Rapid Estimation of TPH Reduction in Oil-Contaminated Soils Using the MED Method

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ABSTRACT: Oil-contaminated soil and sludge generated during federal well plugging activities in northwestern Pennsylvania are currently remediated on small landfarm sites in lieu of more expensive landfill disposal. Bioremediation success at these sites in the past has been gauged by the decrease in total petroleum hydrocarbon (TPH) concentrations to less than 10,000 mg/kg measured using EPA Method 418.1. We tested the "molarity of ethanol droplet" (MED) water repellency test as a rapid indicator of TPH concentration in soil at one landfarm near Bradford, PA. MED was estimated by determining the minimum ethanol concentration (0 – 6 M) required to penetrate air-dried and sieved soil samples within 10 sec. TPH in soil was analyzed by rapid fluorometric analysis of methanol soil extracts, which correlated well with EPA Method 1664. Uncontaminated landfarm site soil amended with increasing concentrations of waste oil sludge showed a high correlation between MED and TPH. MED values exceeded the upper limit of 6 M as TPH estimates exceed ca. 25,000 mg/kg. MED and TPH at the land farm were sampled monthly during summer months over two years in a grid pattern that allowed spatial comparisons of site remediation effectiveness. MED and TPH decreased at a constant rate over time and remained highly correlated. Inexpensive alternatives to reagent-grade ethanol gave comparable results. The simple MED approach served as an inexpensive alternative to the routine laboratory analysis of TPH during the monitoring of oily waste bioremediation at this landfarm site.

INTRODUCTION

The great commercial drilling of petroleum in the United States began at the Drake Well near Titusville, PA in 1859. For the next few decades, Pennsylvania was the world's largest producer of oil. Today, oil still seeps to the surface of uncapped and abandoned wells, while old storage tanks and relicts of the oil industry litter the former oil fields. Federal and state agencies continue to plug wells and recycle waste oil as time and money allow. Small landfarms are used in the Bradford oil field of northwestern PA to remediate oil-contaminated soils and tank bottoms that have been stockpiled during plugging operations, instead of sending those materials to landfills.

The target concentration for landfarm closure at these sites is ca. 10,000 mg/kg total petroleum hydrocarbons (TPH), based primarily on various plant toxicity guidelines (Deuel, 1991). Monitoring of the landfarms typically involves the biweekly collection of ten randomized soil samples to prepare a single composite sample for TPH analysis by an outside certified laboratory. During the course of our study of these landfarms, we found that rapid TPH estimates based on the fluorometric analysis of methanol extracts of soil (Sitelab Corp., West Newbury, MA) correlated well with laboratory TPH analyses (Edenborn et al., unpublished data). We also used the "molarity of ethanol droplet" (MED) method to evaluate the spatial and temporal variability of water repellency in landfarm soils. The MED method has been used previously to investigate the development of water repellency in various natural soils (King, 1981; Franco et al., 2000) as well as those contaminated by petroleum hydrocarbons (Roy et al., 1999; Roy and McGill, 2000; Litvina et al., 2003; Roy et al., 2003). In the current study, we examined the use of this relatively easy and inexpensive test to evaluate the rate of TPH decrease in a landfarm designed and maintained for that purpose.

Site Description. The study landfarm was located near Bradford, PA. It was established in June 2003 to remediate waste oil sludge and tank bottoms collected during well plugging operations carried out on a lease along a nearby stream. A level area approx. 11 x 18 m was cleared of small brush and cultivated with a rototiller. The eastern half of the site was amended with oily soil previously located in a nearby landfarm that became waterlogged and ineffective. The western half of the landfarm was amended with waste oil sludge (tank bottoms, non-recyclable oil) that had been collected during more recent well plugging operations. Thus, the western half of the site received a greater initial loading of less weathered oily material than did the eastern half. The landfarm and surrounding soil was characterized as a coarse-loamy, mixed, mesic Fluvaquentic Dystrochrept of the Basher series (Churchill, 1987).

MATERIALS AND METHODS

Soil Collection. A sampling grid of twelve uniformly spaced locations was established within the landfarm plot, with three additional control locations located in adjacent uncontaminated soil. Surface soil samples were collected in 125-ml pre-cleaned wide mouth glass jars (Eagle Picher Technologies; #130-04C). The jars were sealed with Teflon-lined polypropylene caps and kept cool in an ice chest until they were returned to the laboratory and stored at 4°C prior to further analysis within 48 h.

