Freeze-Thaw Processes Degrade Post-fire Water Repellency in Wet Soils

Ekaterina Rakhmatulina*[1] and Sally Thompson[1,2]

[1]Civil and Environmental Engineering, University of California Berkeley, Berkeley, California

[2]Civil, Environmental and Mining Engineering, University of Western Australia, 35 Stirling Hwy, Crawley, Western Australia

Abstract

Wildfires are a cause of soil water repellency (hydrophobicity), which reduces infiltration while increasing erosion and flooding from post-fire rainfall. Post-fire soil water repellency degrades over time, often in response to repeated wetting and drying of the soil. However, in mountainous fire-prone forests such as those in the Western USA, the fire season often terminates in a cold and wet winter, during which soils not only wet and dry, but also freeze and thaw. Little is know about the effect of repeated freezing and thawing of soil on the breakdown of post-fire hydrophobicity. This study characterized the changes in hydrophobicity of Sierra Nevada mountain soils exposed to different combinations of wet-dry and freeze-thaw cycling. Following each cycle, hydrophobicity was measured using the Molarity of Ethanol test. Hydrophobicity declined similarly across all experiments that included a wetting cycle. Repeated freezing and thawing of dry soil did not degrade soil water repellency. Total soil organic matter content was not different between soils of contrasting hydrophobicity. Macroscopic changes such as fissures and cracks were observed to form as soil hydrophobicity decayed. Microscopic changes revealed

*Corresponding author: erakhmat@berkeley.edu

by scanning electron microscope imagery suggest different levels of soil aggregation occurred in samples with distinct hydrophobicities, although the size of aggregates was not clearly correlated to the change in water repellency due to wet-dry and freeze-thaw cycling. A nine year climate and soil moisture record from Providence Critical Zone Observatory was combined with the laboratory results to estimate that hydrophobicity would persist an average of 144 days post-fire at this well-characterized, typical mid-elevation Sierra Nevada site. Most of the breakdown in soil water repellency (79%) under these climate conditions would be attributable to freeze-thaw cycling, underscoring the importance of this process in soil recovery from fire in the Sierra Nevada.

1 Introduction

A century-long policy of fire suppression in California's Sierra Nevada Mountains, like much of the rest of the Western United States, has favored the growth of dense forests with high fuel loads that lead to more frequent catastrophic fires (Collins, 2014; Collins et al., 2011; Miller et al., 2009). Catastrophic fires are large in extent and also include large areas of high severity burn, (Keyser and Westerling, 2017; Schweizer et al., 2020), which dramatically changes landscapes, soils and hydrological processes (Martin, 2016; Robinne et al., 2016). Increased runoff generation and elevated erosion rates are well known consequences of severe fire (Burch et al., 1989; Kinoshita and Hogue, 2015; Moody and Martin, 2001b; Tiedemann, 1979, e.g.). For example, fires are responsible for up to 60% of long-term sediment production rates in some regions (Robichaud, 2000). In the Sierra Nevada, up to 3 orders of magnitude increases in annual sediment yield (up to 120 tonnes ha^{-1} per year) have been reported following fires (Moody and Martin, 2009). Post-fire debris flows can be immediate and acute, moving rapidly over large areas, threatening lives and costing hundreds of millions of (US) dollars (e.g. the 2018 Thomas Fire in coastal CA, Cui et al., 2018). Extensive infrastructure damage due to sediment mobilization into water systems is also reported. For example, the 2002 Hayman Fire in the Rocky Mountains deposited $\approx 765,000$ m^3 of sediment into water supply reservoirs, requiring \$30 million worth of dredging (Bladon et al., 2014). Post-fire erosion impacts can also be chronic; in the

1996 Buffalo Creek wildfire in Colorado, the immediate sediment input into reservoirs was only a fraction of the total sediment load from the fire, 67% of which was deposited in stream beds and is expected to be exported gradually over a 300-year period (Moody and Martin, 2001a).

Both vegetation loss and physicochemical changes in topsoil after fires contribute to elevated runoff and erosion rates (Caon et al., 2014; Keeley, 2009; Mataix-Solera et al., 2011; Stoof et al., 2015, 2011). Vegetation canopies mitigate runoff and erosion by reducing throughfall volumes via canopy interception (e.g. Ahlgren, 1981), maintaining higher infiltration rates by protecting the soil surface from rain splash and soil seal formation (Assouline and Mualem, 1997), mechanically increasing soil cohesion (Gyssels et al., 2005), and slowing flow and trapping suspended sediments (Stoof et al., 2015). Loss of vegetation cover thus contributes to increased runoff and erosion through multiple pathways (Larsen et al., 2009a). The impacts of these process changes are enhanced when fire also produces physiochemical changes to topsoils, including inducing soil water repellency (DeBano, 2000). Soil water repellency is attributed to the volatilization and subsequent condensation of organic chemical species on soil grains (DeBano and Krammes, 1966), which are derived from the complex humic fraction of the soil (DeBano, 2000; Doerr et al., 2000). The deposition of these chemicals coats soil grains in a mixture of nonpolar (insoluble in water) and amphiphilic (partially soluble in water) compounds that tend to inhibit infiltration. By cementing soil grains together, decreasing porosity and increasing the stability of soil aggregates (coherent units formed by chemically or physically bound soil particles, Giovannini et al., 1983; Kořenková and Matúš, 2015; Nimmo, 2005), hydrophobic compounds can further inhibit water entry into soil. Hydrophobicity usually manifests as a water repellent layer within the top 8 cm of the soil (DeBano et al., 1970; Ebel and Moody, 2020), with its precise depth and extent depending on the vegetation type and properties of the fire (DeBano, 2000; DeBano et al., 1970). Many techniques are available to measure hydrophobicity, all of which assess the physics of water interaction with soils (e.g. the time taken to infiltrate a droplet of water (Letey, 1969), the contact angle of water on the soil surface (Bachmann et al., 2000), or the extent of capillary rise within the soil (Letey et al., 1962)). In this study, hydrophobicity was measured with Molarity of Ethanol Test (MED) which identifies the molarity of ethanol in water needed for a drop of the solution to infiltrate into the soil in a fixed 10 second time period (King, 1981; Watson and Letey, 1970). We implemented MED tests using ethanol solutions ranging from 0% to 22% molarity, in increments of 0.5%. Soil is deemed moderately hydrophobic above 5.5% (King, 1981).

