Effect of the Addition of Clay and Wetting/Drying Cycles to the Contaminated Soils at the National Crude Oil Spill Fate and Natural Attenuation Research Site (NCOSFNARS)

B. Wendt, Undergraduate Researcher, Bioproducts and Biosystems Engineering Department,
University of Minnesota, 1390 Eckles Ave, St. Paul, MN 55108, wendt153@umn.edu

Abstract

Although thirty-three years have passed since the 1979 pipeline break at the NCOSFNARS near Bemidji, Minnesota the soil within the zone sprayed by pipeline oil exhibits strong signs of oil contamination. The soils found within the spray zone are water repellent due to this contamination, and in result affects the growth of non-woody and woody vegetation. In the pursuit of providing alleviation techniques for oil-contaminated soils, a study has been initiated to evaluate the effectiveness of clay addition to alleviate soil hydrophobicity. This will be done by first conducting particle size distributions of the soil. Secondly, clay will be added at various rates and water repellency will be tested for using the molarity of ethanol (MED) test and water drop penetration time (WDPT) test. Lastly, wetting/drying cycles will be imposed on the sample and retested for water repellency.

1. Introduction

Hydrophobicity (water repellency) in soils can occur naturally (Dekker & Ritsema, 2000; Jaramillo et al., 2000; Bauters et al., 2000) or result from hydrocarbon contamination (Ellis and Adams, 1961; Roy et al., 1999; Adams et al., 2008). As a result of the 1979 pipeline break near Bemidji, MN, roughly 1.7 million liters of crude oil sprayed onto 7500 m^2 of vegetated land called the spray zone (Essaid et al., 2011). Initially, 75% of the crude was removed from the environment, but the remaining 25% moved through a porous medium of sand and loose gravel contaminating the soil and the groundwater aquifer. From 1994-2000, 27% of the remaining oil was removed from the underlying groundwater through induced depression pumping (Essaid et al., 2011). The residual oil in the vadose zone overlying the groundwater has remained in place since the time of the spill, there having been no remediation of the soil or underlying unsaturated zone. This residual oil has been bound to soil particles in the unsaturated zone since then, causing the soil to become hydrophobic to varying degrees of severity depending on depth.

Up until recently no research had been conducted in the vadose zone at the National Crude Oil Spill Fate and Natural Attenuation Research Site NCOSFNARS. The first work at the site began with staking out a grid of sites and the marking and mapping the GPS locations. The soil at these sites was tested for their physical and hydrologic characteristics (Nieber et al. 2011). The next area of interest was to consider alleviation methods for the oil-contaminated soil. In order to conduct this research, samples were collected from the site in Bemidji and brought back to the laboratory for testing. The goal of this project was to see how the addition of clay to the oil-contaminated soils affected the water repellency of the soils. It was of interest also to how the water repellency of the clay amended soils would respond to subsequent wetting/drying cycles.

2. Experiments and Methods

Five test sites were chosen, B49, B33, B79, B4, and B15 (shown on figure 1). These sites were chosen based on water repellency observed at the NCOSFNARS, in Bemidji Minnesota in order to get multiple water repellency classes represented in the data. Beyond this, the sites were chosen arbitrarily and ample soil was collected from the sites and placed in Ziploc bags.

Two tests were used in order to measure water repellency, the molarity of ethanol droplet (MED) and water drop penetration time (WDPT) tests. Both tests have advantages and disadvantages in the lab. The MED test must be conducted on samples with no moisture, a disadvantage to the WDPT test. Once samples are dried, the MED test has several advantages when testing water repellency. First, the test is very quick, 10 seconds is the maximum time before trying a different solution. One of the greatest challenges with putting drops of water on the surface of the soil is determining the point at which the drop begins to infiltrate. In the WDPT test this challenge is a cause of greater error as it is increasingly difficult when the drop takes over an hour of time to infiltrate. For this reason, the MED test makes testing very water repellent soils in the lab faster, easier, and more accurate.