Soil TPH Estimates. The UVF analytical test kit (Sitelab Corp.) was used to estimate TPH concentrations in soil via fluorometric analysis of methanol extracts of soil. The EDRO C10-C40 aromatics calibration kit (CAL-042), containing weathered diesel fuel, was used to estimate the hydrocarbon content of the extracts. Because the fluorometer only detects aromatic compounds in the extracted material, a relationship between the measured value and independently-determined TPH by standard methods must be established. Comparison of TPH analyses using EPA Method 1664 A versus the Sitelab method using EDRO calibration standards gave a linear correlation of $r^2 = 0.863$ ($n = 20$) between 0 and 50,000 mg/kg TPH. Washed sea sand was used as control to ensure cleanliness of reagent blanks and materials. All TPH data were converted to mg/kg dry weight (24 h, 105°C) to account for variability in soil moisture of field samples on different dates.

MED Analysis. The MED test on soils was conducted using protocols similar to those described in Roy and McGill (2002). This method estimates the relative water repellency of soil by determining the minimum ethanol concentration (0 – 6 M) required to completely penetrate the surface of an air-dried and sieved sample within 10 sec (Figure 1).

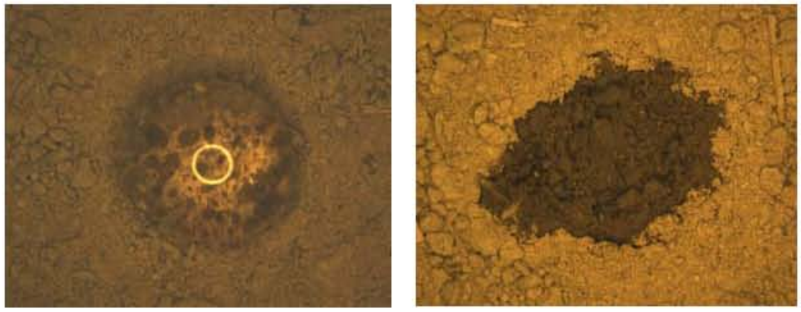

FIGURE 1. Appearance of water droplets added to oily (left) and uncontaminated (right) soil samples. The MED method determines the minimum ethanol molarity required for an added drop to completely enter the soil in less than 10 sec.

Field collected soil was first air-dried under a laminar flow hood for at least 24 h. After gentle crushing, the material was passed through a #14 (1.168 mm) sieve and air-dried for an additional 24 h. MED test solutions were prepared in 0.2 M intervals between 0 and 6 M by diluting denatured 95% ethanol in MilliQ-quality deionized water. Alternative test solutions were also prepared from dehydrated 100% ethanol, 40% ethanol (commercial vodka), and 91% isopropyl alcohol for comparative purposes. Approx. 20 gm dried soil was added to an aluminum weigh pan and droplet disappearance into soil was observed under a Leica Wild M3Z dissection microscope at 6.5x magnification. Test solution droplets were added to the soil surface using disposable transfer pipettes and the time for complete droplet penetration after initial solution-soil contact was measured using a stopwatch. MED was reported as the lowest molarity solution that was able to completely penetrate the soil surface in 10 sec or less. MED values and TPH concentrations were plotted as contour maps using the Kriging gridding method (Surfer for Windows, version 6; Golden Software, Inc., Golden, CO).

Oil Sludge Amendments to Soil. Oil sludge stockpiled for amendment to the landfarm site was added to uncontaminated air-dried and 2 mm-sieved soil collected adjacent to the test site. About 75 gm of soil were placed in each of 7 pre-cleaned 125-ml wide mouth glass jars. Oil sludge was added to the soil resulting in final concentrations of 0, 0.5, 1, 2.5, 5, 10, and 15% (w/w) added sludge. Soils and sludge were well-mixed with a spatula and allowed to incubate at room temperature for 72 h. At that time, soil aliquots were removed and analyzed for TPH and MED as described previously.

RESULTS AND DISCUSSION

The effect of adding oily waste sludge stockpiled for addition to the landfarm site to uncontaminated soil from the same location is shown in Figure 2. A linear relationship between the MED values and the TPH concentration estimates was observed as 0 - 15% (w/w) sludge was added to the soil.