Post-fire soil hydrophobicity is not a permanent soil property, but decreases at a variable rate, typically returning to pre-fire levels within 1 to 6 years (Leelamanie and Karube, 2007; Shakesby, 2011). There are some clear associations between hydrophobicity levels and the environmental conditions experienced by soil, including temporary increases in wettability with increasing soil moisture content (Doerr et al., 2000), more permanent increases following repeated cycles of wetting and drying (Doerr et al., 2000; Quyum et al., 2002), and increases in wettablity following soil agitation (Horne and McIntosh, 2000; King, 1981; Mashum and Farmer, 1985). The underlying mechanisms responsible for degradation via these environmental drivers remain unclear, with chemical leaching (Doerr and Thomas, 2003), chemical transformation of hydrophobic compounds (Simkovic et al., 2008), destruction of aggregates (Horne and McIntosh, 2000; King, 1981; Mashum and Farmer, 1985), and creation of preferential flow paths all finding inconsistent support across studies (Jordan et al., 2017; Leelamanie and Karube, 2007). Additionally, several studies suggest that complex surface chemical processes, such as changes in isomer configuration or ion exchange states could cause reversible changes to hydrophobicity (Doerr et al., 2000; Horne and McIntosh, 2000; Kleber et al., 2007).

In the Sierra Nevada (and much of the western US), the fire season is followed by a cold, wet winter. In these environments, the wet-dry cycling that is linked to loss of soil hydrophobicity also involves freeze-thaw cycles at the soil surface. Freeze-thaw processes in soils are known to generate a range of physical (Ferrick and Gatto, 2005; Fitzhugh et al., 2001, e.g. frost heave), chemical (DeLuca et al., 1992; Herrmann and Witter, 2002, e.g. enhanced mineralization), and biological (Yanai et al., 2004, e.g. depression of enzyme reaction kinetics and degrataion rates) changes (Henry, 2007; Marion, 1995). In particular, freeze-thaw cycles have been repeatedly shown to reduce soil aggregate stability (Kværnø and Øygarden, 2006; Oztas and Fayetorbay, 2003; Zhang et al., 2016), a reduction often associated with the degradation of soil hydrophobicity (Giovannini et al., 1983; Horne and McIntosh, 2000; King, 1981; Kořenková and Matúš, 2015; Mashum and Farmer, 1985). To date, however, there is almost no information measuring how soil hydrophobicity degrades following exposure to freeze-thaw cycling, and how this degradation compares to that induced by the better known process of soil wetting and drying. One study reported that *freeze-drying* converted a severely water-repellent soil into a readily wettable soil, although rewetting and oven drying restored water repellency (Mashum and Farmer, 1985). No *in situ* or laboratory studies have been undertaken to explore freeze-thaw cycling effects on hydrophobicity in contexts similar to those in the field (e.g. repeated freezing, thawing, wettting and drying processes).

To begin to fill this knowledge gap, we tested the effects of freeze-thaw cycles on the degradation of heat induced soil hydrophobicity in a laboratory study. Hydrophobicity was measured using MED on soil samples subjected to repeated and varied combinations of wet-dry and freeze-thaw cycles. To constrain potential degradation mechanisms, the soil samples were characterized chemically, physically, and at the granular level (via electron microscopy) under contrasting MED conditions. The relationships obtained between soil hydrophobicity and soil exposure to different freeze-thaw and wet-day cycles were then used to estimate the timescale over which post-fire hydrophobicity would decay in the field under Sierra Nevada climate conditions, and to assess the significance of freeze-thaw processes for recovery of soil wettability in this area.

2 Methods

2.1 Soil Preparation

Soil samples were obtained from the Jennie Lakes Wilderness (36.71403°N, -118.75708°E) located in the Californian Sierra Nevada at an elevation of 2530 m. Soils were sampled from beneath a canopy mix of Jeffrey pine (*Pinus jeffreyi*), lodgepole pine (*Pinus contorta*), white fir (*Abies concolor*), and red fir (*Abies magnifica*). No fires were recorded in the sampling location since local records for the Sequoia Kings Canyon National Park began in 1910 (see fire perimeter data at https://frap.fire.ca.gov/mapping/gis-data). Soil samples were taken from the top 5 cm of mineral soil after first removing the surface litter layer, which consisted of pine needles and duff. Approximately 5 gallons of soil were collected, and air dried at room temperature (25 °C) in a laboratory at UC Berkeley, until the soil weight stabilized. The dry soil was sieved at 2 mm and homogenized (Figure 1-A). The soil was sandy (75% sand, 6% clay,and 19% silt). The MED of the soil sample was 6.5%, indicating that a low level of hydrophobicity was present in the native soil. Even in the absence of wildfires, hydrophobicity is observed in many sandy soils, especially under *Pinus* species (Doerr et al., 2009; Zavala et al., 2014).

To determine optimal heating conditions, soil sub-samples were held in a furnace at temperatures ranging from 150 to 285 °C for 15 and 20 min. Once cooled, their hydrophobicity was assessed with the MED test. The highest MED value of 16% ('very hydrophobic') was achieved for soils that were heated for 15 minutes at 260°C (data not shown). Then, sixty aluminium baking trays, each containing 6 separate pans, were filled with 8-12 g of soil in each pan. Each tray was heated once for 15 minutes at 260°C (1-B). Throughout heating, the furnace (*Fisher Scientific Isotemp Muffle Furnace 650-14*) fluctuated ±1°C. The soil was cooled before any further treatments were applied.

Reference samples of both hydrophobic and hydrophilic soils were also prepared. We considered two kinds of hydrophilic soils: the original, sieved and homogenized field soils, which are referred to as 'non-heated' soils, and hydrophilic soils prepared by burning off the soil organic fraction, referred to as 'heated hydrophilic' soils. Heated hydrophilic soil was prepared by heating field soil at 260^0C for >20 min (at which point the soil began to smoke). The MED for these soils was 0% with pure water droplets infiltrating instantly. Finally, reference samples of heated hydrophobic soils were also prepared, similarly to the treatment soils, by holding field-collected soil (homogenized and sieved) at 260^0C for 15 min.

