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Wettability decay in an oil-contaminated waste-mineral mixture with dry-wet cycles

Sérgio D.N. Lourenço[1], School of Earth and Ocean Sciences, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK, lourenco@hku.hk , T: +852 39172672

Clare F. Wakefield, School of Earth and Ocean Sciences, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

Christopher P. Morley, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, UK

Stefan H. Doerr, Institute of Environmental Sustainability, School of the Environment and Society, Swansea University, Singleton Park, Swansea SA2 8PP, UK

Robert Bryant, School of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, UK

Current address: Department of Civil Engineering, The University of Hong Kong, Haking Wong Building, Pokfulam Road, Hong Kong SAR

HIGHLIGHTS

- We subjected an oil-contaminated waste-soil mixture to dry-wet cycles over a period of 8 months
- The oil-contaminated mixture tended to water repellent with drying and wettable with wetting
- Continuous dry-wet cycles made the mixture more wettable
- Reasons for the wettability decay include biofilm formation and mineral precipitation

ABSTRACT

The dependency of soil particle wettability on soil water content implies that soils subjected to drying-wetting cycles become wettable with wetting and water repellent with drying. While this has been demonstrated widely, the results are contradictory when water repellent soils are subjected to a sequence of cycles. Added to this, past wettability measurements were seldom done in batches of samples collected from the field at natural or dry water contents, with little appreciation that slight particle size variations, different drying-wetting histories and fabric (as required by different wettability measurement methods) may alter the results. This note presents soil particle wettability – soil water content relations by means of an index test (the Water Droplet Penetration Time) following staged drying and wetting paths over a period of 8 months for an untreated, oil contaminated anthropogenic soil (a mixture of waste and mineral particles) from Barry Docks (UK), a site formally used for oil storage, which is to be remediated and redeveloped for housing. The results revealed (1) wettability decay with wetting and drying cycles possibly due to mineralization and bacterial activity and, (2) switches in wettability possibly controlled by reorientation of molecules at the air-oil interface.

KEYWORDS: oil spills, soil particle wettability, dry-wet cycles

1. INTRODUCTION

Oil spills impregnate soil particles with water repellent organic coatings (Roy et al., 1998). Reclamation materials and soils contaminated by crude oil from Alberta's Oil Sands developed water repellency or reduced wettability (Hunter, 2011; Quyum et al., 2002). The known dependency of soil particle wettability on soil water content implies that soils become wettable with wetting and water repellent with drying. While this is well known, the results are contradictory when water repellent soils are subjected to a sequence of drying-wetting cycles. Quyum et al. (2002) reported that soil particle wettability increased with the drying-wetting cycles in infiltration tests in oil contaminated soils, while Zhang et al. (2004) reported increased soil water repellency with the cycles in repacked degraded soil. In addition, little is known whether such relation is, like wettable soils, hysteretic (with the wetting path position below the drying path) and, how it relates to the critical water content at which wettability switches. These discrepancies are frequently explained by an interplay of microbiological activity (Jex et al., 1985), organic carbon dynamics (removal, transport and deposition) (Denef et al., 2001), and molecular re-arrangements (Graber et al., 2009).

Wettability measurements are frequently done in batches of samples collected from the field at a wide range of water contents (natural, air dried and oven dried), with little appreciation that variable particle size distributions, drying-wetting histories and fabric (sample preparation method) may influence the results (King, 1981; Dekker and Ritsema, 1994, 2000; de Jonge et al., 1999, 2007; Poulenard et al., 2004). There is therefore a need to conduct wettability measurements in the same samples as they dry or wet mimicking the Soil Water Retention Curve procedure for wettable unsaturated soils.

The aim of this study is to characterize the wettability behaviour (soil particle wettability versus soil water content) for an anthropogenic soil (an oil contaminated mixture of waste and mineral particles) collected from a former industrial site at Barry Docks, South Wales, United Kingdom subjected to continuous drying-wetting cycles.

2. STUDY SITE AND MATERIALS

The Barry Docks tank farm site (UK grid reference ST 11355 67047) is a highly heterogeneous fill of man-made materials, transported and *in-situ* soils. Barry Docks was until the 1970's a coal port. The current site was in part reclaimed from to the sea and extended by tipping locally sourced materials and furnace wastes. The land has had various industrial uses, the most recent being as an oil storage facility housing an extensive tank farm. The site is soon to be regenerated by the construction of residential dwellings. An engineered gravel cap has been installed across the site to prevent contact with the oil contaminants within the soil. With depth, the soil profile comprises made-ground of slag, coal particles, fly-ash, silica and limestone particles, which in turn are underlain by estuarine alluvium. A limestone (the St. Mary's Well Bay Formation) is the bedrock (Waters and Lawrence, 1987). The oil contaminated soil was collected from a number of locations around the site using a hand auger and trowel (Fig. 1). Samples were sealed in plastic bags to preserve the natural water content.