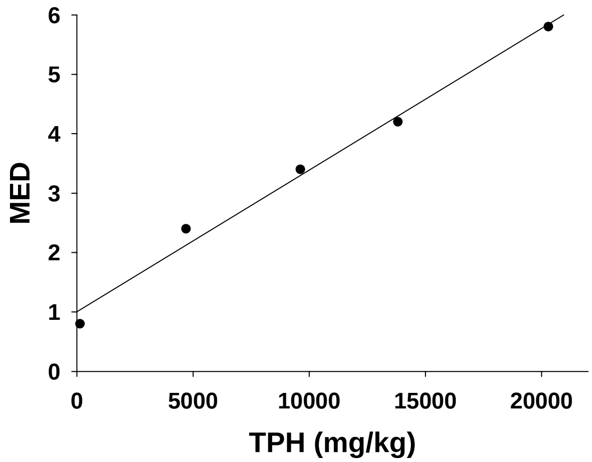

FIGURE 2. Effect of increasing concentrations of added oily sludge on the MED and TPH of uncontaminated landfarm soil. A linear relationship (r^2 = 0.99) between the two variables was observed.

When all field data collected over a two-year period of time were plotted in the same way, a more scattered, but similar linear trend was observed between 0 – 20,000 mg/kg TPH (Figure 3).

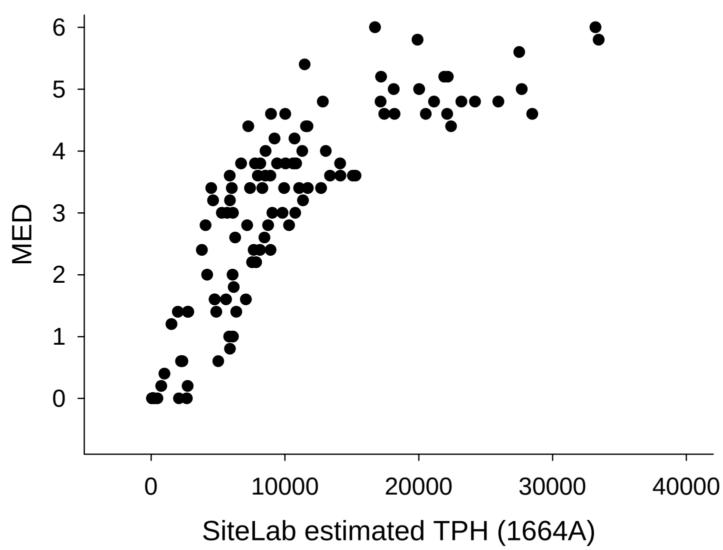

FIGURE 3. Relationship between MED and TPH for all landfarm samples collected over 2 years of study (n=127). Soils with MED values > 6.0 M (the upper limit of detection) were eliminated from this data set.

At higher concentrations of TPH, MED values approached their upper limit of 6 M, and many soil samples taken when oily sludge was first applied to the landfarm exceeded this value. These field data show that, for this particular landfarm, MED values above ca. 4.5 M rarely suggested TPH estimates below 10,000 mg/kg, nor were MED values less than ca. 3 M ever indicative of TPH estimates above this concentration. This suggests the potential value of this approach as a simple screening tool to alert landfarm managers when TPH remediation is approaching the point where more robust laboratory TPH analyses are needed to make decisions regarding closure, etc.

The use of either reagent-grade ethanol, 95% denatured ethanol, or commercial vodka to prepare test solutions for use in the MED test resulted in identical water repellency estimates (+/- 0.2 M). Isopropyl alcohol (rubbing alcohol) also served as an effective solvent substitute, although molar "MED-equivalent" values were roughly one half of those measured using ethanol. This provided an added advantage, however, in providing an indication of water repellency (and TPH) in extremely contaminated soils that would otherwise exceed the maximum MED (ethanol-based) test value of 6 M.

Despite the expected heterogeneity of TPH distribution within the landfarm plot, simple contour maps of TPH and MED based on only 12 points demonstrated not only the common spatial distribution of these two variables, but similar patterns of decreasing water repellency and TPH over time as well (Figure 4).

