kg kg$^{-1}$) (Fig. 7b):

$$w_{NON} = 3.150 \text{ OC} - 0.0355 \text{ pH} + 0.246 \tag{6}$$

For the $w_{NON}$, the addition of pH as input variable had a minor positive effect on the accuracy to which we could explain the variation in this parameter. However, the increased accuracy obtained from using both OC and pH as input variables was not enough to justify the addition of an extra input parameter, since the AIC value remained the same using either OC or OC and pH in combination (Figs. 6b and 7b).

Further, a high significant correlation between $SWR_{AREA}$ and $w_{NON}$ was found (R = 0.93; p < 0.001) (Table 2) as already described in several previous studies (Kawamoto et al., 2007; Regalado and Ritter, 2005). Accordingly, the addition of $w_{NON}$ as input variable for the MLR expression for $SWR_{AREA}$ resulted in an RMSE of 1.21 mN m$^{-1}$ kg kg$^{-1}$ and an $R^2$ of 0.89 (Eq. (7), Fig. 7c). Thus, the accuracy increased significantly (AIC = 238).

$$SWR_{AREA} = 26.195 \text{ OC} - 0.858 \text{ pH} + 24.760 \, w_{NON} + 2.915 \tag{7}$$

We also performed a MLR for $SWR_{AREA}$ utilizing only OC and $w_{NON}$ as input variables, which resulted in an $R^2$ of 0.88, an RMSE of 1.26 mN m$^{-1}$ kg kg$^{-1}$ and an AIC of 242, demonstrating that adding pH in the model contributed only slightly positively to the accuracy of this MLR expression. The study of Regalado et al. (2008) similarly utilized organic matter and $w_{NON}$ to improve the prediction of $SWR_{AREA}$ compared to utilizing only organic matter.
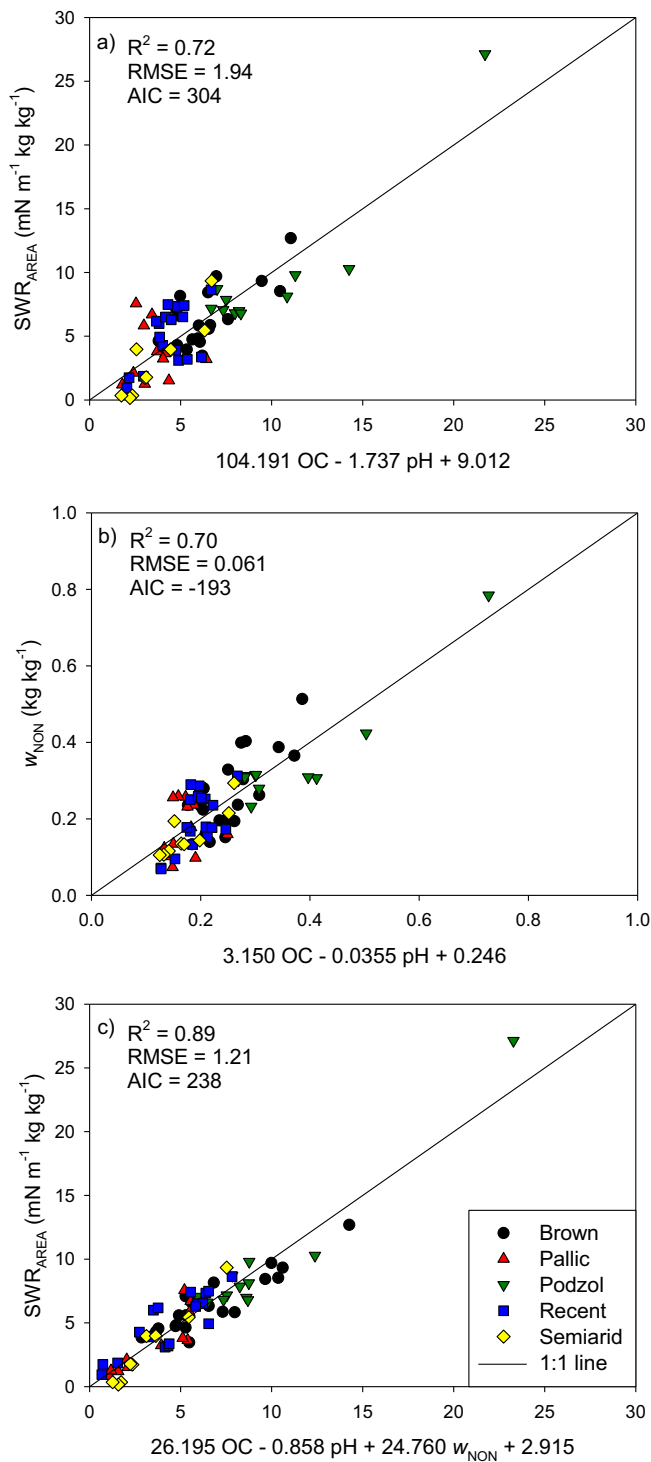
## 4. Conclusion