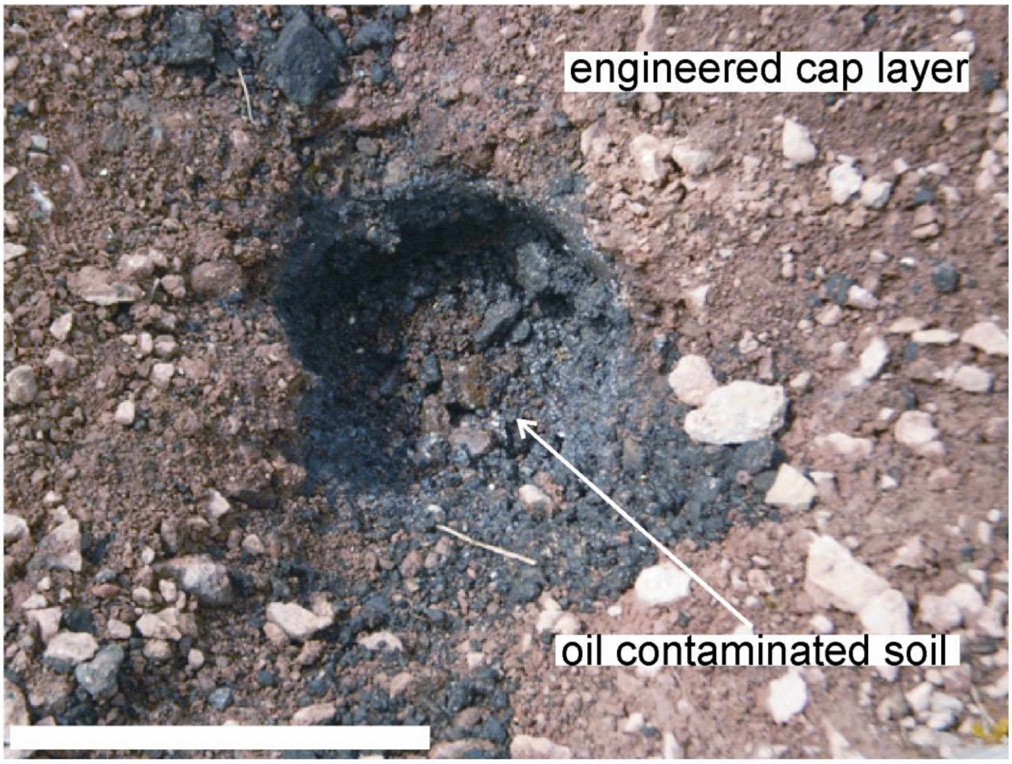


Figure 1: Photograph showing the oil contaminated soils underlying the engineering cap layer (bar = 10cm)

The oil contaminated soils were characterised by the following: natural water content (oven drying at 105 °C), grain size distribution, mineralogy using X-ray powder diffraction (XRD) methods, specific gravity and loss on ignition test (at 400 °C) for total organic carbon content. For the specific gravity and loss on ignition tests, the measurements were conducted for three samples and the results averaged. Imaging to characterize the grain surface characteristics of representative samples were carried out using optical microscopy and environmental scanning electron microscopy (ESEM). Spot analysis using the energy dispersive X-ray analyser (SEM-EDX) was also undertaken to assist mineral identification.

The general properties of the soil samples are summarized in Table 1. The soils were predominantly granular, coarse sand-sized (size 0.1-4.0 mm), with a natural water content ranging between 16.4% and 23.0%. The specific gravity ranged between 2.48 and 2.05, the lower values probably due to the presence of fly ash and coal (Kim et al., 2005). The initial total organic carbon content ranged between 6.6% and 13.9%. These values include both the oil coatings and plant matter (fine roots). X-ray diffractograms for samples B7 and B8 identify a high silica content (attributed to quartz sand grains and silicate slag materials). Samples B11 and B12, were shown to be high in calcium carbonate (sourced from the nearby limestone cliff). B7, B8, B14, B15 were also enriched by iron phases associated with the slag component. Some secondary mineralisation was observed from the SEM images. Clays were present in residual amounts in samples B11, B12, B14, B15. Exact mineral proportions could not be established since coal fragments, a component of the samples, cannot be detected by XRD (coal does not have a crystalline structure).

