EVALUATION OF A NEW FIELD TEST KIT FOR DETERMINING TOTAL PETROLEUM HYDROCARBON CONCENTRATIONS IN SOIL AT A SITE CONTAMINATED BY DIESEL FUEL

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ABSTRACT

Dexsil[1] Corporation's new PetroFLAG™ field test kit for determining Total Petroleum Hydrocarbon (TPH) concentrations in soil was used to field-test soil contaminated by diesel fuel. The test was used at a bioremediation site to analyze remediating soil to determine existing concentrations of TPH after approximately ten months of remediation. The average diesel concentrations before remediation began were approximately 1000 parts per million (ppm) as determined by EPA laboratory method 3550A/8015 for diesel. Several hot spots having very strong diesel odor were also present within the soil at the time the remediation started. Twenty-one (21) soil samples were collected during this study. Duplicate soil samples were analyzed using both the PetroFLAG field test and EPA laboratory method 3550A/8015 for diesel (TPH-D) as well as method EPA 418.1 adapted for soils. The sampling plan and field testing were approved and witnessed by the Senior Environmental Health Specialist from the Local Implementing Agency (LIA). The LIA in this case was the County Environmental Management Department. The results of the comparative statistical analysis of the EPA method 3550A/8015 for diesel data, the EPA method 418.1 for soil data, and the PetroFLAG field data show that the PetroFLAG test kit correlates well with both laboratory methods (R^2 =0.89 and 0.92 for the two comparisons).

INTRODUCTION

Hydrocarbon contamination of soil in the United States is a serious problem that is well recognized by the United States Environmental Protection Agency (EPA). Whether the contamination source was a leaking underground fuel storage tank, surface spills, or the result of many years of poor housekeeping practices or sloppy handling of petroleum products at large industrial sites, the results are the same: compromise to the quality of the environment and potential impact to soil, surface waters, and groundwater resources. To protect the environment from further compromise, the EPA requires corrective action be taken to clean up contaminated sites. A directive (Number 9650.13) issued from the EPA's Office of Solid Waste and Emergency Response (OSWER) in November of 1992 and Titled "Streamlined Implementation of UST Corrective Action Requirements" was issued to states and their Local Implementing Agencies (LIAs) to help provide guidance on streamlining corrective actions. The EPA's major priority, as stated in the directive, is to help make the clean-up of contaminated sites faster, more effective and less expensive. The objective of the directive is to identify and discuss opportunities for carrying out federal underground storage tank (UST) regulations (40 CFR 280 Sub part F) in more flexible, efficient and cost effective ways. The directive lists 40 CFR 280.65 Sub-part F, "Field Measurements", as one section of the regulations that should be viewed more flexibly to help implement the directive. The directive, as it pertains to this section (Field Measurements), suggests that by using field measurement methods in place of laboratory analyses to investigate a contaminated site, the investigator can analyze more samples more quickly and at a lower cost. The field test data can then be used to select additional sampling points eliminating delays caused by laboratory processing time while improving the quality of the investigation. Some

laboratory analyses are still required to confirm the results of the field testing, but large numbers of expensive and time consuming laboratory analyses can be reduced.

Corporation's PetroFLAG field test for TPH is an inexpensive field test that provides high quality data in minutes. The test has been developed to be used at a variety of TPH contaminated sites, whether they be UST investigations, remediation efforts, or evaluations of the lateral and vertical extent of TPH distribution and migration on the surface and through the vadose zone at large and small contaminated sites. The use of the PetroFLAG test kit will allow project managers to use a more systematic approach when performing site assessments. Field test results generated using the PetroFLAG test kit can be used to quickly build a statistically supportable data base for on-site project planning and future project management.

By using the PetroFLAG field test kit at hydrocarbon contaminated sites, the EPA's objective of streamlining corrective actions by making them faster and less expensive is brought one step closer to being fulfilled.