The soils used in this study were sampled across 26 sites under pasture in the South Island of New Zealand, representing the most dominant soil orders under pasture. About 92% of the soil samples were water repellent to some degree. For the SWR-$w$ curves exhibiting bimodal behavior, the global maximum was always located in the second peak.

The Podzols exhibited the highest $SWR_{AREA}$ and $w_{NON}$ within the five soil orders included in this data set. Further, the Semiarid soils were the least water repellent soils.

OC was the most important soil property for explaining the total degree of SWR ($SWR_{AREA}$) and the critical soil water content ($w_{NON}$). However, pH also slightly affected $SWR_{AREA}$. Further, the inclusion of both $w_{NON}$, OC, and pH in an MLR expression for $SWR_{AREA}$ significantly improved the accuracy of determining this parameter.

The $w_{NON}$ was linearly correlated with OC content, which explained

**Table 2**

Pearson Product Moment correlation matrix of organic carbon (OC), clay (< 0.002 mm), silt (0.002–0.050 mm), sand and pH, SWR after drying the samples at 60 °C ($SWR_{60}$) and 105 °C ($SWR_{105}$), the total degree of soil water repellency ($SWR_{AREA}$), the critical soil-water content ($w_{NON}$), and the integrative repellency dynamic index (IRDI) for the 72 hydrophobic soil samples.

| | OC | Clay | Silt | Sand | pH | $SWR_{105}$ | $SWR_{60}$ | $SWR_{AREA}$ | $w_{NON}$ | IRDI |
|---|---|---|---|---|---|---|---|---|---|---|
| OC | 1 | −0.04 | −0.17 | 0.17 | 0.14 | 0.41*** | 0.33** | 0.82*** | 0.83*** | 0.35** |
| Clay | | 1 | −0.03 | −0.45*** | −0.20 | 0.08 | 0.16 | 0.02 | −0.06 | 0.21 |
| Silt | | | 1 | −0.88*** | −0.18 | 0.31** | 0.36** | 0.00 | −0.12 | 0.19 |
| Sand | | | | 1 | 0.25* | −0.32** | −0.40*** | −0.01 | 0.14 | −0.27* |
| pH | | | | | 1 | -0.24 | −0.14 | −0.09 | −0.02 | −0.31** |
| $SWR_{105}$ | | | | | | 1 | 0.89*** | −0.39*** | −0.21 | 0.56*** |
| $SWR_{60}$ | | | | | | | 1 | −0.40*** | −0.18 | 0.66*** |
| $SWR_{AREA}$ | | | | | | | | 1 | 0.93*** | 0.61*** |
| $w_{NON}$ | | | | | | | | | 1 | 0.38*** |
| IRDI | | | | | | | | | | 1 |

a: Probability levels of *0.05, **0.01, and ***0.001.

**Fig. 7.** Multiple linear regressions (MLR) for the a) trapezoidal integrated area under the soil water repellency curve ($SWR_{AREA}$) and b) soil water repellency critical soil-water content ($w_{NON}$) using organic carbon (OC) and pH as input variables. c) MLR for the $SWR_{AREA}$ using OC, pH, and $w_{NON}$, as input variables.

68% of the variability. With regard to the linear $w_{NON}$ relationship with OC, a safety margin of $0.1 \, \text{kg} \, \text{kg}^{-1}$ water content was added to capture the spread around the regression line. The upper limit critical water content could be used to derive a threshold water content above which SWR and the related degradation in soil functions could be eliminated.

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