Table 1: Initial and final physical and chemical parameters for the WDPT tests; mineral proportions: high >50%, low <50%, residual <1%

Sample	**Mineral proportions**				**Total organic carbon content (%)**			**Natural water content (%)**	**Specific gravity**
	Quartz	Calcite	Magnetite & Maghemite	Illite	Initial (bulk material)	Final (bulk material)	Final (surface material)		
B7	High	Residual	Low	Not detected	10.7	9.7	6.2	19.8	2.40
B11	Low	High	Not detected	Residual	6.6	6.1	3.7	16.4	2.48
B14	Low	Low	Low	Residual	13.9	16.4	11.6	23.0	2.05

To situate the waste-mineral samples in the context of other soil water repellency studies, soil particle wettability was measured in an air-dried state (after the first drying) by two index tests, its soil water repellency persistence by the Water Droplet

Penetration Time (WDPT), the degree of water repellency by the Molarity of an Ethanol Droplet (MED) and the direct measurement of the apparent contact angles via the Sessile Droplet Method (SDM). The MED is an index test that quantifies soil water repellency as the lowest ethanol concentration permitting a droplet penetration within 5 s. The SDM consists on placing a droplet of water onto a surface of soil particles by means of a syringe, and determining its contact angle by using a microscope. Table 2 shows variability in the persistence of water repellency (between moderate to extreme), but consistency in the degree of water repellency (very strong to extreme). The apparent contact angles averaged 132° for sample B6.

Table 2: Wettability of the waste-mineral samples in an air dried condition (after first drying)

Sample	**Test**	**Measure unit**	**Classification**[c]
B7	WDPT	38 minutes	Severe
B8	MED[a]	35 mNm^{-1}	Very strong - extreme
B11	WDPT	2.6 minutes	Moderate
B12	MED	42 mNm^{-1}	Very strong
B14	WDPT	120 minutes	Extreme
B15	MED	37 mNm^{-1}	Very strong - extreme
B6	SDM[b]	132°	-

[a] The MED test involved placing droplets (80 μl) of aqueous ethanol solutions of increasing concentration (and thus decreasing surface tension), and recording the concentration of the weakest solution that infiltrates the surface (within 3 seconds). Dilute ethanol solutions (1-36% ethanol) were prepared which equate to surface tension thresholds of 66.9 mNm^{-1} (1%) and 33.1 mNm^{-1} (36%).

[b] The apparent contact angles may be higher; the snapshots by the SDM were conducted with an optical microscope in 'camera' mode within an average time of 17 seconds to allow time to focus.

[c] Doerr et al. (2006)

3. METHODS

3.1. Measurement of soil particle wettability during the drying-wetting cycles

The Water Drop Penetration Time was used to measure soil particle wettability during the wetting-drying cycles. The WDPT is an index test widely used amongst soil scientists (Letey et al., 2000), enabling wide comparison with values published in the literature and measurements in wetter and drier sandy samples. However, it may change the particle surface characteristics with the dissolution of organic carbon (Zhang et al., 2004). Its infiltration times are also expected to decrease in drier samples due to a reduction in the unsaturated hydraulic conductivity, but should only present a problem for finer soils or lightly water repellent soils. The WDPT involves placing 3 de-ionized water droplets (each 80 μl) with a pipette on to the sample surface and recording the times for their complete infiltration. The average infiltration time of the three droplets is taken. Water repellent soils have longer infiltration times than wettable soils.

The sample preparation consisted of sieving to remove grains larger than 4 mm and consolidating in an oedometer (Bryant et al., 2007) at 50 kPa at constant water content conditions. The sample was then removed from the oedometer proving-ring and placed in a Petri dish. Liquid paraffin wax was used to fill the annulus between the sample and the Petri dish wall to provide lateral support.

The procedure for the drying-wetting cycles followed that of a Soil Water Retention Curve whereby the same sample is dried or wetted in stages and pore water pressure/water content measurements conducted at equilibrium conditions (e.g. Lourenço et al., 2011). The detailed procedure, in Fig. 2, consisted on the following stages:

1) Drying or wetting – the sample was dried in the atmosphere for a period ranging between 2-3 hours, at an ambient temperature of 20°C; wetting of the sample was from water vapour (to ensure homogeneous wetting) with the sample placed on a grid on a closed box above the water for a period <8 hours; water vapour was created by submerged mist generators (Mendes et al., 2008);
2) Equalization – the Petri dish was closed for a period of 48 hours to ensure water redistribution within the soil;
3) Mass measurement – recording of the mass of the sample on a balance (0.01 g accuracy);
4) WDPT – placement of three water droplets on the sample's surface and recording with stop-watches the time for the three water droplets to infiltrate; to minimize drying from the sample's surface, the droplets were placed immediately after opening the Petri dish and closing afterwards; for the drying path, the placement of the droplets may have induced local wettability reversals (the area was locally wetted followed by the whole drying of the sample), this was unavoidable and represents a disadvantage of the WDPT.