BACKGROUND

The site was selected to demonstrate the ability of the PetroFLAG field test kit to provide an accurate on-site analysis of the existing concentrations of diesel hydrocarbon contamination remaining in remediating soil. The contaminated soil was discovered when a 5,000 gallon underground fuel storage tank was excavated and removed from the ground. The UST had been underground for more than 20 years, and recent tank tightness tests had indicated that the tank leaked. Upon excavation, soil contamination appeared to be located around the fill end and the supply line end of the tank. The contamination encountered at the fill end of the tank affected the soil on top of the tank and along both sidewalls of the excavation. This contamination appeared to be the result of overfilling the tank, and strong diesel odors emanated from the soil in this area. The contamination encountered at the supply line end of the tank appeared to be the result of a loose pipe fitting that was leaking, and strong diesel odors were also evident in this area. The soil beneath the tank was not contaminated and upon excavation, the bottom and sides of the tank were examined and found to be free of holes, and the tank appeared to be in good condition. The leaking pipe joint was most likely the only leak in the system. Upon removal of the tank, the contaminated soil was removed and stockpiled on-site. Several treatment options were considered before on-site passive bioremediation was determined to be the method that best suited the client's needs and budget.

A remediation cell was constructed using 10 millimeter Visqueen™ as a liner, and straw bales for erosion control. The contaminated soil was then placed on the visqueen, spread to a depth of 16-18 inches, amended with fertilizer and organic matter, and treated to adjust the pH to neutral (7.0). The soil was then rototilled, watered, covered with Visqueen, fenced and allowed to remediate. Beginning diesel concentrations were approximately 1000 ppm as determined by EPA laboratory method 3550A/8015 modified for diesel, but several hot spots having strong "diesel" odors were observed within the bioremediation soil. At the 5 month point of the remediation, the soil was tested for nutrient deficiencies and other possible imbalances. Deficiencies and imbalances were corrected, water was added where needed, and the soil was again rototilled. The remediating soil was then re-covered with Visqueen and allowed to continue to bioremediate. No laboratory tests were performed at this time. Soil testing using the PetroFLAG field test kit and laboratory analysis by EPA methods 3550A/8015 for diesel and 418.1 for soil, as presented in this paper, began at 10 months into the bioremediation effort when cursory field observations failed to detect the presence of hydrocarbon contamination.

SOIL SAMPLING

Soil sampling points were selected from an evenly spaced grid that was laid out in the field. The grid pattern allowed for a systematic method of sampling and testing the remediating soil. The systematic sampling method was selected over several other sampling methods because it provided an efficient method for determining potential hot spots that

might exist within the remediating mass of soil while providing a valid estimate of the sample mean. Soil sampling was witnessed by Mr. Jeff Russert, the Senior Environmental Health Specialist for the County Environmental Management Department (LIA). Soil samples were collected from each sampling point using the same protocol, which consisted of digging a hole using a man-powered shovel until the Visqueen liner was visible (approximately 16"-18" deep). The hole was then cleaned to expose an undisturbed vertical section of the soil. The sampling containers, glass jars purchased from an environmental supplier, were then opened and the rim of the jar was gently scraped along the soil, vertically, beginning at the bottom of the section and moving to the top of the pile. This method provided a vertical composite sample from each discrete location. Clean Latex gloves were worn by the sampler during the collection of each sample. After each sample was collected it was sealed, labeled and immediately placed into a cooler containing crushed ice. Soil sampling was performed by a geologist who is both a certified professional soil scientist and California registered environmental assessor. A total of 20 soil samples were collected from the bioremediation soil. One background sample was collected from an undisturbed area at the site. Site preparation and soil sampling required 2 hours and 12 minutes to complete. The background sample collected at the site was used to make three site-specific soil standards of 100 ppm, 500 ppm and 1000 ppm. All of the soil samples were collected before any field testing using the PetroFLAG kit was performed. When sample collection was complete, the soil samples in the glass containers were removed from the cooler, one by one, mixed thoroughly by rotating the jar, and 10 grams of soil were removed from each jar. This soil was placed into extraction test tubes supplied with the PetroFLAG field test kit. Each jar was then placed back into the cooler. The 21 duplicate samples were shipped to an accredited environmental laboratory. The laboratory analyzed the samples using EPA method 3550A (Ultrasonic Extraction) followed by 8015 (Nonhalogenated Organics Using GC/FID) for Diesel. The laboratory also analyzed the samples using EPA method 418.1 (TRPH) adapted for soil.

Decontamination procedures between sample collections consisted of washing the sampling tools in a solution of deionized water containing trisodium phosphate (TSP), followed by two deionized water rinses.