2.2 Experimental Treatments

The hydrophobic soils were subjected to different treatments (Figure 1-C), comprising different, physically plausible, combinations of wet-dry and freeze-thaw cycling. These treatments are:

- repeated wet/dry cycles (WD)
- repeated wet/freeze/thaw/dry cycles (WFTD)
- repeated wet/dry/freeze/thaw (WDFT)
- repeated freeze/thaw cycles on dry soils (DFT)
- repeated freeze/thaw on wet soils (WFT).

To wet the soil (as required in the WD, WFTD, WDFT, WFT cycles), de-ionized water was applied using a misting spray bottle. The mist application was selected to minimize the impact of drop splash on the soil surface. Water was sprayed onto the surface until free water ponded to a depth of approximately 1 cm on the soil surface, after which the sample was left undisturbed for 12 hours. Perforation in the aluminum baking pans allowed for water to drain if it fully infiltrated the soil column. Any remaining ponded water was removed from the soil surface with a pipette after 12 hours. This situation often occurred in the first treatment cycles while soils were highly hydrophobic. For the WFT treatment, soil samples were wetted once and the trays with soil were stored in sealed plastic bags to prevent drying. Each sample was allowed to dry once only, immediately prior to the MED measurement. To dry the soil (as required to measure MED for the WFT treatment, and as part of the regular treatment cycle for the WD, WFTD, WDFT, DFT treatments), soil samples sat for twelve hours at room temperature ($\tilde{2}5^0$C). To freeze the soil (as required for the WFTD, WDFT, DFT, WFT treatments), soil samples were placed in a temperature stable freezer at -20^0C for at least 6 hours. To thaw the soil, frozen soil samples were left at room temperature for at least 6 hours. The time periods used were determined following experimental pilots which found that the soil samples dried (to the point where no further weight change was recorded with further drying) after 12 hours, and that water without soil would freeze and thaw in the freezer and at room temperature within 6 hours.

Each treatment was applied to 12 separate soil samples (i.e. 2 of the aluminium trays). For each treatment, one sample was used to measure MED after induction of hydrophobicity and before treatment application. The remaining 11 samples were subject to between 1 and 11 repeated treatment applications referred to as "cycles" (Figure 1-C). Each treatment was replicated six times. After each treatment cycle, MED was measured for one sample. The location of the samples used for each cycle was randomized across all treatments to avoid any systematic biases associated with location within the trays. Figure 1-B illustrates this schematically for one treatment.

Figure 1: GOES HERE

2.3 Total Organic Carbon

Three replicas from each cycle and treatment were used to assess changes in total organic carbon content via the Walkley-Black test according to a standard protocol following Nelson and Sommers (1965) at UC Davis Analytical Laboratory (https://anlab.ucdavis.edu/). The Walkley-Black method was chosen because it is accurate on soils with low total organic matter (<15%). The entire soil sample was analyzed in each case. In total, 180 samples were measured, including 20 duplicates used to check reproducibility.

2.4 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to visualise the surface topography of non-heated soil, heated hydrophobic soil, and heated hydrophilic soil. We also made one opportunistic measurement of a soil sample that went through seven cycles of wet/dry/freeze/thaw (WDFT): this was the only undisturbed treated sample available for SEM scanning. Untreated soil samples were evenly sprinkled on a mount while surface soil from the WDFT sample was carefully removed and placed on a mount: the SEM imagery of the WDFT soil therefore imaged the undisturbed soil surface.

All samples were sputter coated with a thin gold/palladium film. Subsequently, samples were examined with a Hitachi TM4000 microscope. Imagery of samples was taken using backscattered electrons (BSE), second electrons (SE), and Mix (mixture of SE and BSE) detection modes with an acceleration potential of

15 kV at resolutions of 100, 300, 400, 500, and 1000 times. We present images at ×100 resolution in the BSE mode, in which individual aggregates are most distinguishable. In this analysis, aggregates are identified as individual particles, or collections of particles clumped together and including not only the mineral substrate but also the organic matter.

Using ImageJ software (Rasband and Ferreira, 2012), aggregate size analysis was performed for ×100 BSE and Mix images of non-heated, heated hydrophobic, heated hydrophilic, and 7th cycle of WDFT soil samples. First, each image was binarized into aggregates and void space using a grayscale threshold (image intensity value from a range of 0-256). All void pixels enclosed within aggregate pixels were reclassified as aggregate pixels using the "Fill Holes" tool. The, "Watershed" tool was used to separate individual aggregates. The tool successfully separated adjacent particles, but in some cases erroneously broke down aggregates into smaller pieces. We manually examined all images and removed watershed lines that incorrectly separated parts of an aggregate, focusing on the largest aggregates. Finally, the "Particle Size Analysis" tool was used to calculate an area for individual aggregates and generate the cumulative aggregate size curve, showing the percentage of aggregates smaller than a given area.

Following this methodology, aggregate area is sensitive to the threshold used to binarize the image. To standardize, we selected thresholds as the 40%, 50%, and 60% percentiles of the grayscale intensity distribution of each image. Although we did not have multiple images to compare the analysis across, we tested for sampling bias and variability by repeating the analysis (with the 50% threshold level) on three random, non-overlapping sub-samples of each image. We report both the cumulative aggregate size distribution curves and the percentage the largest ten particles occupy out of the total aggregate area based on the analysis of the four ×100 BSE images using 50% threshold.