In speaking with Dr. Randy Adams, an expert in remediated contaminated soils, he was interested in the amount of clay necessary to alleviate water repellency in the field (Dr. R. Adams, personal communication, September 19th, 2012). Although the MED test and WDPT test both measure degrees of hydrophobicity, because of other soil properties beyond hydrophobicity, there is no MED value that one could say that the soil is "alleviated" of its hydrophobicity to a degree of normalcy in its ecosystem. On the other hand, the WDPT test directly measures how long it takes water to infiltrate the soil, very useful and relevant in alleviation of oil-contaminated hydrophobic soils. According to Dr. Randy Adams, if an oven-dried soil can infiltrate a drop of water within 30 seconds to a minute, it would be considered to be remediated. It is reasonable to say in finding the critical point using the WDPT test, that if a droplet of water infiltrates within 60 seconds, it could be considered remediated of hydrophobicity.

2.1 Particle Size Distribution

Particle size distribution tests were conducted on all 5 samples using 1 liter graduated cylinders and hydrometers. In this way the amount of clay present in the sample to begin with could be determined. A mixture of 400 mL distilled water, 100 mL of 5% Calgon, and 3 drops of antifoam B emulsion was mixed for 5 minutes and added to another 500 mL of distilled water in the graduated cylinder. Hydrometer readings were taken three times at .5, 1, and 3 minutes and then once at 10, 20, 60, 90, 120 and 1440 minutes. After 1440 minutes, the samples were wet sieved using a 0.074 mm (#200) sieve and dried at 105 °C for 24 hours. After 24 hours, each sample was dry-sieved for 4 minutes using 2.38, 0.420, 0.177, 0.105, and 0.074 mm (#8, #40, #80, #120, and #200) sieves (Nieber et al. 2011).

2.2 MED Test

Before mixing, the sample soil was sieved at 2mm, in order to rid the samples of pebbles, roots, and other organic matter, removing between 1.9 and 9% of the oven dried samples. Roy and McGill included this step in their proposed standard procedure for running a MED test (Roy & Mcgill 2002). This procedure was followed to achieve consistency in results. #6 Kaolin Tile Clay was added to 10g samples at rate of 0%, .2%, .4%, .8%, and 1.6%. The samples were mixed in a test tube and placed in small aluminum dishes, as seen in figure 2, which had a volume of around 10mL. The experiment was replicated two times and with the results averaged.

Samples were tested using molar concentrations of ethanol of 0M-5M in .5M increments. Drops were placed on the surface, and the smallest concentration solution that began to infiltrate the soil within 10 seconds was recorded. If the soil held a 5M concentration for much longer than 10 seconds, it was recorded as 6M in order to indicate >5M.