SAMPLE DESCRIPTION AND FIELD OBSERVATIONS

The average soil texture within the bioremediation cell consists of a sandy clay loam. Soil moisture content within the bioremediation cell varied from 26% to less than 5% at the time the soil samples were collected. Bedrock in the area consists of mostly basic schist. The soil within the bioremediation cell contained approximately 5 to 10% organic matter. A background soil sample was collected from the C horizon of native undisturbed soil in an area adjacent to the site. This sample was tested using the PetroFLAG test to determine natural background levels of hydrocarbons and other possible interferences in the native soil, if any, and then was also used to make three site-specific and matrix-specific spiked soil standards of 100, 500, and 1000 ppm diesel. The field standards were then tested exactly the same as all of the other samples and were used to produce a standard curve that enabled colorimetric measurements to be plotted verses ppm. This allowed the hydrocarbon concentration (TPH-D) in each soil sample to be determined quickly in the field.

Soil samples C-5, B-13, C-21, C-37 and the Background sample contained less than 5% moisture content. The remaining soil samples contained 5% to 26% moisture. The soil appeared to be uniform in texture, gravel and rock content, and color with soil moisture being the most variable soil condition observed. No soil discoloration was observed and no hydrocarbon odors were detected in any of the soil samples, making commonly used visual and olfactory detection methods ineffective for determining hot spots and impossible for determining if the soil was still contaminated or completely remediated.

THE PETROFLAG FIELD TEST KIT

The PetroFLAG field test kit for determining petroleum hydrocarbon contamination levels in soil samples

is a portable test kit designed to provide high quality data, inexpensively and quickly on-site at a variety of hydrocarbon contaminated sites. The test can just as easily be performed in an office setting, or in an environmental laboratory. A single sample requires 15 minutes to analyze. When multiple samples are being tested concurrently, analysis time per sample is greatly reduced. The PetroFLAG field test requires 10 grams of soil. The test kit comes prepackaged with plastic screw top test tubes, premeasured extraction solutions in vials, filtering syringes and premeasured color development solutions in screw top cuvettes. The PetroFLAG test kit is **Freon™ free** and uses only environmentally safe reagents. The test also comes with a portable electronic balance. Samples are quantified using Dexsil Corporation's specially configured hand-held colorimeter. The test also comes with prepackaged easy to use ampulized spiking solutions for making specific hydrocarbon standards.

The PetroFLAG field test procedure is easy to learn and quickly memorized. The procedure for the is as follows:

1. Weigh 10 grams of soil into a plastic screw top test tube using a clean spatula.
2. Add premeasured extraction solution to the soil in the test tube and mix for 5 minutes.
3. Add the mixture to the filter syringe and filter the solution into the screw top cuvette containing the premeasured development solution.
4. At the end of a 10 minute development period place the cuvette into the specially designed Dexsil colorimeter and record the reading.

PETROFLAG FIELD TESTING

A total of 24 soil samples were analyzed to determine total petroleum hydrocarbon concentrations as diesel (TPH-D), on-site, using the PetroFLAG field test kit. Of the 24 samples, 20 were collected from hydrocarbon contaminated soil that had been bioremediating for 10 months. One soil sample was collected from the site in an area that appeared to be clean and undisturbed. This sample was used as a background sample, site-specific zero for the test, and to prepare three matrix-specific standards, allowing for a high degree of accuracy. Each soil sample was tested using the PetroFLAG test procedure listed above. All soil samples were weighed using the PetroFLAG's portable electronic balance. At the completion of the development stage, each cuvette was placed into the colorimeter and the reading was recorded. The colorimeter was zeroed using the site specific zero between each reading. The testing of the 24 samples and standards, including weighing the samples, took 169 minutes or seven (7) minutes per sample. All field testing was performed in the field on the tailgate of a truck.

ANALYTICAL RESULTS

The spike recovery data obtained from the laboratory QA/QC indicated an extraction efficiency for EPA method 3550A/8015 of approximately 54%. Method 418.1 data showed an extraction efficiency of approximately 63% as indicated by laboratory spike recovery data. The PetroFLAG test kit uses a soil spike to calibrate the instrument, therefore, a correction for extraction efficiency is incorporated into the reported result. The resulting realized efficiency is greater than 90%. When comparing the PetroFLAG results with the laboratory results, it is important to account for these differences in extraction efficiency.

The PetroFLAG test results and the laboratory data are summarized in Table 1. The PetroFLAG data indicated existing hydrocarbon concentrations in the soil to be between 45 and 700 ppm. The laboratory 3550A/8015 data indicated existing diesel concentrations to be between 13 and 400 ppm. The laboratory 418.1 data indicated existing TRPH concentrations to be between 34 and 470 ppm. As expected, the PetroFLAG results indicated a higher hydrocarbon concentration than either of the two lab methods. The magnitude of the disparity reflects the differences in the extraction efficiencies of the methods.

