

Treatment of water-repellent petroleum-contaminated soil from Bemidji, Minnesota, by alkaline desorption

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Abstract A pipeline right-of-way contaminated with light crude in 1979 and subsequently burned shows severe hydrophobicity, poor infiltration rates, and loss of vegetative cover. To evaluate alkaline desorption as a treatment method, surface soil samples were collected and analyzed pre- and post-treatment. Samples had total petroleum hydrocarbon concentrations of 2800–63,100 mg/kg, severe water repellency, critical moisture 2–5 times above the in situ moisture content, but no acute toxicity. Thus, water repellency, rather than toxicity, is causing the loss of vegetation. Samples were treated with 0.1 N NaOH in two doses (1:3; soil/solution), with complete drainage between doses. Finally, each soil sample was washed with an equal volume of water and allowed to drain completely. For more hydrophobic samples, repeated treatments, without rinsing between each treatment, were made. Post-treatment, the samples were re-analyzed for water repellency and critical moisture content. In samples with initial water repellency values in the range of 5.0–6.7 M, the repellency was reduced 94–100 % and below critical levels to avoid soil hydrophobicity in field conditions. The other samples with initial water repellency values in the range of 10–13 M could not be recovered with single treatment, but sequential treatments reduced the hydrocarbon content up to 87 % and reduced the hydrophobicity to levels low enough or

nearly low enough to avoid severe water repellency in the field. Currently, field studies are being carried out to evaluate this treatment method at the site, as a stand-alone method and in combination with organic amendment.

Keywords Critical moisture content · Hydrocarbon · Hydrophobicity · Remediation

Introduction

Water repellency is a problem that presents itself in a variety of soils. It is the incapacity of soil to re-absorb water after an extended dry period. This results in the reduction in the soil moisture content and difficulty in maintaining a vegetative cover, and finally, soil erosion (Jaramillo 2006). There are certain species of plants which are more resistant to these dry conditions and that could possibly maintain themselves established in the soil. For example, “Alicia” grass (*Cynodon dactylon*), which is used in tropical and subtropical areas, is very tolerant to a variety of problems including dryness, salinity, etc. However, this species does not produce much pasture and is not very nutritious for cattle (FAO 2005).

Although water repellency can occur in many different kinds of soils, it is more common in sandy soils (Roy et al. 2000). It has also been related to certain kinds of vegetation: conifer forests, low chaparral (Mediterranean) forests, eucalyptus, and above all, in sites that have been burnt (Jaramillo 2006). For hydrocarbon-contaminated sites, it is more common in areas that have heavy spills, fires, and after extended drought, when it is easier for the hydrocarbons to adhere to soil surfaces (Roy and McGill 1998, 2000; Roy et al. 2000). Litvina et al. (2003) reported on research related to the nature of water-repellent

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hydrocarbons and their interaction with soil surfaces. These authors proposed a conceptual model in which the hydrocarbons with polar functional groups act as “bridges” between the soil organic material (SOM) and the nonpolar hydrocarbons, permitting the latter to adhere more effectively to the soil surfaces, thereby forming a hydrocarbon layer which interferes with the soil–water interaction, and thus causing water repellency. It appears that the kinds of hydrocarbons implicated (with more polar functional groups) are a result of fire and diagenesis products (from biodegradation or photo-degradation), although they can also be found in low concentrations in crude petroleum, especially in heavy and extraheavy crude. In the USA, the US Environmental Protection Agency (EPA) (Edenborn and Zenone 2007) has proposed the use of water repellency as an alternative means to monitor the bioremediation of petroleum-contaminated sites. However, in these cases the water repellency is usually short-lived and is reduced as the hydrocarbon concentration becomes sufficiently low. In other areas, sites with relatively low hydrocarbon concentrations have been observed which still show water repellency, probably due more to the type of hydrocarbons in the soil, rather than the concentration (Adams et al. 2008; Nieber et al. 2011; Roy et al. 2000).

There are few techniques that have been used for the mitigation of hydrocarbon-contaminated sites that are water repellent. This phenomenon has been studied mostly in Alberta, Canada, principally in the University of Alberta, University of Calgary, and at the Alberta Research Council (Li et al. 1997; Roy and McGill 1998, 2000; Litvina et al. 2003; Roy et al. 2000). There, 26 hydrocarbon-contaminated, water-repellent sites have been identified with areas ranging from 0.03 to 6.4 hectares. The soil at many of these sites shows severe water repellency, a complete loss of structure (disaggregated), some problems with cation exchange capacity, and loss of vegetative cover, resulting in soil erosion. Nonetheless, the concentrations of hydrocarbons in the soil are low and there are no obvious characteristic signs of petroleum contamination, such as hydrocarbon odors or a sticky consistency. Worse yet, the hydrophobic property of the soil at these sites has been observed to be able to be transferred to adjacent soil, possibly by wind action or due to rain water runoff (migration of hydrophobic soil particles) or by transfer of hydrophobic substances as vapors.

In terms of site recovery, it has been noticed that in the long run (decades) these sites slowly begin to recover due to a succession of colonization by more tolerant species, but the previous soil productivity is not fully restored. On the other hand, researchers in Alberta (Roy and McGill, 2000; Roy et al. 2000; Litvina et al. 2003) have found that it is possible to eliminate water repellency in the soil using certain amphiphilic organic solvents, such as $\text{NH}_3/$

isopropanol, ammonium acetate, isopropanol/acetate, or isopropanol/ammonium hydroxide. However, due to the high cost of treatment with these kinds of solvents, they were not considered for remediation at an industrial scale, but rather to understand the interaction between soil surfaces and the hydrocarbons responsible for hydrophobicity. Notably, treatment with nonpolar solvents (dichloromethylene, cyclohexane) or with very polar solvents (ethanol, methanol) did not result in the correction of water repellency. Quyum (2000) had reasonable improvement in water infiltration in petroleum-contaminated hydrophobic soils using organic amendments, dolomite lime, and kaolinite clay. However, it was necessary to add very high quantities of these soil conditioners: 15 % of compost, 20–30 % of dolomite lime, and 10 % of kaolinite clay, which makes this technique of limited use at an industrial scale.