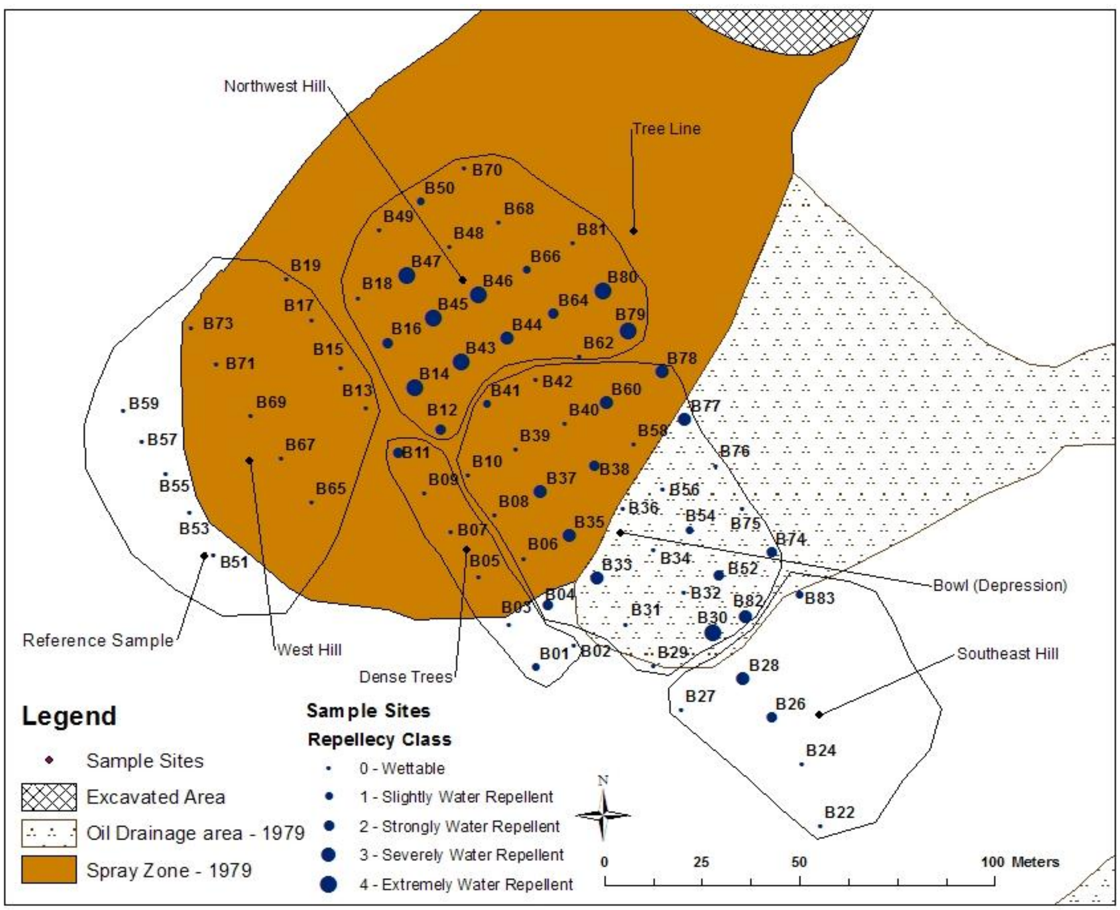


Figure 1. Map showing the spray zones and locations of test locations. Water Drop Penetration Time (WDPT) test was used at field moisture. Repellency classes change as moisture content changes, and oven dried samples will exhibit higher repellency classes.


Figure 2. Shows the mixed samples in the aluminum dishes used for testing.

2.3 Water Drop Penetration Time (WDPT) Test

Samples of soil B49 were prepared in the same way as in 2.2, MED Test, but in this experiment were tested using the Water Drop Penetration Time test. This approach was used to determine the critical point of clay necessary to alleviate the water repellency effects in the soil. Soil B49 was selected as it exhibited water repellent features yet wasn't extremely repellent. Soil from site B49 had an original MED value of 4 in contrast to 5 or higher in soils B33, B79, and B4. This made it possible to conduct the test without requiring penetration times of over an hour. This soil was mixed in the same way from 0% to the amount needed to get a soil that would have a drop penetrate the soil within 60 seconds which would receive the rating of 1 (slightly water repellent) on the WDPT rating scale. If the oven-dried sample will allow a drop to penetrate in 60 seconds, in the field, soil treated could be considered remediated of hydrophobicity (according to conversation with Dr. Randy Adams).

Then a wet/dry cycle was implemented, to find the critical point of clay necessary to alleviate the water repellency effects in the soil after 1 cycle. This process was repeated a second time, to see if the critical point changes over multiple wet/dry cycles. The experiment was replicated two times and the values were averaged, and recorded in Table 3.2.