A residual analysis of the data revealed that the data for sample C-21 was inconsistent between methods. It was, therefore, eliminated from the data set and the analysis was repeated. The final regression analysis of the field data versus both lab methods indicates that the PetroFLAG results correlate very well with either

method. The correlation coefficient (R^2) in both cases is greater than 0.88 (R^2 =0.886 when regressed against EPA-3550A/8015 and R^2 =0.916 when regressed against EPA 418.1 results) and the intercept in each case was not statistically different from zero (50 ppm compared to EPA-3550A/8015 and 10 ppm when compared to EPA 418.1 data), indicating very little bias. As expected, the slopes of the regression lines are greater than one, reflecting the greater extraction efficiency of the PetroFLAG method. (See figures 1 and 2)

REGULATORY REVIEW

Mr. Russert was given a summary of the data in Table 1. He found that the PetroFLAG data compared quite well with the laboratory data when the extraction efficiencies of each of the methods are taken into account. Mr. Russert also noted that the PetroFLAG test produced no false negative results when compared to the laboratory methods, and the hot spots identified by PetroFLAG were confirmed by laboratory analysis.

CONCLUSIONS

Dexsil's PetroFLAG hydrocarbon field test kit successfully demonstrated the ability to provide accurate on-site analysis of the existing petroleum hydrocarbon contamination remaining in the bioremediating soil. The PetroFLAG results compared very well with EPA laboratory analytical methods 3550A/8015 for diesel and 418.1 for TPH. The PetroFLAG's extraction efficiency was in fact much better than the EPA methods, and this is reflected in the regression analysis of the data.

The PetroFLAG test kit was easy to use and economical, which allowed soil samples to be collected using a grid sampling method. The resulting field-generated data provided a very clear picture for evaluating the status of the bioremediation, in the field while providing high quality, statistically supportable data for on-site project management decisions. This was very important because commonly used visual and olfactory detection methods proved ineffective at this site due to the uniformity of the soil and lack of discernible odors and color changes in the soil. Conventional methods would have included expensive laboratory analysis requiring two weeks waiting time before analytical results could be available for evaluation. By using the PetroFLAG test kit at this site, more samples were tested than conventional methods would have allowed. The PetroFLAG test produced no false negative results when compared to the 8015 and 418.1 analytical results.

The use of the test as approved for evaluation by the senior environmental health specialist from LIA fulfilled the spirit of EPA's OSWER directive of streamlining corrective actions by utilizing field measurements in place of laboratory analyses for site monitoring and assessment. By utilizing the PetroFLAG field test, the investigator was given the luxury of analyzing more samples, more quickly, and at lower cost. The LIA's representative was given the opportunity to evaluate both the field test kit results and the laboratory results. Mr. Russert felt that the field test kit performed quite well, showing no false negative results while identifying the same hot spots as the laboratory methods.

The field data generated by using the PetroFLAG kit improved the quality of the investigation by efficiently identifying and locating "hot spots" while also identifying and locating soil that had been bioremediated to below the regulatory clean-up level. The hot spots could then be tested further to determine if nutrient deficiencies, or other limiting factors may be preventing bacteria growth in those areas. Also, additional PetroFLAG testing could be performed in a grid pattern around the identified hot spots. By doing this, the investigator could determine very accurately the total volume of soil that is still above the regulatory limit. The clean soil could then be removed and a smaller volume of "hot" soil could be given more attention.

The use of Dexsil Corporation's PetroFLAG field test kit provided an inexpensive, easy to use, quick and quantitative on-site field test for determining existing hydrocarbon concentrations at a bioremediation site and should be considered for use on similar projects where hydrocarbon testing is necessary.