Besides the research groups in Alberta, there are few others that have dedicated themselves to the restoration of hydrocarbon-contaminated water-repellent soils (in Oklahoma, Minnesota and Tabasco). Sublette et al. (2010) presented research on the use of a mixture of straw, compost, and hydrogels (polyacrilamide) for treatment of soil contaminated with light crude oil; this had a density value in the American Petroleum Institute (API) classification system of 42 °API. An increase in pasture biomass of 3.8 times was achieved using commercial products containing hydrogels, as well as an increase in vegetative cover of 3.2 times, achieving a maximum cover of 77 %. However, in that study the kind of petroleum used (light crude oil) generally does not cause hydrophobicity in the long run, due to its low content of polar hydrocarbons.

In Bemidji (Minnesota, USA), a group of investigators from the University of Minnesota and the US Geological Survey (USGS) have also been studying the phenomenon of water-repellent hydrocarbon-contaminated soil. This site was contaminated due to a pipeline break in 1979 with light crude oil (37.5 °API), which normally does not cause water repellency. However, part of the most contaminated area at the site was burned to reduce the volume of oil in the environment (Delin et al. 1998). There have been decades of research on this site dedicated to groundwater contamination, and recently, to the problem of water repellency in surface soil (Nieber et al. 2011). To date, they have characterized the surface soil for water repellency and infiltration, evaluated re-colonization by tolerant species, as well as performed tests for the treatment of water repellency using kaolinite clay (Wendt 2012).

In Tabasco, Córdova-Alvarado (2010) ran a study where the restoration of highly water-repellent hydrocarbon-contaminated soil was tried using an organic amendment (sugarcane filter cake—cachasse). In this treatment, it was possible to increase the field capacity by 29 % and reduce

the water repellence severity (the molarity of ethanol in a drop of water able to infiltrate in dry soil in 10 s, known as Molarity Ethanol Drop-MED) by 37 %. The pasture production was increased three times, and the water repellence persistence (the time needed for a drop of pure water to infiltrate the soil, known as the Water Drop Penetration Time-WDPT) decreased more than four orders of magnitude. However, the final WDPT was still over 2 h, which was still too long to obtain an adequate, long-term recovery.

As a followup on this research, a new technique was developed to restore the soil fertility definitively and applied to this site (Adams 2011). This method involves cation exchange using alkaline slurries or solutions [of $\text{Ca}(\text{OH})_2$ or NaOH], in which the cation replaces the positive charges of the SOM, thus sloughing off the SOM-hydrocarbon complex from the soil surface and restoring the wettability of the soil. Organic matter is subsequently replaced by addition of a soil amendment, such as sugarcane cachasse, or other agricultural wastes. Using this method, the WDPT at the site was reduced five orders of magnitude and the field capacity was increased by 20 %. This allowed the establishment of a more productive species of pasture (*Brachiaria humidicola*) which was previously unable to sustain itself in the affected area (Domínguez-Rodríguez and Adams 2011).

Related to these studies on water repellency, but not with respect to hydrocarbon-contaminated soil, various investigators have reported that it is possible to mitigate water repellency (for example in agricultural fields, golf courses, or sports fields) using surfactants, which reduce the superficial tension between the water and the hydrophobic compounds on soil surfaces (see for example, the patents of Petrea et al. 2003a, b). Among recent patents in this area, in 2005, the US Patent and Trademark Office (USPTO) conceded a patent for the use of a surfactant based on alkylpolyglycoside and copolymer-type block EO/PO (ethylene oxide/propylene oxide) to mitigate water repellency in soil (Kostka and Bially 2005). More recently (2009), another patent was conceded to the same inventors for the use of a surfactant based on copolymer-type block EO/PO with low HLB (hydrophilic–lipophilic balance) values, for the same purpose (Kostka and Bially 2009). The use of surfactants is not novel. There are reports in the literature discussing this topic since several decades (see for example Letey et al. 1962), but these patents were conceded for the types of surfactants investigated. It is worth mentioning that the use of surfactants does not eliminate water repellency from the soil in a definitive way, but it allows the soil to moisten and helps to control soil humidity while the soil is irrigated with surfactant solutions.

It is also worth mentioning that there are other studies for the treatment of naturally occurring water-repellent soils which may pertain to the research on petroleum-