2.5 Time frame of hydrophobicity decay in the Sierra Nevada

The laboratory experiment relates changes in MED to the application of successive treatment cycles. To relate these cycles to an estimate of time-since-fire, we used a nine year climate and soil moisture record (October 1, 2008 through October 1, 2017) from the Providence Critical Zone Observatory (CZO) site located in the Southern Sierra (Bales et al., 2011). We obtained air temperature, snowpack depth, and shallow soil moisture measurements at 10 cm depth from the Upper Providence sensor node located on flat aspect and having open canopy (elevation: 1982 meters, lat: 37.0626N, lon: -119.1823E, data: https://eng.ucmerced.edu/snsjho/files/MHWG/Field/SouthernSierraCZOKREW). The reported soil texture at this site is very similar to the soil collected for the main experiment at Jennie Lakes Wilderness, with 79% sand, 6% silt, and 15% clay (Bales et al., 2011). Vegetation around the the Providence CZO instrumentation site is also very similar to our soil sampling location, with 76-99% of the Providence watershed cover comprising of mixed-conifer forest of white fir (*Abies concolor*), ponderosa pine (*Pinus ponderosa*), Jeffrey pine (*Pinus jeffreyi*), sugar pine (*Pinus lambertiana*), and incense cedar (*Calocedrus decurrens*) (Bales et al., 2011).

Daily precipitation data were obtained from the neighboring (within 40 m) Upper Providence Weather Station (data: https://www.fs.usda.gov/rds/archive/catalog/RDS-2018-0028). Missing air temperature records ($\approx 10\%$) were gap filled from the neighboring weather station, and remaining gaps ($< 0.2\%$ of the record) were linearly interpolated. Hourly air temperature data was averaged to a 6 hour resolution to correspond to the timescales of freeze/thaw used in the laboratory cycles. The hourly soil moisture record was smoothed using a cubic smoothing spline function (*smooth.spline* in R) to generate a 6 hour record.

We classified the smoothed soil moisture data, identifying drying events when volumetric water content fell below 6%, and wetting events when volumetric water content rose above 6%. The 6% cutoff is based both on the CZO timeseries at 10 cm depth of minimum soil moisture threshold and studies stating that the critical soil moisture for transition between hydrophobic and hydrophilic soil state can range anywhere between 2-28% at surface (Dekker et al., 2001; Doerr and Thomas, 2003; Doerr et al., 2000).

Where smoothed soil moisture at 10 cm was $< 6\%$ but a precipitation event of > 1cm was recorded, we assumed that the surface soil was wetted and then dried, but that the wetting fronts had not reached the sensor at 10cm. We assumed, however, that these events represented a wet-dry cycle at the soil surface that would impact hydrophobicity. If dry conditions were maintained through repeated days of precipitation, these were treated as a single wet/dry event. Precipitation events were assumed not to contribute to wet/dry cycles when snowpack was over 10 cm, regardless of the soil condition.

To account for the effect of the thermal insulating properties of snowpack, we assumed that no freeze-thaw cycles could be induced in the soil when snowpack depths exceeded 10 cm. Above this depth, snowpack acts as an insulator that de-couples air temperature from soil surface temperature (Chang et al., 2014; Thompson et al., 2018; Zhao et al., 2018). Provided snow depth was < 10cm, then a freeze event was identified when air temperature dropped below 0°C (on 6 hour timescales). Thaw events occurred when sub-zero temperatures then rose above 0°C. Dry freeze/thaw cycles were identified as freeze-thaw cycles occurring when the soil was dry (soil moisture at 10 cm below 6%). Wet freeze/thaw cycles required either wet soil or a freeze/thaw cycle that occurred within 24 hours of a precipitation event on dry soil.

For the nine year data record (2008-2017), we calculated the time taken for each cycle to occur following a hypothetical fire that stopped burning on October 1st. The final hypothetical fire ended in October 2015; this was the last date for which sufficient climate data was available to resolve all 11 cycles. Finally, the different cycles were converted into an estimate of hydrophobicity decline, with drops in hydrophobicity estimated based on the different rates of decline (and the uncertainties in these rates across the experimental replicates) associated with each of the different kinds of wetting-drying or freeze-thaw cycles experienced.

3 Results

3.1 Soil Water Repellency Degradation Mechanisms

After heating soil at 260^0C for 20 min, the mean MED for the soil samples was 16.6% (cycle 0 in Figure 2), classified as very severely hydrophobic (King, 1981). Hydrophobicity remained the same after one cycle of treatments that included a freeze/thaw component of wet soil (WFT, WFTD), and increased by 1.6% MED for cycles with a wet/dry component (WD and WDFT). After 3 cycles of treatment, the MED of the treated samples other than the DFT treatment all declined below a reference condition given by the 'heated hydrophobic' soil. The MED values of the DFT treatment were statistically indistinguishable from the 'heated hydrophobic' reference across all treatment cycles. Freeze-thaw cycles applied to wet soil, however, lead to declines in hydrophobicity, whether or not the soil was allowed to dry between the freeze-thaw cycles. All cycles containing a wetting component lead to similar rates of hydrophobicity decline. However, the wet/freeze/thaw cycles exhibit greater MED variability across replications than the other cycles involving a wet soil phase (standard deviation of 3.1% MED vs 1.7% MED respectively). The soil water repellency returned to conditions similar to the non-heated hydrophobic native soils (MED=6.5%) after the 6th cycle for all treatments other than DFT. By the end of the 11th cycle, the mean MED across treatments (other than DFT) dropped to 1.9%, much lower than the MED of the non-heated soil from the field.

Figure 2: GOES HERE

As multiple treatment cycles progressed, the soil surface became visually different. Photographs of the soil surface for one of the replicas of the wet/freeze/thaw cycles are shown in Figure 3. Small fissures that appeared in the soil surface following treatment are highlighted in white. Fissures developed after 2 cycles, and their number and length increased as treatment applications increased. Similar patterns were observed in all treatments that involved a wetting component. No fissures formed on the soil surface of dry/freeze/thaw cycles (images not shown).

Figure 3: GOES HERE

3.2 Soil Organic Matter

Soil organic matter (SOM) measured for all cycles and treatments with three replicas is presented in Figure 4. Prior to treatment applications, the mean SOM (cycle 0) was 10.9% $\pm$ 0.68 (1.2% $\pm$ 0.54); here, the standard deviation across treatments is shown in brackets, and errors are based on the differences between 20 replicate samples. By the 11th cycle, SOM had decreased by 1.8% SOM which is significantly different from the pre-treatment (cycle 0) SOM, based on a 2-sided Kolmogorov-Smirnov test. The overall change, however, is small. There is a weak correlation of 0.27 (data not shown) between treatments' SOM content and measured MED. There is no significant difference in SOM between treatment types. Potentially these SOM results were diluted by measuring SOM for the whole soil sample, rather than the soil surface only. We estimate that the soil surface represents $\sim 10\%$ of the entire soil sample.