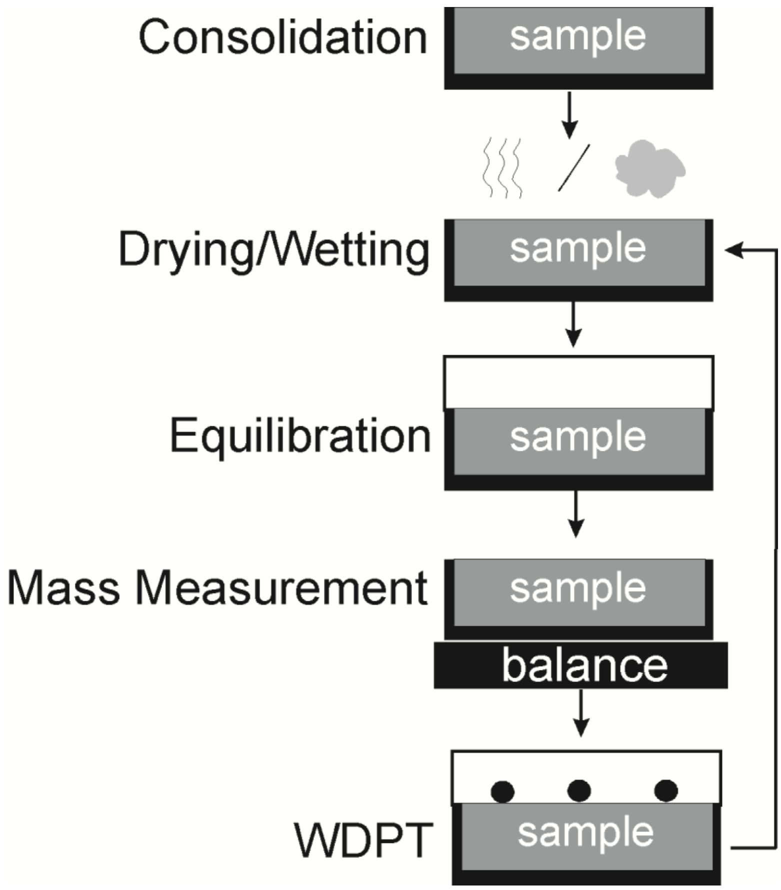


Figure 2: Testing sequence

The measurements started with the samples, untreated, at their natural water contents and steps 1) to 4) were repeated until the samples had air-dried. The process was then reversed, with the samples wetted until they regained their initial masses. The water contents varied between 25% (water clogged pores with no water penetrating) and 5% (a visibly dry condition). All WDPT samples were subjected to 3 drying and wetting cycles. The total period of testing was 8 months.

4. RESULTS AND DISCUSSION

4.1. Soil particle wettability – water content relations

Gradual decay of wettability was observed with the cycles of drying and wetting (Table 3). Sample B7 was wettable from 20% to 17% water content, with the penetration times increasing to 38 minutes at 7% water content (Fig. 3). In the following cycles, the penetration time at the lowest water content (7%) decreased to 27 minutes in the wetting path 1, 14 minutes in the drying path 2 and 5 minutes in the wetting path 2. Sample B14 revealed a similar behaviour, with the penetration time at the lowest water content (14%) decreasing from 120 minutes, in drying path 1, to nearly 25 minutes in drying path 2 (Fig. 4). Sample B11 revealed a similar trend despite the results obtained for wetting path 1, which had led to it becoming wettable at the end of drying path 1 or the start of the wetting path 1 (Fig. 5). An interpretation for this wettability switch is provided in the next section.

Table 3: Wettability decay (WDPT) for samples B7, B11, B14 for each path at 10% water content

Sample	WDPT (minutes)			
	Drying path 1	Wetting path 1	Drying path 2	Wetting path 2
B7	9.0	0.7	2.3	0.8
B11	1.8	1.1	0.5	-
B14*	-	202.7	25.0	-