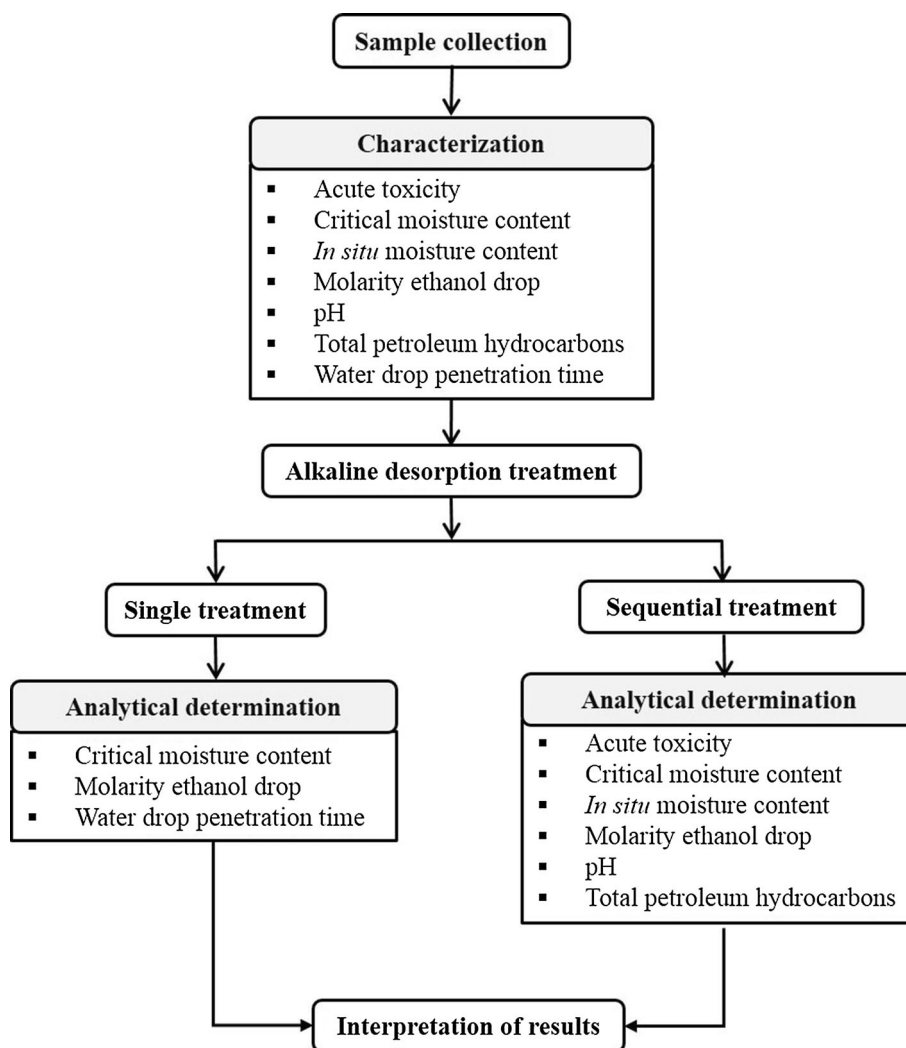
contaminated soils. The area in which this has been most studied is arguably in agricultural soils in Southern and Western Australia. Due to the kinds of vegetation present in this area, and historical use of fire both previous to, and after European colonization, hydrophobic compounds have accumulated on the soil surfaces causing water repellency and problems with soil moisture and erosion, especially in areas tilled for agricultural purposes or with heavy cattle use. To overcome this problem, several techniques have been investigated. Managing areas to increase natural biodegradation of waxy substances in the soil has been suggested by Roper (2006), as an alternative to the incorporation of clay in sandy soil (McKissock et al. 2002). This investigator (Roper) was able to reduce water repellency by inoculating soil with wax-degrading bacteria to adequate levels in 150 days, although it was considered not to be economically practical at field scale. Cann (2000) has shown that sandy water-repellent soils can be successfully treated by incorporating clays, although generally, at least 100 t/ha is needed, and so it is only practical for soils where clay exists on site (such as in a layer of subsoil). It is worth noting that these studies were made on soils with water repellency generally in the 2–3 MED range, which is much lower than that typically encountered in petroleum-contaminated sites (Adams et al. 2008; Roy et al. 2000; Wendt 2012).

The purpose of the present study was to evaluate and develop remediation techniques to ameliorate water repellency in petroleum-contaminated soils, specifically for application in the Bemidji National Crude Oil Spill Fate and Natural Attenuation Research Site (Minnesota, USA). Contaminated samples from the site had different concentrations of total petroleum hydrocarbons (TPH) and different in situ moisture contents (ISM). These parameters were considered independent variables in these experiments which were related to the dependent variables of water repellency, in particular MED, WDPT, and critical moisture content (CMC) values. Likewise, different treatments (single or sequential) were applied to contaminated soil, and the treatment method was also considered an independent variable. Additionally, the acute toxicity test was considered a dependent variable with respect to the hydrocarbon concentrations in soil samples collected in the field. This research was carried out between September 2012 and August 2015 in the Remediation Laboratory of the Universidad Juárez Autónoma de Tabasco, Villahermosa, Tabasco, Mexico.

Materials and methods

In Fig. 1, the overall scheme of the experiments carried out is presented in brief; the details are explained subsequently.

Fig. 1 Experimental scheme and sequence



Soil sampling

Surface soil samples (0–4 cm) were collected in or near the spray zone of the site, to the northwest of Bemidji, Minnesota, USA (Fig. 2). The environmental conditions on the day of sampling were partially cloudy with a light wind from the east and a daytime temperature of about 13 °C. Samples were placed in opaque, plastic screw cap jars and stored at room temperature. A description of the surface samples and characteristics is presented in Table 1.

Hydrocarbon concentration and characterization

The TPH concentration in soil was determined according to Adams et al. (2008) by US EPA method 418.1, using perchloroethylene as an extraction solvent and incorporating a sample cleanup with silica gel to remove naturally occurring organic compounds (EPA 1997). TPH were measured with an Infracal TOG/TPH analyzer-Wilks Enterprise. Also, at one of the sampling points (Gs-7) additional soil from 0 to 10 cm

was collected for characterization of the hydrocarbon type. Oil was obtained from this sample with perchloroethylene in three sequential extractions using equal volumes in an Erlenmeyer flask and the extract filtered through a column of fiberglass. The filtrate was placed in shallow porcelain bowls and evaporated to dryness in a chemical hood over several days. The oil recovered was then analyzed for °API (and hence specific gravity), using the dilution-extrapolation hydrometer method of Morales-Bautista et al. (2013).

ISMC, CMC, and water repellency analyses

Previous to any subsequent tests, the samples were analyzed for water repellency at the ISMC before drying. Samples were also analyzed for ISMC gravimetrically as per Mexican norm NOM-021-SEMARNAT-2000 (SEMARNAT 2002). Subsequently, WDPT and MED were determined from the penetration time versus molarity of ethanol function (usually an exponential decay function), as per Adams et al. (2008).