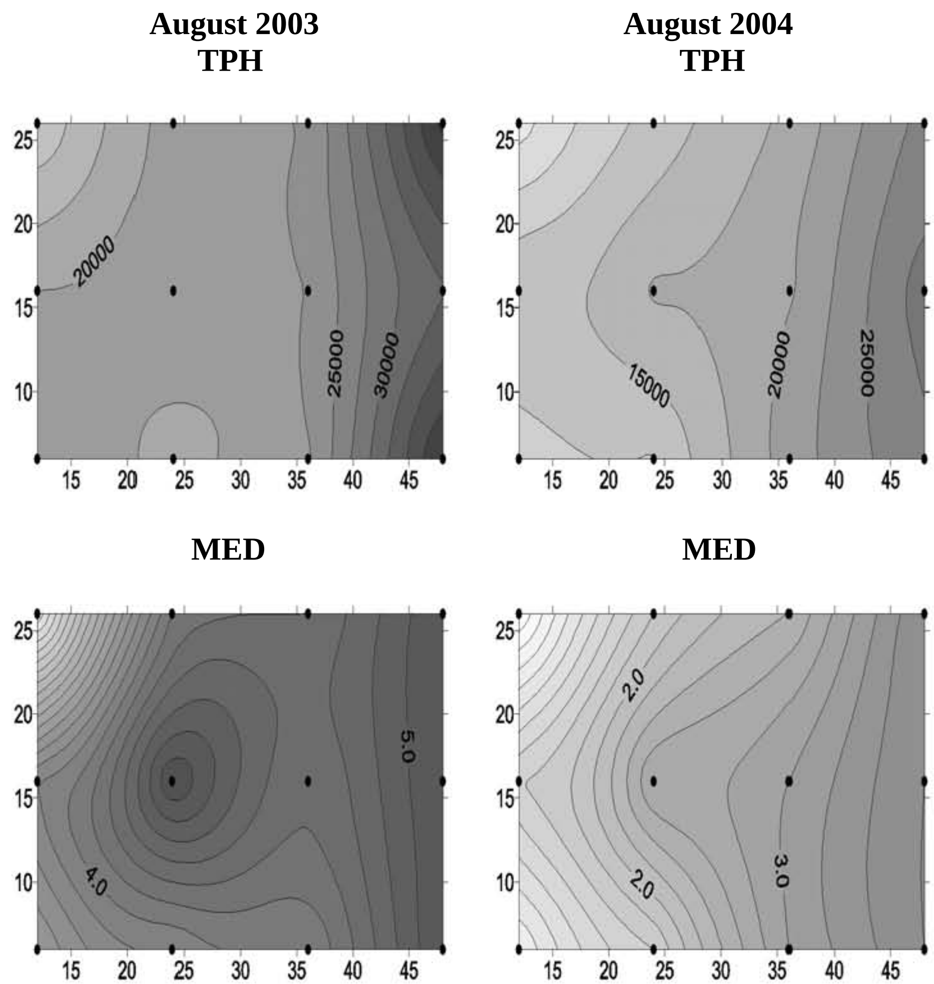

FIGURE 4. Contour maps showing areal distribution of estimated TPH and MED values at the 11 x 18 m study site. Darker shades indicate higher values.

The seasonal trends for MED and TPH can be even more clearly seen when simple averages of these variables are plotted over time (Figure 5).

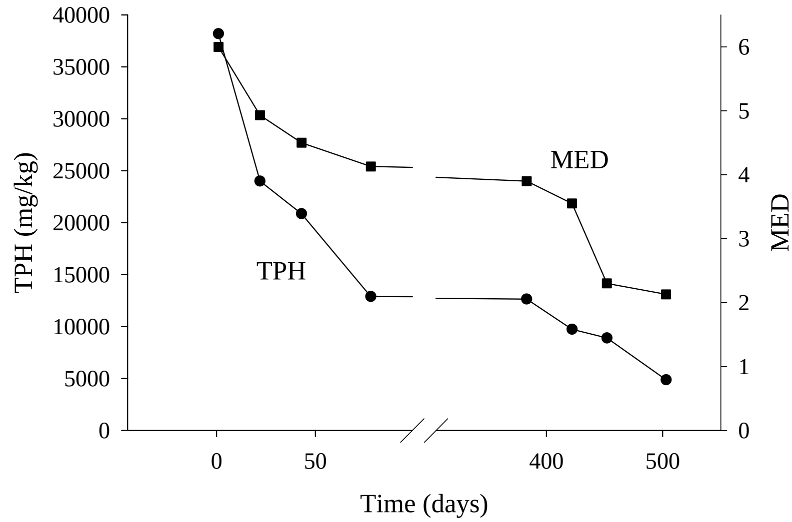

Figure 5. Decrease in estimated TPH and MED values over the study period, expressed as the arithmetic mean of 12 sampling points in the landfarm.