* At 14% water content

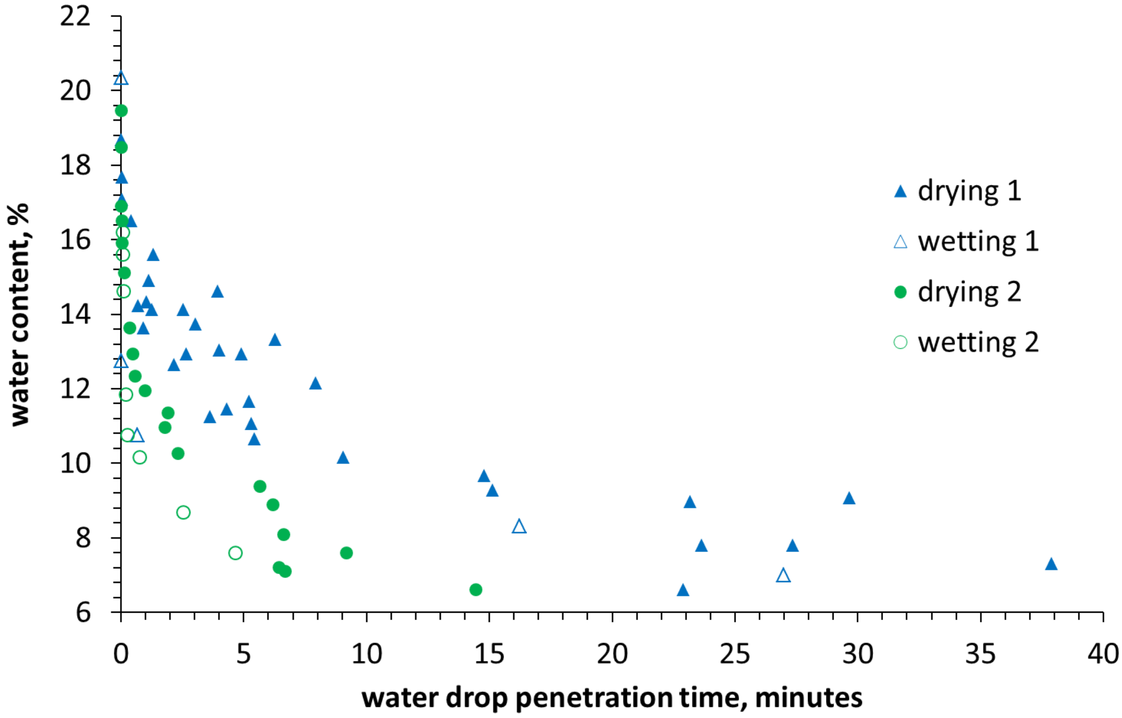


Figure 3: Relations between the water drop penetration time and water content for 2 drying and wetting cycles (sample B7)

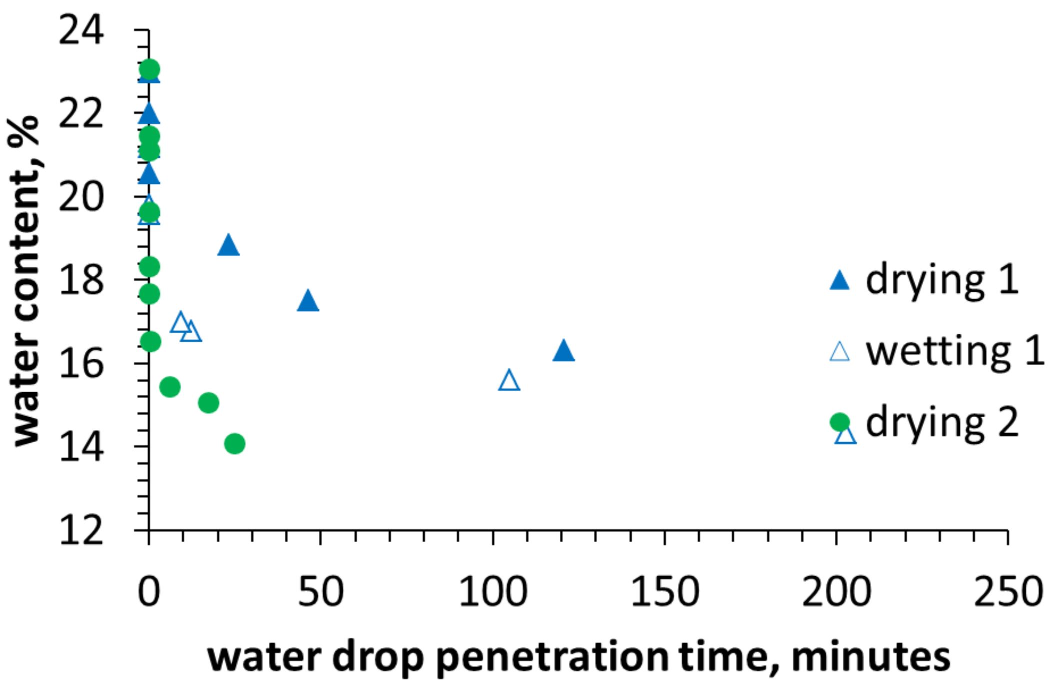


Figure 4: Relations between the water drop penetration time and water content for 1 drying and wetting cycle followed by 1 drying path (sample B14)