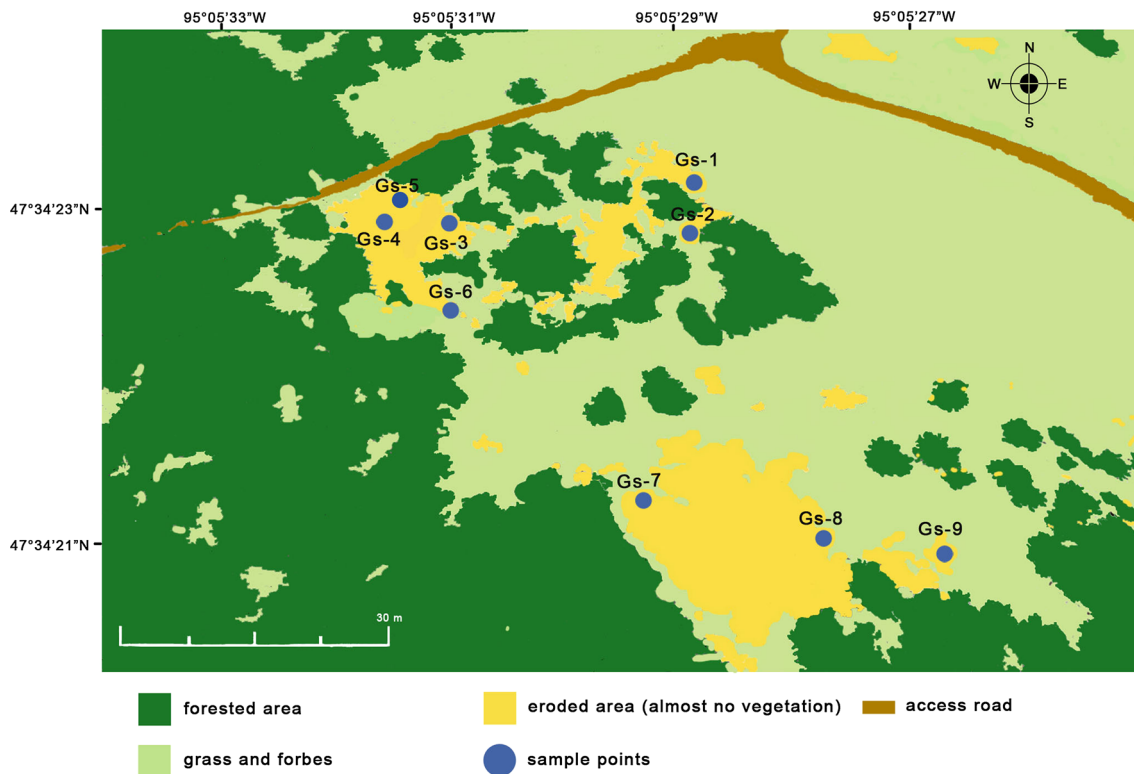


Fig. 2 Location of sampling points

Table 1 Description of sampling points

Sample	Coordinates	Description
Gs-1	N47.57317 W95.0913	Near pipeline right-of-way. Light color, looks like clean sand
Gs-2	N47.57305 W95.0913	Degraded area between right-of-way and northern spray area (hill). Some limited vegetation. Soil color dark brown from petroleum contamination
Gs-3	N47.57306 W95.09182	Dark, very burnt area. Hard and semi-consolidated. In north hill
Gs-4	N47.57306 W95.09196	Compacted area, very contaminated. High spot in north hill area. Without vegetation
Gs-5	N47.57309 W95.09187	Very superficial (approximately 0–2 cm) material near Gs-4. Not compacted, slightly lighter in color. Approximately 3 m east of Gs-4
Gs-6	N47.57289 W95.09177	Area below north hill, from uncompacted area, about halfway down the hill. Some vegetation (natural recovery)
Gs-7	N47.57258 W95.09134	Lower part of southeast hill, runoff receiving area from sandy and gravelly area uphill (east)
Gs-8	N47.57252 W95.09103	High spot on southeast hill. Surface has a lot of loose sand
Gs-9	N47.5725 W95.09083	To the southeast of hill, in an area receiving runoff to the southeast, before entering woods. Surface slightly compacted

In these standard analyses, the water repellency is determined on dry soil. However, water repellency has been shown to be dependent on the moisture content in the soil (Dekker and Ritsema 1994, Lichner et al. 2006). In the field, even during the driest part of the year, there may still be some moisture in the soil, which could mitigate water repellency. To determine the CMC at which water repellency is manifested, direct measurement of penetration times of deionized water was made to determine CMC for absorption at <5 and <60 s (non-

repellent to slightly repellent range, according to Dekker and Jungerius 1990), as per Guzmán-Osorio and Adams (2015).

pH

pH determinations were made in the laboratory using 1:2.5 proportions of soil to deionized water and a pH electrode as per Mexican norm NOM-021-SEMARNAT-2000 (SEMARNAT 2002), on fresh and treated samples.

Acute toxicity

Toxicity was determined using the Microtox bioassay with *Vibrio fischeri*, based on the method in the Mexican norm NMX-AA-112-1995-SCFI (SECOFI 1996), and Adams et al. (2014). The toxicity was determined as EC₅₀ (effective concentration 50, concentration of sample which reduces the bioluminescence 50 %), and subsequently calculated as toxicity units (TU), using the relationship: $TU = (1/EC_{50})$.

Additionally, preliminary earthworm (*Eisenia foetida*) bioassays were run using the 48-h filter paper tests according to Palafox-Alejo et al. (2012).

Single alkaline desorption treatment

Single alkaline desorption treatment (experiment 1) consisted in applying a 0.1 N solution of NaOH in a proportion of 1:3 soil to solution (on a dry weight basis for soil). One hundred grams of air-dried soil was treated by mixing in 15 ml of 0.1 N NaOH and letting the mixture set for 48 h. Subsequently, another 18.3 ml of alkaline solution was mixed in. After mixing, the soil was transferred to a plastic cup with small holes (1–2 mm) perforated in the bottom, to let drain for 48 h. After this period, 33.3 ml of deionized water was added and mixed in, and the excess water was allowed to drain from the soil. After draining completely (48 h), the soil was air-dried for several days until completely dry. This air-dried treated material was then re-tested for water-repellent properties.

Sequential alkaline desorption treatment

Although this was effective for some of the samples, in the more contaminated areas a single treatment was not sufficient to reduce the CMC to below the ISMC typical during the dry seasons in the region. Subsequently, repeated treatments were made on these more recalcitrant samples. Subsamples from the jars containing the original samples were re-tested for pH and TPH, as well as the CMC to avoid WDPT above 5 and 60 s. For these samples with sequential alkaline desorption (experiment 2), no fresh water washes were made between treatments, only at the end of several treatments and upon finalizing the experimental work.

Results and discussion

Characterization of untreated soil

Hydrocarbons concentration

The TPH concentration in untreated soil was approximately between 2800 and 63,100 mg/kg (Table 2). The

subsamples for experiment 2 showed greater variability, although they were taken from the same jars.