CONCLUSIONS

The MED test was shown to be an effective estimator of TPH concentration in a northwestern Pennsylvania landfarm. Since 10,000 mg/kg is still a typical target concentration for the closure of such sites, it appears that the MED method could be used as a cost effective way to estimate approximate TPH concentrations as they approach this level. More samples can be run in a shorter period of time and more inexpensively than by conventional lab analysis, also providing information about the distribution of TPH contamination not provided by composite samples. In addition, specialized equipment is not required, and alternatives to reagent grade ethanol used in the test can be easily obtained in the field.

ACKNOWLEDGMENTS

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RAPID ESTIMATION OF TPH REDUCTION IN OIL-CONTAMINATED SOILS USING THE MED METHOD

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ABSTRACT: Oil-contaminated soil and sludge generated during federal well plugging activities in northwestern Pennsylvania are currently remediated on small landfarm sites in lieu of more expensive landfill disposal. Bioremediation success at these sites in the past has been gauged by the decrease in total petroleum hydrocarbon (TPH) concentrations to less than 10,000 mg/kg measured using EPA Method 418.1. We tested the "molarity of ethanol droplet" (MED) water repellency test as a rapid indicator of TPH concentration in soil at one landfarm near Bradford, PA. MED was estimated by determining the minimum ethanol concentration (0 – 6 M) required to penetrate air-dried and sieved soil samples within 10 sec. TPH in soil was analyzed by rapid fluorometric analysis of methanol soil extracts, which correlated well with EPA Method 1664. Uncontaminated landfarm site soil amended with increasing concentrations of waste oil sludge showed a high correlation between MED and TPH. MED values exceeded the upper limit of 6 M as TPH estimates exceed ca. 25,000 mg/kg. MED and TPH at the land farm were sampled monthly during summer months over two years in a grid pattern that allowed spatial comparisons of site remediation effectiveness. MED and TPH decreased at a constant rate over time and remained highly correlated. Inexpensive alternatives to reagent-grade ethanol gave comparable results. The simple MED approach served as an inexpensive alternative to the routine laboratory analysis of TPH during the monitoring of oily waste bioremediation at this landfarm site.

Northwestern Pennsylvania, 1865

Well plugging operation, Bradford, PA

Landfarming operation, Bradford, PA

Introduction

The great commercial drilling of petroleum in the United States began at the Drake Well near Titusville, PA in 1859. For the next few decades, Pennsylvania was the world's largest producer of oil. Today, oil still seeps to the surface of uncapped and abandoned wells. The U.S. EPA and PA Department of Environmental Protection continue to plug abandoned wells that threaten to pollute surface waters, as time and money allow. Small landfarms are used by the EPA in the Bradford (McKean Co., PA) region to remediate oil-contaminated soils that accumulate during these plugging operations instead of sending the material to landfills.

The EPA target concentration for landfill closure at these sites is ca. 10,000 mg/kg total petroleum hydrocarbons (TPH), based on human toxicity guidelines. Typical monitoring of the landfarms involves the biweekly collection of 10 randomized soil samples to prepare a single composite sample for TPH analysis by an outside laboratory. During the course of our study of these landfarms, we found that rapid TPH estimates by fluorometric analysis of methanol extracts (siteLAB method) correlated well with laboratory TPH analyses. We also routinely used the "molarity of ethanol droplet" (MED) method to evaluate the spatial and temporal variability of soil water repellency in the landfarm soils. These studies revealed that the simple and inexpensive MED test was effective at estimating the TPH concentration in landfarm soils in this region, and that the method could be used to rapidly evaluate relative remediation efficiency in the field.