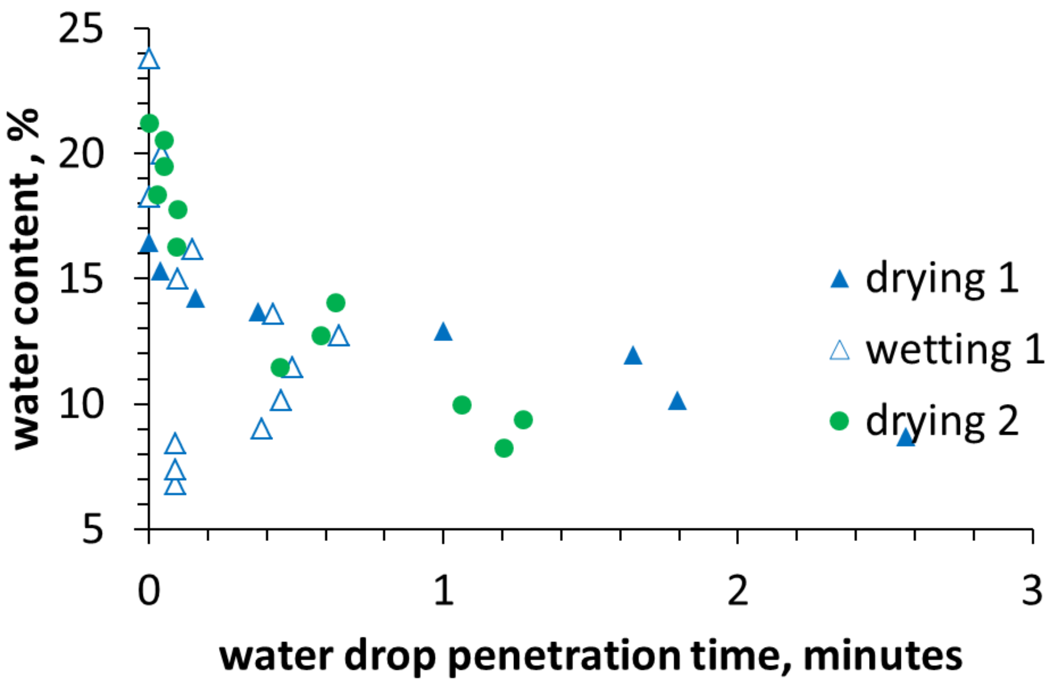


Figure 5: Relations between the water drop penetration time and water content for 1 drying and wetting cycle followed by 1 drying path (sample B11)

Most samples remained fully wettable for increasing ranges of soil water content. Sample B7 remained wettable from 20% to 14% water content in drying path 1, increasing from 20% to 12% in drying path 2. Sample B14 revealed a similar trend, remaining wettable from 23% to 20 % water content in drying path 1, increasing the from 23% to 17% water content in the subsequent paths. Sample B11 behaved differently, remaining in a virtually wettable condition for the same water content range in the 3 paths: 23% to 15%.

In an air-dried state, soil particle wettability correlates with the total organic carbon content (Table 1). Sample B14, with the highest penetration times, had the highest initial total organic carbon content (13.9%), followed by sample B7 with 10.7% total organic carbon content, and sample B11 with 6.6% total organic carbon content. This observed decrease in soil particle wettability with increasing total organic carbon content is in agreement with several studies (e.g. Dekker & Ritsema, 1994).

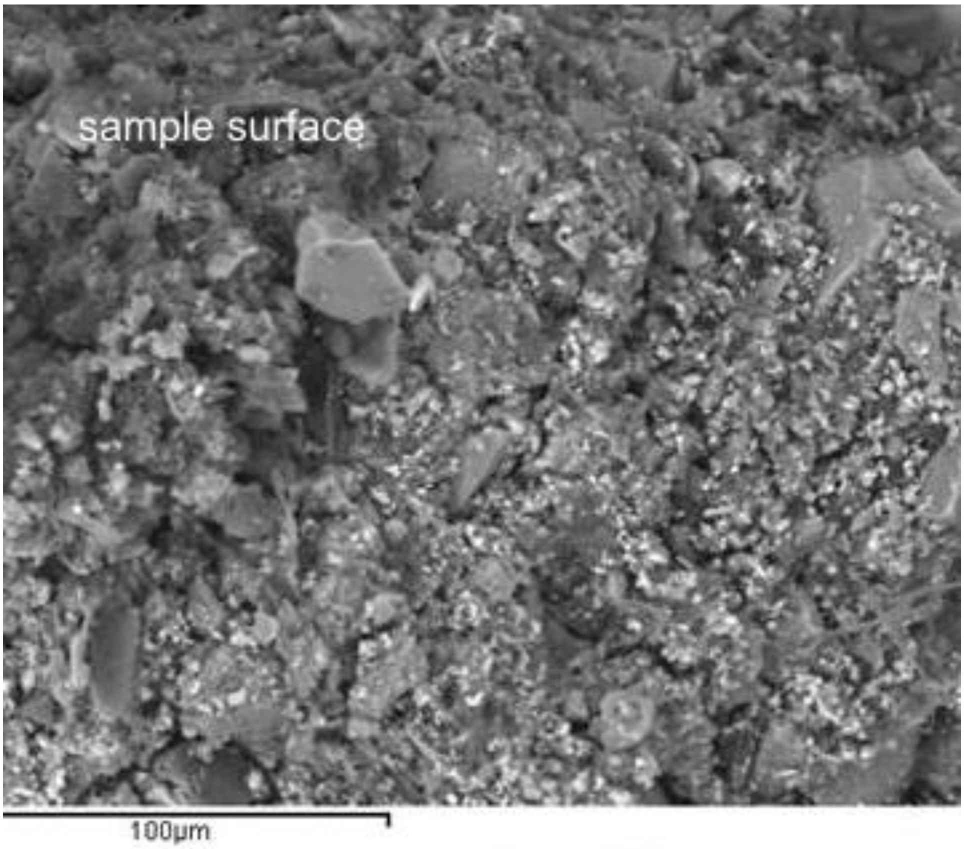
Note that the start of the wetting paths were frequently at lower water contents than the end of the drying curves (the case of the wetting path 1 in samples B11 and B14). This was possibly due to a lower Relative Humidity (RH) in the closed box at the initial stages of wetting. With time, the mist generators raised RH to near saturation water vapour inducing condensation onto the sample and increasing its water content.