Even though the oil spilled at the site over 35 years ago was light crude (37.5°API), it has been highly degraded. Probably due to the fire induced post-spill (to reduce the amount of oil in the environment), and/or biodegradation or photo-degradation, the residual oil is a mixture of hydrocarbons resembling heavy crude, with only 17.4°API. If one assumes that the hydrocarbons that were destroyed in the fire were principally low molecular weight compounds, similar in composition to gasoline, with a specific gravity of about 0.76 g/cm³ (Pemex refinación 2012), the amount of oil consumed in the fire was about half, at least in the superficial soil (not including that which infiltrated into the subsoil and aquifer). Due to the fire and natural attenuation, the resulting residual mixture of hydrocarbons is much more viscous and more difficult to biodegrade. It is also likely that the mixture has a greater quantity of polar functional groups, causing greater water repellency (Morales-Bautista et al. 2016).

ISMC, CMC, and water repellency for experiment 1

In Table 3, some of the important water repellency data are shown for untreated soil in experiment 1. All samples failed to wet at the moisture content that was already present in the soil. The CMC and MED were both relatively low in samples Gs-1 and Gs-7 (CMC < 1.1, MED < 5 M). Note that even though the ISMC was greater than the CMC in sample Gs-5 (ISMC/CMC = 1.28), the sample tested before drying could not be wetted (water repellent). Thus, it appears that there may be some imprecision in the CMC value and it may possibly be different depending on whether it is determined on the wetting cycle or drying cycle due to hysteresis (these were measured on the drying cycle).

A dose–response-type relationship between the TPH concentration and CMC was observed in these samples (Fig. 3). In this figure, sample Gs-5 was not included since

Table 2 TPH concentration in untreated soil

Sample	Experiment 1 TPH (mg/kg)	Experiment 2 ^a TPH (mg/kg)
Gs-1	2809	–
Gs-2	20,223	32,701
Gs-3	35,522	63,109
Gs-4	24,634	37,511
Gs-5	12,518	–
Gs-6	17,652	–
Gs-7	2986	–
Gs-8	12,715	16,113
Gs-9	19,423	19,131

^a The concentrations in experiment 2 are from subsamples of the soil samples in experiment 1



Table 3 Water repellency characteristics of untreated soil (experiment 1)

Sample	ISMC (%)	MED	WDPT (s)	CMC (%) (for WDPT < 60 s)	Ratio ISMC/CMC
Gs-1	0.50	5.08	21,652,098	0.99	0.51
Gs-2	0.73	12.89	2.1×10^{10}	3.82	0.19
Gs-3	1.26	10.27	7.5×10^{22}	5.36	0.24
Gs-4	0.72	11.71	2.2×10^{47}	4.66	0.15
Gs-5	0.93	6.32	8,417,827,077	0.73	1.27
Gs-6	0.84	6.67	32,553,673	2.33	0.36
Gs-7	0.58	5.03	425,598	1.01	0.57
Gs-8	0.47	11.44	1.7×10^{105}	2.09	0.22
Gs-9	0.72	11.74	4.9×10^{33}	3.34	0.22

ISMC in situ moisture content, MED molarity ethanol drop, WDPT water drop penetration time, CMC critical moisture content

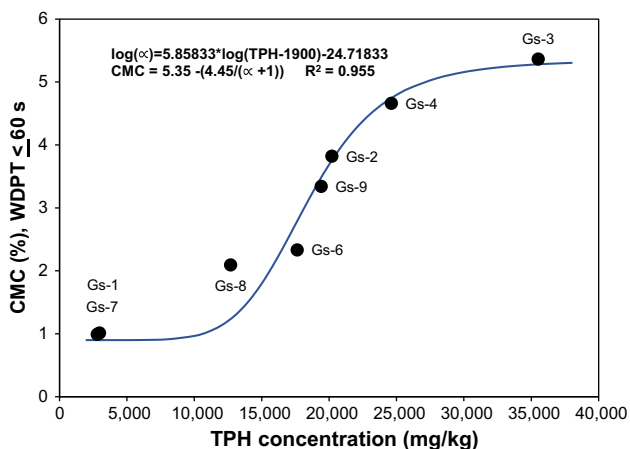


Fig. 3 Relationship between the CMC (for WDPT < 60 s) and the initial TPH concentration

it was very superficial (0–2 cm) and may not be representative. At around 1.5–2 % TPH (15,000–20,000 ppm), there appears to be a threshold, above which the CMC increases rapidly but only up to a certain level. This rapid increase in water-repellent properties was also found for sandy soil in Tabasco (Adams et al. 2008) and is probably due to the limited surface area of sandy soils that are quickly saturated by hydrocarbons. This leaves very little available surface area in the soil to interact with water, and when the moisture level in the soil drops to <4 %, water repellency may become manifest.

CMC, pH, and water repellency for experiment 2

In Table 4, the initial water repellency data are shown for untreated soil in experiment 2. All the subsamples showed a very severe water repellency (MED > 3.2 M) and a pH between 5.8 and 5.9, being classified as moderately acidic as per Mexican Norm NOM-021-SEMARNAT-2000. According to Palma-López et al. (2007), this pH is typical of the A horizon in sandy soils.

Table 4 Water repellency characteristics of untreated soil (experiment 2)

Sample	MED	CMC (%) (for WDPT < 5 s)	CMC (%) (for WDPT < 60 s)
Gs-2	11.2	6.25	4.52
Gs-3	10.3	10.15	5.62
Gs-4	11.6	6.75	1.91
Gs-8	11.1	3.72	1.39
Gs-9	10.9	4.43	2.43

MED molarity ethanol drop, CMC critical moisture content

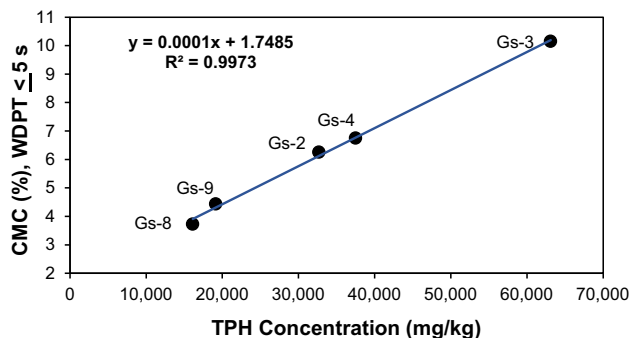


Fig. 4 Relationship between the CMC (WDPT < 5 s) and TPH concentration

As shown in Fig. 4, at least the onset of water repellency (WDPT > 5 s) is directly proportional to the TPH concentration ($R^2 = 0.9973$). This suggests that (at least in these very sandy soils), the quantity of surfaces covered with petroleum is greater with higher oil content, thus causing a linear increase in the onset of water repellency (WDPT > 5 s). Thus, it would require a higher moisture content to overcome the critical moisture level to completely avoid water repellency.