McCracken landfarm

Materials & Methods

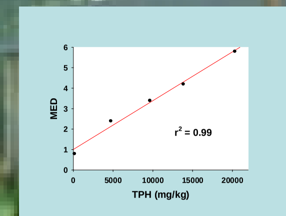
The McCracken landfarm was established in June 2003 to remediate oily sludge obtained from plugged wells in the immediate vicinity. The landfarm was rototilled 3 times per week during the growing season, weather permitting. Fertilizer and soil bulking agents (leaf litter) were also periodically added. The landfarm was sampled monthly during periods of operation in 2003 and 2004. The tilled area of the landfarm was ca. 190 m^2 (10 x 19 m).

Soil TPH was estimated by fluorometric analysis of methanol extractions of soil obtained after 2 min shaking. Estimates obtained using EDRO standards correlated well with laboratory analysis of TPH performed using EPA Method 1664 (data not shown).

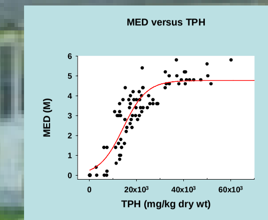
The MED method was used to estimate the degree of soil water repellency in landfarm soils. Basically, procedures were followed as described in detail by Roy and McGill (**Soil Science** *167*:83-97; 2002). Soil samples were air-dried for 72 hr prior to gentle crushing with a mortar and pestle, followed by sieving through a 1.4 mm mesh sieve, and an additional 24 hr of air-drying. Oven-drying was not used, as volatile hydrocarbons were driven off by this step. Samples were then evaluated for water repellency by applying droplets of ethanol solution, previously prepared in 0.2 M increments between 0 and 6 M, to the soil surface. The molarity of the least concentrated ethanol solution whose droplets were adsorbed into the soil within 10 sec was observed under a microscope (6x) and recorded as the MED value for that sample. 95% denatured ethanol was used as the standard reagent, although comparative experiments were also done using 40% ethanol (vodka) and isopropyl alcohol as starting reagents.

Examples of ethanol droplet appearance on soil surface during MED test

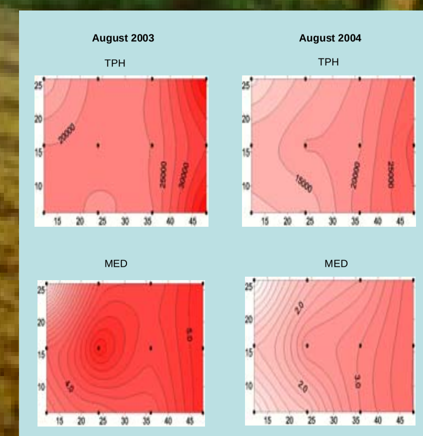
RESULTS



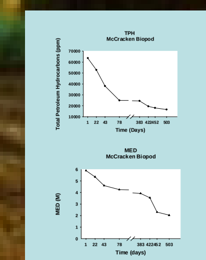
Addition of increasing amounts of oily sludge to uncontaminated soils showed excellent correlation between siteLAB TPH and MED methods.



Correlation between TPH and MED for all landfarm soils sampled in 2003 and 2004 was less linear at higher TPH concentrations. However, MED provided a good estimate of landfarm TPH as concentrations approached the desired 10,000 ppm TPH target.



Contour mapping of TPH and MED data revealed similar spatial distributions for the two variables. Both methods yielded far more information in a shorter time than did EPA-collected composite samples. The observed trend of higher TPH and MED on the right side of the landfarm was consistent with the initial placement of greater amounts of oily sludge in that location. Ethanol solutions prepared using 95% denatured alcohol and 40% vodka gave identical MED values. Lower molarity solutions of isopropyl (rubbing) alcohol gave comparable results.



TPH and MED measurements (shown as average values for 12 points in the landfarm) both yielded similar temporal data, showing similar decreases in TPH and general water repellency over the summers of 2003 and 2004.

CONCLUSIONS

The MED test was shown to be an effective estimator of TPH concentrations in Bradford landfarm soils. Since 10,000 mg/kg TPH is a typical target concentration for the closure of these sites, it appears that the method could be used as a cost effective way to estimate TPH at these sites. More samples can be run in a shorter period of time and more inexpensively than by conventional lab analysis, avoiding the need for composite samples that give little information about the distribution of oil contamination. In addition, specialized equipment is not generally required, and alternative reagents to 100% ethanol can be easily obtained in the field.

Used MED sample. This research was endorsed by Mandy the cat.