4.2. Mineralization and microbiological activity

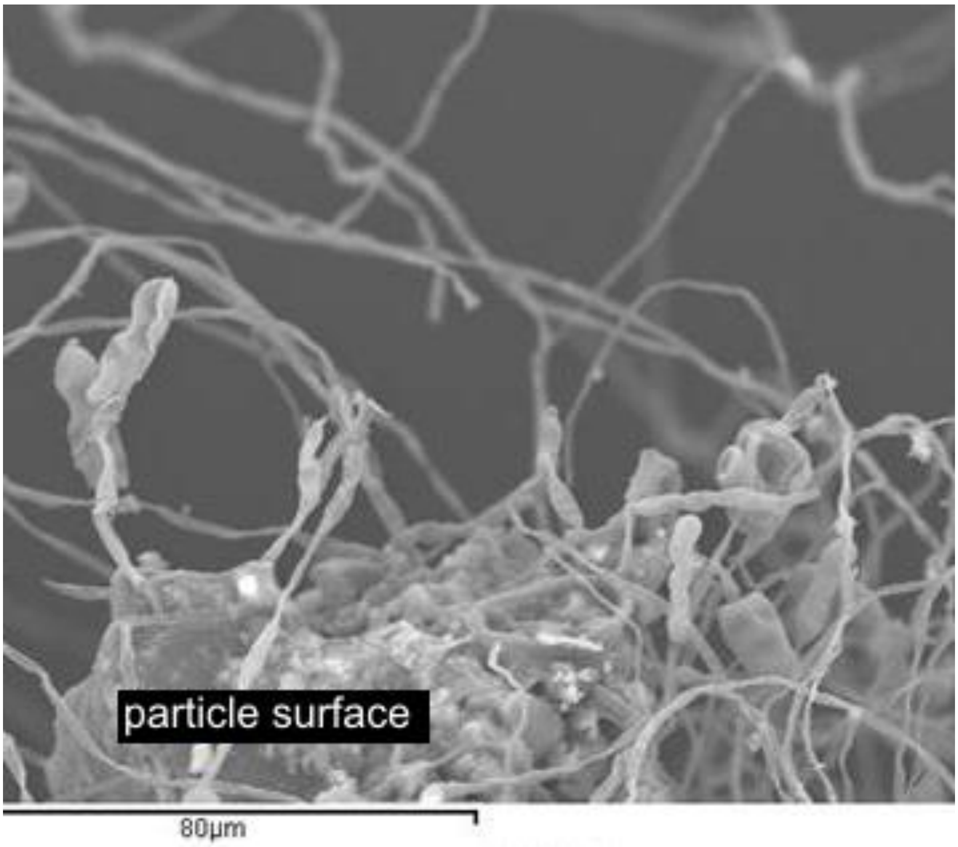
The samples developed a series of white patches across the surface with the sequence of drying-wetting cycles. Imaging of the white patches with an optical microscope and SEM-EDX revealed the following: (1) calcite precipitates (μm to mm sized) with a distinctive white colour that contrasted with the surrounding dark oil coatings (Fig. 6a); (2) loose filaments crossing the pores and covering the particles and, micron sized open cylindrical structures attached to the surface of the grains (Fig. 6b). From their sizes, shapes and arrangements these structures were found to be biofilms, a mixture of microbial cells, extracellular polymeric material (Fig. 6c) produced by bacteria, and fungi. The bacteria are similar to *Actimomycetes* (typical soil bacteria) (Parkes & Sass, 2012). An interpretation is that the initial oil coated calcite particles may have dissolved during wetting and precipitated during drying as new carbonates (without the oil coating). The bacteria may have also contributed to the formation of the new particles (biomineralization). Microorganisms contribute towards the formation of minerals, in particular in limestone formations (Klappa, 1979; Strong et al., 1992). The long-term duration of the cycles (8 months) may have also played a role, allowing sufficient time for the biofilm growth, together with the elevated temperature created by the mist generators during the wetting stages.