Results

3.1 Particle Size Distribution

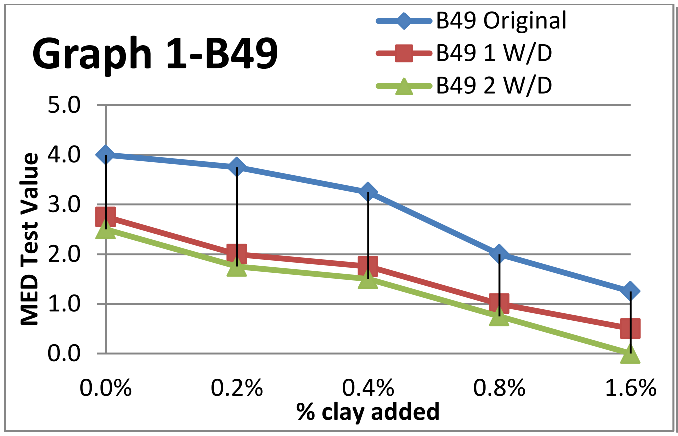
In general, the soils of northern Minnesota are very sandy soils, so it was predicted to find very low distributions of clay and silt. As seen in Table 1, soil from sites B49, B33, B79, and B4 all had a clay distribution of 0% or 1%, and sand concentrations over 91%. When considering the soils with the least clay with the water repellencies in Graphs 1-4 show that a correlation exists, although certainly other factors affect water repellency.

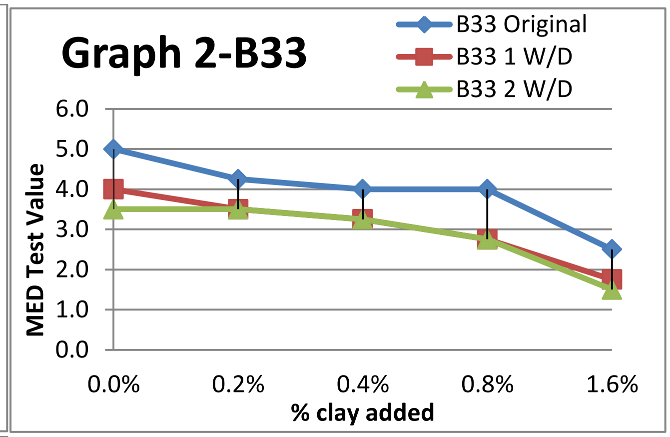
Table 1. Percent Distributions of Size of Particles in Soil

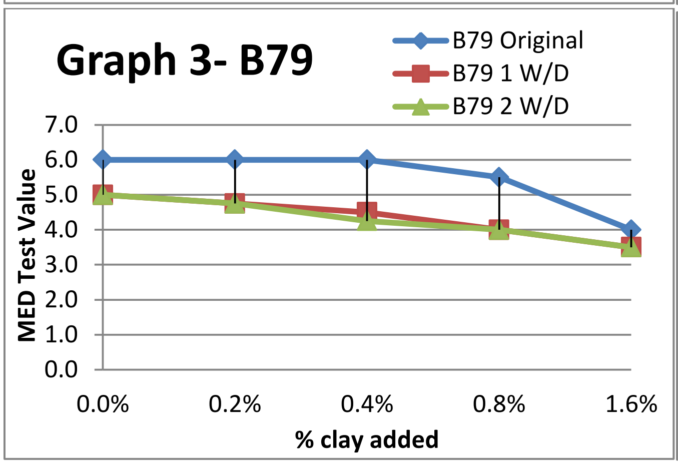
Site Number	% Clay	%Silt	%Sand
B49	0	7	93
B33	1	7	92
B79	0	2	98
B4	1	8	91
B15	3	6	91