Toxicity (Vibrio fischeri bioassay)

The samples showed very low toxicity with a $CE_{50} > 200,000$ ppm and < 5 TU (Toxicity Units, Table 5).

Table 5 Toxicity in untreated soil samples

Sample	EC ₅₀	UT	Toxicity level
Gs-1	838,952	1.2	Not toxic
Gs-2	237,264	4.2	Not toxic
Gs-3	199,979	5.0	Not toxic
Gs-4	330,494	3.0	Not toxic
Gs-5	500,430	2.0	Not toxic
Gs-6	372,389	2.7	Not toxic
Gs-7	1,161,227	0.9	Not toxic
Gs-8	668,088	1.5	Not toxic
Gs-9	597,264	1.7	Not toxic

This is likely because the spill occurred over 35 years ago and the hydrocarbons have been heavily weathered (besides being burned). During this period, the lighter and more toxic molecules have either volatilized or been biodegraded or photo-degraded, leaving only the heaviest fraction which has a higher proportion of resins, polars, and asphaltenes than the original light crude that was spilled. This residual fraction with these characteristics is practically non-biodegradable by microorganisms or plants, remaining in the soil for decades (Shahriari et al. 2007). Roy and McGill (2002) considered that concentrations of heavy hydrocarbons above 20,000 mg/kg would promote serious problems for fertility in sandy soils.

Single alkaline desorption treatment

Water repellency

After applying the single alkaline desorption treatment, samples Gs-1 and Gs-7 changed from severely water repellent to merely slightly repellent (WDPT < 60 s, Table 6), probably since the initial TPH concentrations were low (TPH < 3000 mg/kg), and the starting water repellency was also relatively low (MED < 6 M), compared to the other samples. Likewise, in those samples with

greater initial hydrocarbon concentrations (Gs-2, Gs-3, Gs-4, Gs-8 and Gs-9), little reduction in water repellency severity was observed. Nonetheless, in samples Gs-5 and Gs-6 the CMC was reduced to values similar to those found in samples Gs-1 and Gs-7 prior to treatment (Table 3).

CMC reduction

As can be seen in Fig. 5, in some of the samples the CMC was completely reduced (Gs-1 and Gs-7), or nearly completely reduced (Gs-5 and Gs-6, approximately 95 % reduction), other samples showed moderate reduction (Gs-3 and Gs-9 with approximately 30–60 % reduction), while a few of the samples had very little reduction (Gs-2, Gs-4 and Gs-8, with approximately 5–15 % reduction). In samples Gs-5 and Gs-6, the bars in Fig. 5 show negative values. In these samples, at zero moisture content, the WDPT was less than 60 s and thus the calculated value of soil moisture corresponding to a WDPT = 60 s gave negative values.

The samples with initial MED values of about 5 M (Gs-1, Gs-7, Table 3) were able to be treated with just one treatment, and those samples with initial MED values in the 6–7 M range (Gs-5, Gs-6) could nearly be treated with just one application. However, in samples with greater initial water repellency, single treatments were not able to reduce to CMC sufficiently to overcome water repellency. Therefore, sequential treatments were investigated.

Sequential alkaline desorption treatment

Water repellency

After the sequential alkaline desorption treatment, the water repellency severity in the subsamples was reduced (MED < 5 M). The final CMC (for WDPT < 5 s) was greater in samples with higher MED values (Table 7). The

Table 6 Water repellency after single alkaline desorption treatment

Sample	MED	WDPT (s)	CMC (%) (for WDPT < 60 s)	Ratio ISMC/CMC	Percent reduction CMC (%)
Gs-1	ND ^a	25	ND ^a	–	100.0
Gs-2	10.89	1.6 × 10 ¹⁹	3.64	0.20	4.8
Gs-3	9.02	8.2 × 10 ²⁷	1.97	0.64	63.3
Gs-4	11.41	2.9 × 10 ³¹	3.98	0.18	14.5
Gs-5	4.36	6002	−0.05 ^b	–	93.7
Gs-6	4.95	124,079	−0.10 ^b	–	95.9
Gs-7	ND ^a	50	ND ^a	–	100.0
Gs-8	8.85	1.5 × 10 ¹⁴	1.90	0.25	9.0
Gs-9	11.3	4,293,386,635	2.35	0.31	29.6

^a Not determined

^b Negative CMC values; these samples should not be water repellent even at a zero soil moisture content; however, they were still water repellent

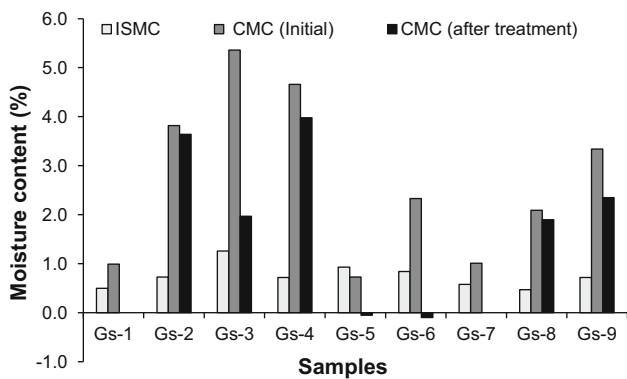


Fig. 5 ISMC prior to treatment, and CMC before and after treatment

samples with the highest TPH concentration (Gs-3) also maintained a very severe water repellency (MED > 3.2 M).