Figure 4: GOES HERE

3.3 Scanning Electron Microscopy

The SEM images in Figure 5 did not reveal any differences in the organic matter matrix that has been reported by others (Jiménez-Morillo et al., 2017). This may be due to the organic coating being too thin for the SEM to detect (Doerr et al., 2000). Though at $\times 100$ resolution, there were differences in aggregate size distribution between soils of different MED (Figure 6).

Figure 5: GOES HERE

Based on the aggregate size distribution curves, the ten largest aggregates make up 58% of the total aggregate area for cycle 7 of WDFT, followed by 44% for the heated hydrophobic soil, 33% for the non-heated soil, and 21% for the heated hydrophilic soil samples. The aggregate size below which 50% of the aggregates are finer is 2.9, 0.9, 0.5, and 0.3 cm^2 for the 7th WDFT cycle, heated hydrophobic, non-heated hydrophobic, and heated hydrophilic respectively. Based on these two metrics, there is a positive correlation between MED and aggregate size among non treated samples. However, this relationship does not hold when the treated (7th cycle of WDFT) sample is included; even though its MED of 4% is relatively low, cycle 7 of WDFT treatment has larger aggregates among all of the samples.

Analysis using different grayscale thresholds and image sub-sampling (data not shown) produced aggregate size distribution curves with the same relative relationship as in Figure 6, making our analysis robust.

Figure 6: GOES HERE

3.4 Sierra Nevada Climate and Hydrophobicity Decay

Fifty-nine freeze-thaw events and 38 wet-dry events were identified in the nine year climate and soil moisture record from Upper Providence CZO, as shown in Figure 7-A,C. The identification of these events for the 2013 water year is shown in Figure 7-B and -D.

Figure 7: GOES HERE

Figure 8-A shows the timing of the first eleven successive WFT, WDFT, or WD cycle relative to October 1st over the eight analysed years. In Figure 8-B, the hydrophobicity distribution associated with each cycle is shown as a function of the median number of days since October 1st when that cycle occurred. Seventy-one percent of the first eleven cycles over eight years were wet/freeze/thaw cycles. The most rapid loss of hydrophobicity during the analysed period was for winter 2011-2012, when all eleven cycles occurred in 79 days and were primarily wet freeze/thaw cycles. The longest duration of hydrophobicity was associated with the severe warm California drought from 2014-2015: hydrophobic soils induced prior to that winter would have persisted for 562 days. On average, the eleven cycles considered occurred within 350 days. Hydrophobicity was typically reduced to the 'non-heated hydrophobic' reference condition within six cycles, requiring a mean of 144 days.

Figure 8: GOES HERE

4 Discussion

The experimental results indicate that freeze-thaw cycling on wet soils resulted in a similar magnitude and rate of hydrophobicity loss as did more conventionally considered wet-dry cycling, or wet-dry cycling combined with freeze-thaw cycling; suggesting the potential for freeze-thaw processes to be important mechanisms of soil physico-chemical recovery following fire.

Analysis of climate and soil moisture data to identify the occurrence of freeze/thaw and wet/dry cycles in surface soils of a well-monitored mid-elevation Sierra Nevada site confirmed that freeze-thaw processes are likely to have pragmatic importance in post-firer soil recovery. Most of the area burned by fires in the Sierra Nevada burns in the period from October to December (Williams et al., 2019); these late-season wildfires occur under low fuel and soil moisture conditions, which are conducive to soil heating and the generation of hydrophobic soil layers. It is the arrival of winter rain and low temperatures that typically ends the Sierra Nevada fire season: as represented in this analysis by a hypothetical October 1st end-of-fire date. Over the eight-years of data analysed, hydrophobic soils generated by this hypothetical fire would return to pre-fire wettability conditions over a mean period of 144 days. This relatively rapid rate of degradation of hydrophobicity would be mostly attributed to freeze-thaw cycling, representing approximately 80% of the soil changes that contributed to hydrophobicity loss. Thus, it is likely that freeze-thaw cycling is of practical importance in regulating the recovery of soils from post-fire hydrophobicity in the Sierra Nevada.

The experimental results do not clearly identify the mechanisms by which soil hydrophobicity is lost as repeated wetting, drying, freeze and thaw cycles are imposed on soil. They do, however, constrain some of the possibilities. First, it is clear that degradation is not simply a function of time, given that no change in hydrophobicity of the dry freeze-thaw samples was observed. Second, it seems unlikely that removal of hydrophobic compounds via leaching was the main mechanism responsible. Two strands of evidence contradict this. Firstly, although leaching was possible in treatment cycles that involved repeated wetting and drying, it was not possible in the freeze-thaw cycles applied to a wet soil. Yet the decay in hydrophobicity in the wet freeze-thaw cycling was comparable, if more variable across replicates, to that in other treatment cycles involving repeated wetting and drying. Secondly, although soil organic matter declined in all treatments, this decline was modest in magnitude (less than 2 percentage points decline relative to an initial mean SOM of 10.9%), only weakly correlated to MED, and not statistically different between the hydrophobic samples from the dry freeze/thaw cycle (MED=16.9%) and the hydrophilic samples across all samples following eleven treatment cycles (MED=1.9%). Third, there is suggestive if inconclusive evidence that physical changes in the soil structure at macro- and micro-scales. Fissure length and number increased as MED decreased over repeated wet/dry (or wet freeze/thaw) cycles. In the absence of chemical changes, these fissures may have provided flow pathways that were less influenced by surface hydrophobicity (e.g. due to smaller surface area to volume ratios) than the original soil pores. Similarly, the SEM images indicated that soil surfaces with distinct MED patterns were also distinguished by different aggregate sizes. Amongst untreated soils, there was a clear trend towards increasing MED and hydrophobicity with aggregate size. The opportunistic measurement made on the treated soil sample suggests that its distribution of surface aggregate sizes was also distinct from the untreated soils. However, due to its different treatment history, and the fact that this sample was an intact soil surface rather than a homogenised soil sample, makes a direct comparison of aggregate size distributions between the untreated and treated soils impossible. It is, however, again suggestive that differences in soil wettability were, to some extent, reflected in differences in soil aggregate structures at the microscopic level.