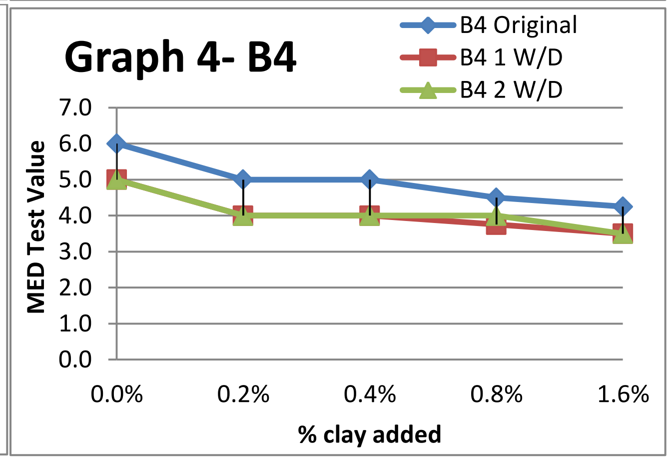
3.2 MED Test

The soil samples from site B15, reported an original MED value of 0.0M. When clay was added to the B15 soils, it remained a MED value of 0.0M, as expected. Adding clay to a wettable soil resulted in no change, and therefore no graph or further data is expressed. Although the B79 data suggests that from 0.0% clay added to 0.4% clay had no impact, they were all significantly greater than 5.0M and therefore ~6M solution was recorded, as a result the data is reported as having a 6.0M value. Therefore, it was not possible to show exactly the difference between soils in this case. With a broader range of solutions of ethanol, the extremely water repellent soils could have been analyzed.









3.2 B49 Water Drop Penetration Time (WDPT) test

The point of this experiment was to find the critical point that the soil would infiltrate a drop of water within 60 seconds. Soil from site B49 was used, as explained in section 2.3, because it was of intermediate water repellency. Results in Table 2 shows that without a wet/dry cycle the soil from site B49 and 2.0% clay added allowed a droplet of water to infiltrate in 35 seconds. This amount of clay without a wet/dry cycle would be sufficient to alleviate water repellency. After a wet/dry cycle, the data in Table 2 shows a significant decrease in time to infiltrate a droplet. With 0.8% clay added, the soil infiltrates a droplet in 30 seconds, and would be sufficient to alleviate water repellency after one wet/dry cycle. A second wet/dry cycle doesn't show little difference, and 0.8% clay is still necessary. In the field, wet/dry cycles occur regularly; therefore the relevant necessary addition of clay is 0.8%, for the soil at site B49.

Table 2. B49 WDPT Test

% Clay added	Original WDPT (sec)	1 W/D (sec)	2 W/D (sec)
2.0%	35	0	0
1.6%	3600	0	0
0.8%	>3600	30	10
0.4%	>3600	600	1000
0.2%	>3600	>3600	2400

4. Conclusion

As predicted the particle size distributions show the high content of sand in the soils, and very low content of clay. The MED test shows that the soil from B79, which had 0% clay and was 98% sand, was the one with the highest water repellency rating. Additionally, soil from B15, which had the most clay (3%), was a wettable soil. Although there certainly are other factors affecting the soil water repellency in these cases; nevertheless a correlation exists. The addition of clays to the soils immediately reduces the water repellency ratings in every sample.

For B49, the critical point for clay addition without a wet/dry cycle was 2.0% clay. After a wet/dry cycle, a critical point for wettability is 0.8% clay. In Cann's study in the field, clay was applied in the top 7.5 cm of soil (Cann, 2000). If 2%

clay was necessary, 44 tons/hectare would be necessary to achieve 2.0% clay in top 7.5 cm of soil, while only 17 tons/hectare would be necessary to achieve 0.8% clay in top 7.5 cm of soil. With costs of kaolin clay around $200 per ton, the clay necessary would cost only $3,400 per hectare as opposed to $8,800 per hectare. Over many hectares, this cost difference is becomes even more significant. This quick cost analysis is dependent on many aspects, such as cost of clay, depth of application, and mass of soil. Nevertheless, it illustrates the significance of a wet/dry cycle to the application of clay to water repellent soils. A second wet/dry cycle appears to have very little impact on wettability in this critical point which confirms the data that the MED tests show.

The initial wetting and drying cycle had an impact on the water repellency ratings. In both experiments, and at each percentage showed a reduction of water repellency ratings. This could be for many different reasons. It may be as simple as the clay is more equally dispersed within the soil when a wet/dry cycle occurs. It could be that the clay is able to cover the hydrophobic surfaces of the sand grains after a wet/dry cycle (Cann 2000). An electron microscope and further testing would be necessary to figure out exactly what is occurring on the molecular level.

Acknowledgements

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