In Fig. 6, a reduction in water repellency severity is observed in samples Gs-2, Gs-8 and Gs-9, with each treatment. In sample Gs-3, during the first three treatments, the reduction in severity (MED) was only 10 % in comparison with the rest of the samples, probably due to the initial high hydrocarbon concentration and corresponding high water repellency, making it more difficult for the NaOH solution to wet and penetrate the soil. Notice that sample Gs-4 had an even higher initial MED value, but a much lower initial TPH concentration and that alkaline desorption was more effective.

Relationship between MED values and TPH concentrations

The initial TPH concentration was directly proportional ($R^2 = 0.9987$) to the MED after three sequential treatments (Fig. 7), except for Gs-8, which was much lower. Probably, the TPH after three treatments would also be proportional to the MED after three treatments, if the TPH had been determined. It is possible that at the lower initial TPH of Gs-8 (16,113 ppm), there was sufficient wetting to overcome a threshold and have increased alkaline desorption (the alkaline desorption was more effective). This threshold may also be observed in Fig. 1, with much greater water repellency above a TPH concentration of about 15,000–20,000 ppm.

After sequential treatment a reduction of up to 78 % in water repellency severity (MED), levels that were at or near those sufficient to only manifest slight water repellency in

the field (ISMC > CMC = 60 s), and a reduction of up to 87 % in TPH concentration were achieved. Additionally, after sequential treatment, the water repellency (MED) was directly proportional to the final TPH concentration ($R^2 = 0.9987$, see Fig. 8). Thus, at a lower final TPH concentration there was a corresponding reduction in the severity of water repellency in the soil. Sample Gs-3 maintained a very severe water repellency (MED > 3.2 M), however, possibly due to the high final TPH concentration.

Several methods have been established for the evaluation of water repellency in soil. The WDPT and MED methods are simple, rapid, and precise (Buczko et al. 2005; Doerr 1998). In recent studies, MED has been related to soil texture and pH. Regalado and Ritter (2007) evaluated persistence (WDPT) with respect to severity (MED), and the repellency curves obtained with the MED method were better than those described using the WDPT method. For this reason, many researchers use MED as the preferred metric for evaluation of water repellency in sandy soils.

During the initial characterization, prior to alkaline desorption, a poor relationship was observed between MED and the TPH concentration, when the repellency was very high (MED > 10 M). However, the CMC (for WDPT < 5 s) showed an excellent correlation, even when the TPH concentration was high (TPH > 16,000 mg/kg). After applying the sequential treatment, when the MED was reduced to less than 4.5 M, the MED value had an excellent correlation to the final TPH concentration ($R^2 = 0.998$). These metrics permitted the evaluation of the treatment efficacy in the alkaline desorption treatments.

Toxicity (earthworm bioassay) and pH

Preliminary data from this experiment (Table 8) indicated null to low mortality. Nonetheless, there were high levels of non-lethal effects that in longer tests would probably lead to mortality. This is especially apparent in samples Gs-2 and Gs-3, a little less in Gs-4 and Gs-9, and lower in Gs-8. The cause of these impacts to earthworm health is uncertain, and more studies are needed to determine it. Curiously, the sample with the lowest final TPH concentration (Gs-8) showed the highest mortality (<10 %), which may be due to experimental error (possibly lack of

Table 7 Characteristics of soil after sequential alkaline desorption treatment

Samples	MED	CMC (%) (for WDTP < 5 s)	CMC (%) (WDPT < 60 s)	TPH	ISMC (%)
GS-2	1.8	1.5	0.8	3597	0.73
GS-3	4.5	2.1	0.8	7492	1.26
GS-4	2.9	1.3	0.3	5004	0.72
GS-8	1	a	a	2478	0.47
GS-9	1.3	a	a	2749	0.72

^a WDTP < 180 s

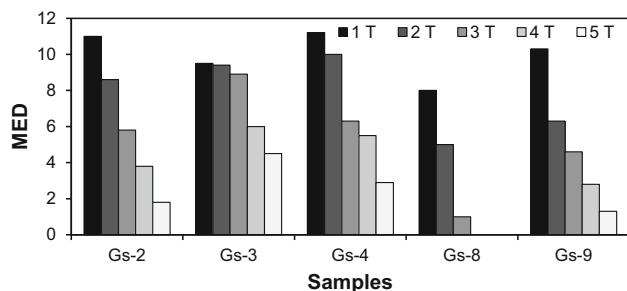


Fig. 6 Reduction in MED values during sequential alkaline desorption treatment

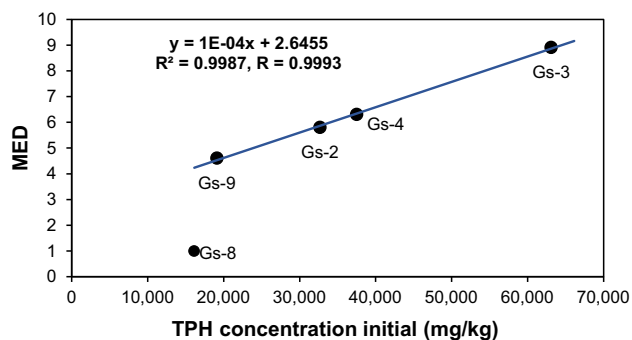


Fig. 7 Reduction in MED after the third sequential treatment with respect to initial TPH concentration

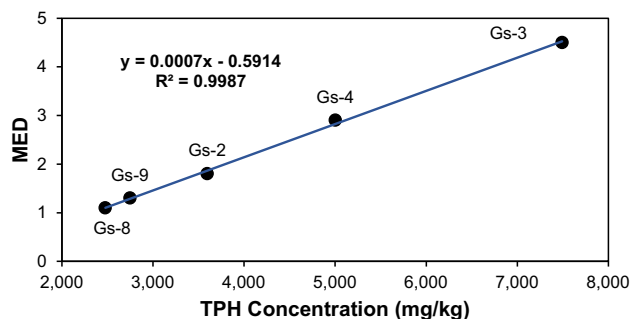


Fig. 8 Relationship between final MED values and TPH concentrations

sufficient moisture during the test or some residual solvent used in applying the soil extract to the filter paper).