Therefore, based on the preliminary evidence collected here, it seems likely that the degradation of hydrophobicity is associated with similar processes amongst the wet/dry and wet freeze/thaw cycles. These processes depend upon water, and may have a physical component, potentially associated with macroscopic and microscopic changes to soil structure induced by drying of wet soil (e.g. shrink-swell behavior) or by expansion of frozen water (e.g. frost-heave processes). It is also possible that other chemical mechanisms, not tested here, could be associated with changing hydrophobicity. For example, changes in the orientation of amphipathic (partially polar) molecules could be induced by varying environmental conditions, leading to changes in hydrophobicity that do not require changes in bulk soil chemistry (Horne and McIntosh, 2000; Kleber et al., 2007).

Regardless of the microscopic mechanisms involved, the significant of freeze/thaw cycling for post-fire soil hydrophobicity in the Sierra Nevada and other montane or seasonally frozen environments suggests the potential for complex feedbacks between fire and hydrological processes subject to climatic warming. As climate warms, the duration and mean depth of snowpack will decline, as will the length of the season in which freeze-thaw cycling occurs. This is likely to have confounding effects on freeze/thaw cycling, which may be more frequent with a shallower snowpack (Decker et al., 2003): in the dataset analysed here, freeze thaw cycles would increase in importance for degrading hydrophobicity (from 79% of cycles to 91% of cycles) in the absence of a snowpack. However, the shorter snow season would tend to reduce the number of such events. The effect of climatic warming will also alter the elevation of the snowline: currently moving upward from its current elevation between 800 and 2800 m across the Sierra Nevada (Lundquist et al., 2008) by as much as 72 m/yr (Hatchett et al., 2017). Below the snowline, warmer temperatures would tend to reduce freeze-thaw cycling. Near the snowline, warmer mean temperatures might be expected to increase the frequency with which air temperatures fluctuate around 0°C while reducing the insulating effect of the snowpack itself (Templer et al., 2017). While well above the snowline, climate warming will probably not greatly alter the frequency of freeze/thaw events. The loss of snowpack and freeze-thaw dynamics along with the increased fire risk anticipated with warming and drying at low elevations may also exacerbate the risks to soil and water quality following fires, due to the loss of freeze/thaw mechanisms to restore soil wettability.

We conclude that freeze-thaw cycling could be an important factor mitigating against long-term water quality, erosion, and flood risks from fire in the Sierra Nevada. These cycles, which do not in themselves produce risks of erosion or flood exacerbation, appear to enable substantial soil wettability recovery in the first winter after late summer fires. Of course, this mechanism does not prevent flooding and erosion impacts from fire in the Sierra Nevada, as the effects of vegetation loss remain (Berg and Azuma, 2010; Larsen et al., 2009b). The potential relevance of freeze-thaw cycles for post-fire soil recovery merits further investigation, both to resolve the underlying mechanisms by which hydrophobicity is degraded, and to quantify the importance of freeze/thaw processes *in situ* for recovery of soil hydraulic properties post fire. The latter may be particularly important to an improved understanding of fire impacts in the Sierra Nevada and similar mountain ecosystems as climates continue to warm.

References

Ahlgren, C. E. (1981). Seventeen-year changes in climatic elements following prescribed burning. Forest Science, 27(1):33–39.

Assouline, S. and Mualem, Y. (1997). Modeling the dynamics of seal formation and its effect on infiltration as related to soil and rainfall characteristics. Water Resources Research, 33(7):1527–1536.

Bachmann, J., Ellies, A., and Hartge, K. (2000). Development and application of a new sessile drop contact angle method to assess soil water repellency. Journal of Hydrology, 231-232:66–75.

Bales, R. C., Hopmans, J. W., OGeen, A. T., Meadows, M., Hartsough, P. C., Kirchner, P., Hunsaker, C. T., and Beaudette, D. (2011). Soil moisture response to snowmelt and rainfall in a sierra nevada mixed-conifer forest. Vadose Zone Journal, 10(3):786–799.

Berg, N. H. and Azuma, D. L. (2010). Bare soil and rill formation following wildfires, fuel reduction treatments, and pine plantations in the southern sierra nevada, california, USA. International Journal of Wildland Fire, 19(4):478.

Bladon, K. D., Emelko, M. B., Silins, U., and Stone, M. (2014). Wildfire and the future of water supply. Environmental Science & Technology, 48(16):8936–8943.

Burch, G. J., Moore, I. D., and Burns, J. (1989). Soil hydrophobic effects on infiltration and catchment runoff. Hydrological Processes, 3(3):211–222.

Caon, L., Vallejo, V. R., Ritsema, C. J., and Geissen, V. (2014). Effects of wildfire on soil nutrients in mediterranean ecosystems. Earth-Science Reviews, 139:47–58.

Chang, J., xu Wang, G., heng Gao, Y., and bo Wang, Y. (2014). The influence of seasonal snow on soil thermal and water dynamics under different vegetation covers in a permafrost region. Journal of Mountain Science, 11(3):727–745.

Collins, B. M. (2014). Fire weather and large fire potential in the northern sierra nevada. Agricultural and Forest Meteorology, 189:30–35.

Collins, B. M., Everett, R. G., and Stephens, S. L. (2011). Impacts of fire exclusion and recent managed fire on forest structure in old growth sierra nevada mixed-conifer forests. Ecosphere, 2(4):1–14.

Cui, Y., Cheng, D., and Chan, D. (2018). Investigation of post-fire debris flows in montecito. ISPRS International Journal of Geo-Information, 8(1):5.

DeBano, L. F. (2000). The role of fire and soil heating on water repellancy in wildland environments: a review. Journal of Hydrology, 231-232:195–206.

DeBano, L. F. and Krammes, J. S. (1966). Water repellent soils and their relation to wildfire temperatures. International Association of Scientific Hydrology. Bulletin, 11(2):14–19.