The total organic carbon content was used to establish whether the observed whitening was due to the loss of the oil coatings during the drying-wetting cycles. After the dry-wet cycles, samples were collected from the bulk material of the samples (below the surface) and also the surface material (that had whitened) for loss on ignition tests. In comparison with the initial total organic carbon contents, the results showed a greater decrease in the total organic carbon at the surface than in the bulk material (Table 1). This could have been due to the physical washing of organic carbon from the surface (during the WDPT tests and when the sample achieved full saturation) and degradation of the organic carbon by the microbial activity. McKenna et al. 2002 showed that *Actimomycetes* ameliorate soil water repellency.

(a)



(b)



(c)

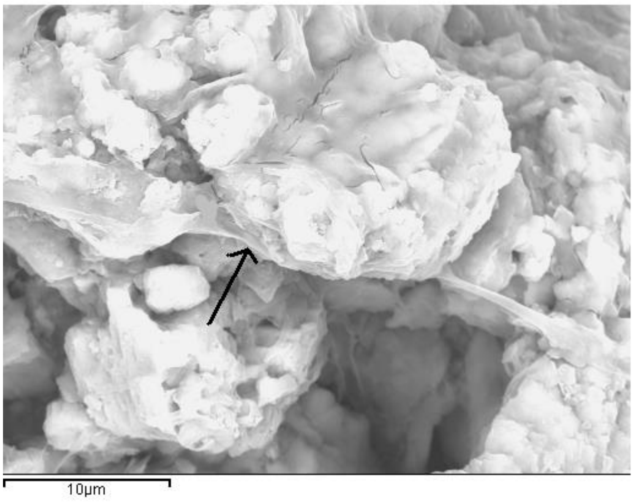


Figure 6: SEM images showing the formation of the new surface) General view of sample surface with white patches of calcite, b) Fungal filaments formed on a particle surface, c) continuous film of extracellular polymeric substances (arrow) wrapping the grains

Distinct mechanisms for the wettability decay are proposed. (1) The mineralization at the surface and formation of biofilms suggests that a new discontinuous surface made of clean minerals and microorganisms was created on top of the oily coatings. Consequently, the penetration times decreased since the new surface is not contaminated with water repellent substances. The decrease in the total organic carbon content at the surface of the sample may have also contributed to the increased wettability. (2) Since no visible changes occurred to the surface of the samples, we hypothesise that the thresholds observed in the WDPT data in wetting path 1 of sample B11 arise from behaviour at the molecular level, and may be attributed to re-orientation of molecules at the air-oil interfaces (Cheng et al., 2009). In very general terms, some of the molecules that populate the air-oil interfaces are wettable at one end and water repellent at the other (Shaw, 1992). When these molecules are oriented with the water repellent end pointing away from the surface, such a configuration makes the oil coated grains water repellent. In the opposite configuration the wettable ends of the molecules are exposed to the atmosphere rendering the oil coated grains wettable (the configuration may thus be influenced by the changing nature of the surface to which the molecules adsorb). (3) Other factors may have contributed to the hysteresis in the drying and wetting paths: differences in the advancing and receding contact angles (Bachman et al., 2006); hydraulic hysteresis, as in wettable soils, due to the emptying and filling of ink-bottle pores (Wheeler et al., 2003); microstructural changes (Monroy et al., 2009). The tendency to wettable with drying-wetting cycles agrees with previous ESEM observations in wettable micron-sized silica spheres (Lourenço et al., 2012).

5. CONCLUSIONS

Soil particle wettability measurements in an oil-contaminated waste-mineral mixture revealed wettability decay with wetting and drying cycles. It is thought the wettability decay can be attributed to mineralization of the surface with calcite and biofilm formation. Wettability switches were observed and probably controlled by reorientation of molecules at the air-oil interface. The results highlight the dynamic nature of soil particle wettability and suggest that it is likely to gain in significance in the future extreme climate change scenarios. The results have applications within the built and natural environment: (1) In Brownfield sites with oil contamination, they highlight the importance of remediating the ground so that water repellency does not develop after dry weather spells, or in the case of dry climates, so that a permanent water repellent condition is avoided. (2) The re-use of oil contaminated soils *per se* or mixed with wettable materials (in fills for instance) is not advisable since it may lead to preferential flow through the wettable areas, and ultimately piping. (3) The increased wettability following wetting and drying cycles due to the precipitation of carbonates and bacterial activity observed here suggests that this phenomenon can occur at other sites with limestone geology.

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