An alkaline pH was produced in these samples from the excess NaOH. After treatment, the subsamples showed a pH in the range of 9.5–9.7, being approximately four units greater than initial readings. According to Mexican Norm 121, they were classified as strongly alkaline. This high pH in soil causes fertility problems. In the field, this would need to be reduced by natural precipitation or rinsing with fresh water. In a tropical monsoon environment, this was accomplished in a few weeks (Domínguez-Rodríguez and Adams 2011); however, in the drier mid-continental climate of northern Minnesota, this may require rinsing or an extended

Table 8 Percent mortality and non-lethal effects in treated samples (earthworm bioassay)

Sample	Mortality (%)	Non-lethal effects ^a (% sum)
Control	ND	28
Gs-2	ND	47
Gs-3	ND	47
Gs-4	ND	37
Gs-8	<10	13
Gs-9	ND	41

ND Not detectable

^a Change in color, loss of response to stimulus, loss of movement

period of natural precipitation. Therefore, for this site, the addition of an organic amendment is suggested. This, in conjunction with natural attenuation (principally precipitation), can buffer the pH. This was observed by Adams et al. (2014) after the addition of a similar alkaline solution [Ca(OH)₂], for the stabilization of hydrocarbon-contaminated soil. In that experiment, the pH increased notably after adding the calcium hydroxide (up to pH = 9.14), but upon adding an organic amendment (sugarcane cachasse) at 4 %, the pH was reduced to near neutral (pH = 6.3–7.6).

Efficacy of single and sequential alkaline desorption treatment

Single alkaline desorption treatment reduced water repellency in those samples with lower initial TPH concentrations and lower CMC (Gs-1 y Gs-7) to below critical levels (ISMC > CMC). However, for those samples with higher TPH concentrations (and more severe water repellency), sequential treatment was required. With sequential treatment, the hydrocarbon concentration was reduced up to 87 % and water repellency was reduced to levels that were at or near those sufficient to only manifest slight water repellency in the field (ISMC > CMC = 60 s). In Fig. 9, the change in color associated with the alkaline desorption of hydrocarbons from the soil is shown in the most contaminated sample. As seen, the treatment desorbs the hydrocarbons from the soil surfaces, causing a reduction in TPH concentration, water repellency and critical moisture content.

In preliminary experiments, treatment with 0.2 M NaOH was tried by itself and in combination with an organic amendment of 4 % (w/w, dry) of sugarcane cachasse (data not shown). The combined treatment resulted in a reduction of about 6.5 M in the MED value. In these preliminary experiments, the CMC was not determined. However, if the organic material is able to increase the field capacity and maintain the ISMC > CMC, it may be possible to overcome the water repellency and establish a vegetative cover, leading to successive colonization and finally overcoming the water

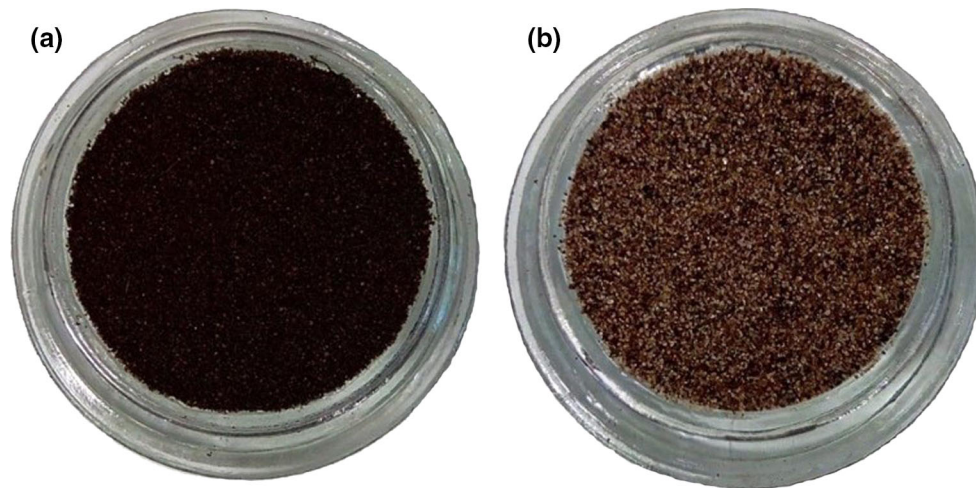


Fig. 9 Subsample Gs-3: **a** initial TPH at 63,109 ppm, **b** TPH at only 7492 ppm after applying sequential treatment

repellency problem in petroleum-contaminated soil in Bemidji and similar sites. Currently field plots at the National Crude Oil Spill Fate and Natural Attenuation Research Site are being conducted in which compost has been incorporated into soil treated by alkaline desorption to test this method.

Conclusion

Different remediation techniques, such as the addition of organic amendments and surfactants, have been used to treat water-repellent, hydrocarbon-contaminated soils with limited results. In the present study, a novel process was tested in a site-specific application, with the ultimate aim of definitive soil fertility restoration. At this site, with very sandy soil, the treatment results showed that this method could really be used to eliminate water repellency under field conditions. The burnt and weathered oil at the site is very viscous and has low biodegradation capacity, but does cause severe water repellency. However, single or sequential alkaline desorption was effective in reducing the water repellency to levels sufficiently low to avoid the manifestation of hydrophobicity under field conditions ($ISM > MCM$). Water repellency was directly related to hydrocarbon concentration when measured as the CMC (for $WDPT < 5$ s) for very repellent soils ($MED > 10$ M) or when measured as MED for less repellent soils ($MED > 4.5$ M). These variables had excellent correlation with the treatment procedures and permitted and effective evaluation of the technology.

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Attenuation Research Site titled: Evaluation of Remediation Methods for Water-Repellent Petroleum Contaminated Sites; and Evaluation of Water Repellency and Vegetation Composition at the Bemidji Oil Spill Site. Funding was provided from the National Crude Oil Spill Fate and Natural Attenuation Research Site, a collaborative venture of the USGS, Enbridge Energy Limited Partnership, the Minnesota Pollution Control Agency, and Beltrami County. Additional support was provided through the U.S. Geological Survey's Toxic Substances Hydrology Program. J.L. Nieber's effort on this project was partially supported by the USDA National Institute of Food and Agriculture, Hatch/Multistate project 12-059.

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