DeBano, L. F., Mann, L. D., and Hamilton, D. A. (1970). Translocation of hydrophobic substances into soil by burning organic litter. Soil Science Society of America Journal, 34(1):130–133.

Decker, K., Wang, D., Waite, C., and Scherbatskoy, T. (2003). Snow removal and ambient air temperature effects of forest soil temperatures in northern vermont. Soil Science Society of America Journal, 67(5):1629–1629.

Dekker, L. W., Doerr, S. H., Oostindie, K., Ziogas, A. K., and Ritsema, C. J. (2001). Water repellency and critical soil water content in a dune sand. Soil Science Society of America Journal, 65(6):1667–1674.

DeLuca, T., Keeney, D., and McCarty, G. (1992). Effect of freeze-thaw events on mineralization of soil nitrogen. Biology and Fertility of Soils, 14(2):116–120.

Doerr, S. and Thomas, A. (2003). Soil moisture: a controlling factor in water repellency? In Soil Water Repellency, pages 137–149. Elsevier.

Doerr, S., Woods, S., Martin, D., and Casimiro, M. (2009). 'natural background' soil water repellency in conifer forests of the north-western USA: Its prediction and relationship to wildfire occurrence. Journal of Hydrology, 371(1-4):12–21.

Doerr, S. H., Shakesby, R. A., and Walsh, R. P. (2000). Soil water repellency: Its causes, characteristics and hydro-geomorphological significance. Earth Science Reviews, 51(1-4):33–65.

Ebel, B. A. and Moody, J. A. (2020). Parameter estimation for multiple post-wildfire hydrologic models. Hydrological Processes.

Ferrick, M. and Gatto, L. W. (2005). Quantifying the effect of a freeze–thaw cycle on soil erosion: laboratory experiments. Earth Surface Processes and Landforms: The Journal of the British Geomorphological Research Group, 30(10):1305–1326.

Fitzhugh, R. D., Driscoll, C. T., Groffman, P. M., Tierney, G. L., Fahey, T. J., and Hardy, J. P. (2001). Effects of soil freezing disturbance on soil solution nitrogen, phosphorus, and carbon chemistry in a northern hardwood ecosystem. Biogeochemistry, 56(2):215–238.

Giovannini, G., Lucchesi, S., and Cervelli, S. (1983). Water-repellent substances and aggregate stability in hydrophobic soil. Soil Science, 135(2).

Gyssels, G., Poesen, J., Bochet, E., and Li, Y. (2005). Impact of plant roots on the resistance of soils to erosion by water: a review. Progress in physical geography, 29(2):189–217.

Hatchett, B., Daudert, B., Garner, C., Oakley, N., Putnam, A., and White, A. (2017). Winter snow level rise in the northern sierra nevada from 2008 to 2017. Water, 9(11):899.

Henry, H. A. (2007). Soil freeze–thaw cycle experiments: trends, methodological weaknesses and suggested improvements. Soil Biology and Biochemistry, 39(5):977–986.

Herrmann, A. and Witter, E. (2002). Sources of c and n contributing to the flush in mineralization upon freeze–thaw cycles in soils. Soil Biology and Biochemistry, 34(10):1495–1505.

Horne, D. and McIntosh, J. (2000). Hydrophobic compounds in sands in new zealand—extraction, characterisation and proposed mechanisms for repellency expression. Journal of Hydrology, 231-232:35–46.

Jiménez-Morillo, N. T., Spangenberg, J. E., Miller, A. Z., Jordán, A., Zavala, L. M., González-Vila, F. J., and González-Pérez, J. A. (2017). Wildfire effects on lipid composition and hydrophobicity of bulk soil and soil size fractions under quercus suber cover (SW-spain). Environmental Research, 159:394–405.

Jordan, C. S., Daniels, J. L., and Langley, W. (2017). The effects of temperature and wet-dry cycling on water-repellent soils. Environmental Geotechnics, 4(4):299–307.

Keeley, J. E. (2009). Fire intensity, fire severity and burn severity: a brief review and suggested usage. International Journal of Wildland Fire, 18(1):116–126.

Keyser, A. and Westerling, A. L. (2017). Climate drives inter-annual variability in probability of high severity fire occurrence in the western united states. Environmental Research Letters, 12(6):065003.

King, P. M. (1981). Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect its measurement. Australian Journal of Soil Research, 19(3):275–285.

Kinoshita, A. M. and Hogue, T. S. (2015). Increased dry season water yield in burned watersheds in southern california. Environmental Research Letters, 10(1):014003.

Kleber, M., Sollins, P., and Sutton, R. (2007). A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry, 85(1):9–24.

Kořenková, L. and Matúš, P. (2015). Role of water repellency in aggregate stability of cultivated soils under simulated raindrop impact. Eurasian Soil Science, 48(7):754–758.

Kværnø, S. H. and Øygarden, L. (2006). The influence of freeze–thaw cycles and soil moisture on aggregate stability of three soils in norway. CATENA, 67(3):175–182.

Larsen, I. J., MacDonald, L. H., Brown, E., Rough, D., Welsh, M. J., Pietraszek, J. H., Libohova, Z., de Dios Benavides-Solorio, J., and Schaffrath, K. (2009a). Causes of post-fire runoff and erosion: water repellency, cover, or soil sealing? Soil Science Society of America Journal, 73(4):1393–1407.

Larsen, I. J., MacDonald, L. H., Brown, E., Rough, D., Welsh, M. J., Pietraszek, J. H., Libohova, Z., de Dios Benavides-Solorio, J., and Schaffrath, K. (2009b). Causes of post-fire runoff and erosion: Water repellency, cover, or soil sealing? Soil Science Society of America Journal, 73(4):1393–1407.

Leelamanie, D. A. L. and Karube, J. (2007). Effects of organic compounds, water content and clay on the water repellency of a model sandy soil. Soil Science and Plant Nutrition, 53(6):711–719.

Letey, J. (1969). Measurement of contact angle, water drop penetration time and critical surface tension.

Letey, J., Osborn, J., and Pelishek, R. E. (1962). Measurement of liquid-solid contact angles in soil and sand.

