

# USE OF THE MED METHOD TO EVALUATE TOTAL PETROLEUM HYDROCARBON REDUCTION DURING BIOREMEDIATION OF OIL-CONTAMINATED SOILS

H.M. Edenborn<sup>1</sup>, K.T. Schroeder<sup>1</sup>, F. Mulcahy<sup>2</sup>, and V.E. Zenone<sup>3</sup>

<sup>1</sup>National Energy Technology Laboratory, U.S. Department of Energy, P.O. Box 10940, Pittsburgh, PA 15236;

<sup>2</sup>Department of Chemistry, Allegheny Institute of Natural History at the University of Pittsburgh - Bradford, 300 Campus Drive, Bradford, PA 16701;

<sup>3</sup>U.S. Environmental Protection Agency, Region III, Removal Response Section (3HS31), Philadelphia, PA 19103

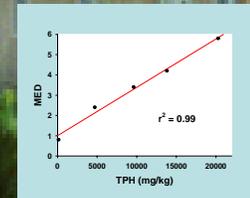
**Abstract.** Oil-contaminated soil generated during federal well plugging activities in NW Pennsylvania is currently incorporated into landfarm sites in lieu of more expensive landfill disposal. Bioremediation "success" at these sites has been gauged by the decrease in total petroleum hydrocarbon (TPH) concentrations to less than 10,000 mg/kg (EPA Method 418.1). We tested the "molarity of ethanol droplet" (MED) method as a rapid indicator of TPH concentration in soil at the McCracken landfarm near Bradford, PA. MED was estimated by determining the minimum ethanol conc. (0 - 6 M) required to penetrate air-dried soil samples within 10 sec. TPH in soil was analyzed by rapid fluorometric analysis of methanol soil extracts (siteLAB), which correlated well with EPA Method 1664. Uncontaminated landfarm soil amended with increasing concentrations of fresh oil sludge showed a high correlation between MED and TPH ( $r^2 = 0.99$ ). MED values exceeded the upper limit of 6 M as added TPH increased above ca. 25,000 mg/kg. The McCracken site was sampled monthly over a two year period on a twelve-point sampling grid during the summers of 2003 and 2004. MED and TPH decreased at a constant rate over time and remained correlated. Spatial analysis of MED and TPH data gave similar 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 these landfarm sites.



McCracken landfarm

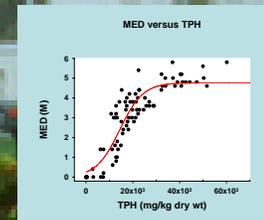


Examples of ethanol droplet appearance on soil surface during MED test



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

## RESULTS



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.

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.

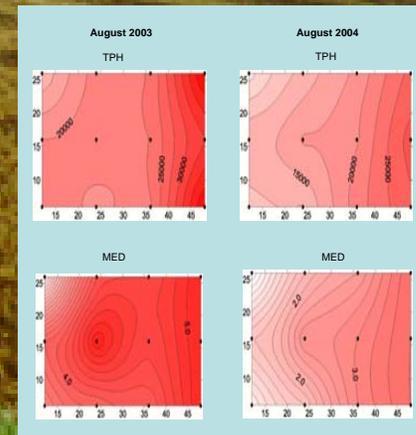
The EPA target concentration for landfill closure at these sites is ca. 10,000 mg/kg total petroleum hydrocarbons (TPH), based on human toxicity guidelines. Typical monitoring of the landfarms involves the biweekly collection of 10 randomized soil samples to prepare a single composite sample for TPH 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.

## Materials & Methods

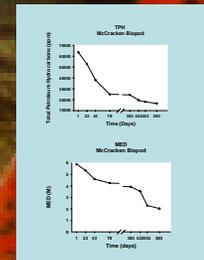
The McCracken landfarm was established in June 2003 to remediate oily sludge obtained from plugged wells in the immediate vicinity. The landfarm was rototilled 3 times per week during the growing season, weather permitting. Fertilizer and soil bulking agents (leaf litter) were also periodically added.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



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.