Lundquist, J. D., Neiman, P. J., Martner, B., White, A. B., Gottas, D. J., and Ralph, F. M. (2008). Rain versus snow in the sierra nevada, california: Comparing doppler profiling radar and surface observations of melting level. Journal of Hydrometeorology, 9(2):194–211.

Marion, G. M. (1995). Freeze-thaw processes and soil chemistry. Technical report, Cold Regions Research and Engineering Lab, Hanover NH.

Martin, D. A. (2016). At the nexus of fire, water and society. Philosophical Transactions of the Royal Society B: Biological Sciences, 371(1696):20150172.

Mashum, M. and Farmer, V. (1985). Origin and assessment of water repellency of a sandy south australian soil. Soil Research, 23(4):623.

Mataix-Solera, J., Cerdà, A., Arcenegui, V., Jordán, A., and Zavala, L. (2011). Fire effects on soil aggregation: A review. Earth-Science Reviews, 109(1-2):44–60.

Miller, J., Safford, H., Crimmins, M., and Thode, A. E. (2009). Quantitative evidence for increasing forest fire severity in the sierra nevada and southern cascade mountains, california and nevada, usa. Ecosystems, 12(1):16–32.

Moody, J. A. and Martin, D. A. (2001a). Initial hydrologic and geomorphic response following a wildfire in the colorado front range. Earth Surface Processes and Landforms, 26(10):1049–1070.

Moody, J. A. and Martin, D. A. (2001b). Post-fire, rainfall intensity–peak discharge relations for three mountainous watersheds in the western usa. Hydrological processes, 15(15):2981–2993.

Moody, J. A. and Martin, D. A. (2009). Synthesis of sediment yields after wildland fire in different rainfall regimes in the western united states. International Journal of Wildland Fire, 18(1):96.

Nelson, D. W. and Sommers, L. E. (1965). Total carbon, organic carbon, and organic matter. In Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, pages 539–579. American Society of Agronomy, Soil Science Society of America.

Nimmo, J. (2005). AGGREGATION | physical aspects. In Encyclopedia of Soils in the Environment, pages 28–35. Elsevier.

Oztas, T. and Fayetorbay, F. (2003). Effect of freezing and thawing processes on soil aggregate stability. CATENA, 52(1):1–8.

Quyum, A., Achari, G., and Goodman, R. (2002). Effect of wetting and drying and dilution on moisture migration through oil contaminated hydrophobic soils. Science of The Total Environment, 296(1-3):77–87.

Rasband, W. and Ferreira, T. (2012). Image j user guide.

Robichaud, P. R. (2000). Forest fire effects on hillslope erosion: what we know. Watershed Management Council Networker, 9(1).

Robinne, F.-N., Miller, C., Parisien, M.-A., Emelko, M. B., Bladon, K. D., Silins, U., and Flannigan, M. (2016). A global index for mapping the exposure of water resources to wildfire. Forests, 7(1):22.

Schweizer, D., Nichols, T., Cisneros, R., Navarro, K., and Procter, T. (2020). Wildland fire, extreme weather and society: Implications of a history of fire suppression in california, usa. In Extreme Weather Events and Human Health, pages 41–57. Springer.

Shakesby, R. (2011). Post-wildfire soil erosion in the mediterranean: Review and future research directions. Earth-Science Reviews, 105(3-4):71–100.

Simkovic, I., Dlapa, P., Doerr, S. H., Mataix-Solera, J., and Sasinkova, V. (2008). Thermal destruction of soil water repellency and associated changes to soil organic matter as observed by FTIR spectroscopy. Catena, 74(3):205–211.

Stoof, C. R., Ferreira, A. J., Mol, W., Van den Berg, J., De Kort, A., Drooger, S., Slingerland, E. C., Mansholt, A. U., Ferreira, C. S., and Ritsema, C. J. (2015). Soil surface changes increase runoff and erosion risk after a low–moderate severity fire. Geoderma, 239:58–67.

Stoof, C. R., Moore, D., Ritsema, C. J., and Dekker, L. W. (2011). Natural and fire-induced soil water repellency in a portuguese shrubland. Soil Science Society of America Journal, 75(6):2283–2295.

Templer, P. H., Reinmann, A. B., Sanders-DeMott, R., Sorensen, P. O., Juice, S. M., Bowles, F., Sofen, L. E., Harrison, J. L., Halm, I., Rustad, L., Martin, M. E., and Grant, N. (2017). Climate change across seasons experiment (CCASE): A new method for simulating future climate in seasonally snow-covered ecosystems. PLOS ONE, 12(2):e0171928.

Thompson, K. L., Zuckerberg, B., Porter, W. P., and Pauli, J. N. (2018). The phenology of the subnivium. Environmental Research Letters, 13(6):064037.

Tiedemann, A. R. (1979). Effects of fire on water: a state-of-knowledge review, volume 10. Department of Agriculture, Forest Service.

Watson, C. and Letey, J. (1970). Indices for characterizing soil-water repellency based upon contact angle-surface tension relationships. Soil Sci. Soc. Am., Proc.; (United States).

Williams, A. P., Abatzoglou, J. T., Gershunov, A., Guzman-Morales, J., Bishop, D. A., Balch, J. K., and Lettenmaier, D. P. (2019). Observed impacts of anthropogenic climate change on wildfire in california. Earths Future, 7(8):892–910.

Yanai, Y., Toyota, K., and Okazaki, M. (2004). Effects of successive soil freeze-thaw cycles on soil microbial biomass and organic matter decomposition potential of soils. Soil science and plant nutrition, 50(6):821–829.

Zavala, L. M., García-Moreno, J., Gordillo-Rivero, Á. J., Jordán, A., and Mataix-Solera, J. (2014). Natural soil water repellency in different types of mediterranean woodlands. Geoderma, 226-227:170–178.

Zhang, Z., Ma, W., Feng, W., Xiao, D., and Hou, X. (2016). Reconstruction of soil particle composition during freeze-thaw cycling: A review. Pedosphere, 26(2):167–179.

Zhao, J., Chen, J., Wu, Q., and Hou, X. (2018). Snow cover influences the thermal regime of active layer in urumqi river source, tianshan mountains, china. Journal of Mountain Science, 15(12):2622–2636.