Table 1: Analytical Results for Both Field and Laboratory Methods

Sample ID	PetroFLAG Results (ppm)	Laboratory 3550A/8015D Results (ppm)	Laboratory 418.1 Results (ppm)
b-13	160	73.4	68
b-29	220	47.4	109
c-5	135	34.2	48
c-21	240	54†	298
c-37	180	84.7	91
g-13	290	89.3	166
g-29	75	71.1	137
h-5	105	57.8	91
h-21	230	95.4	161
h-37	175	69.6	105
l-13	60	60.4	74
l-29	111	49.7	78
m-5	380	256	281
m-21	85	13.4	52
m-37	220	80.1	171
q-13	195	106	132
q-29	130	26	64
r-5	360	217	254
r-21	700	399	466
r-37	45	17.2	34
blank	ND	ND	ND

† Residual analysis indicated that this point was an outlier.
ND = None Detected

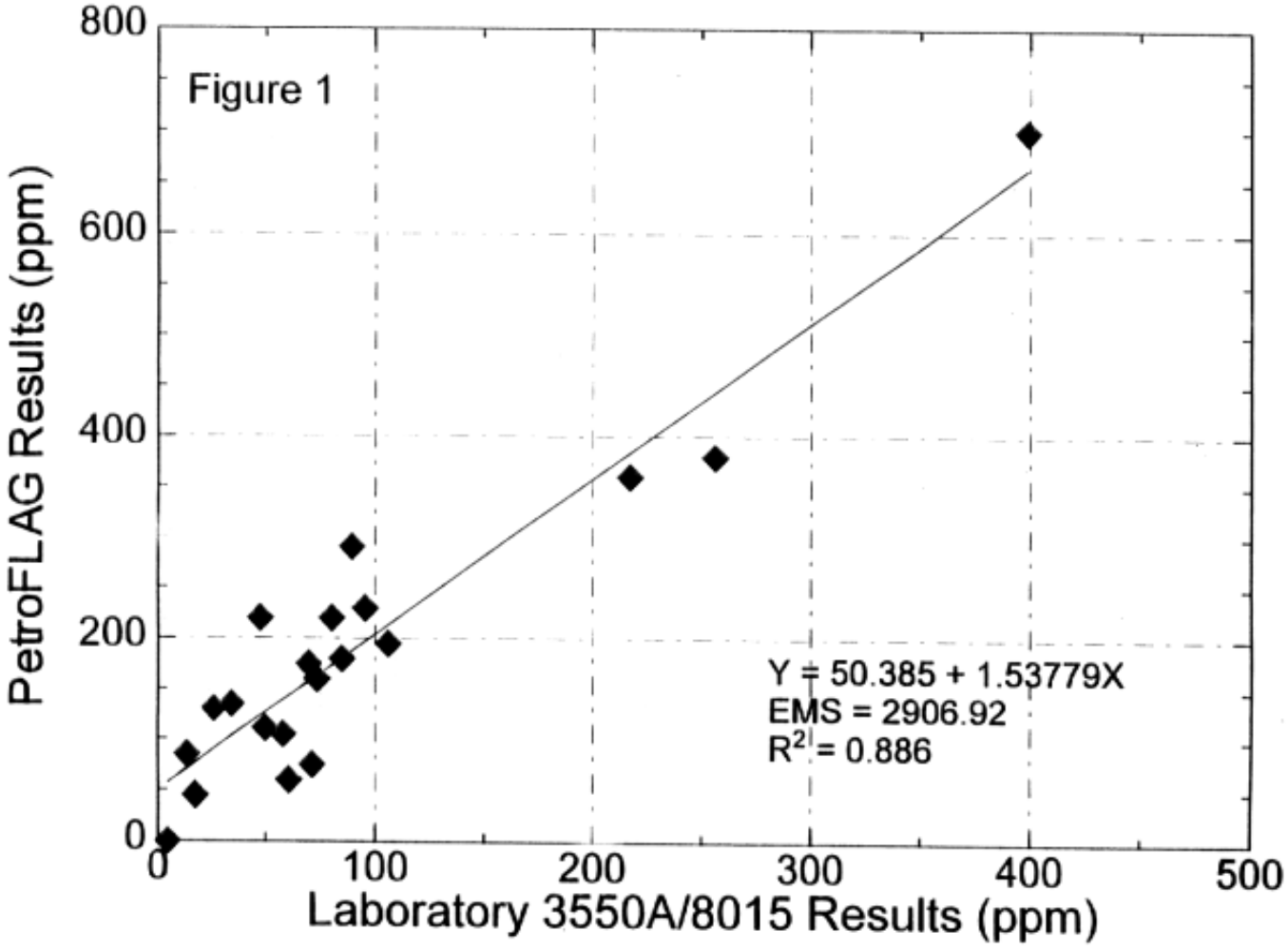
Figure 1
PetroFLAG Results (ppm)
800
600
400
200
0
0
100
200
300
400
500
Laboratory 3550A/8015 Results (ppm)
Y = 50.385 + 1.53779X
EMS = 2906.92
R2 = 0.886

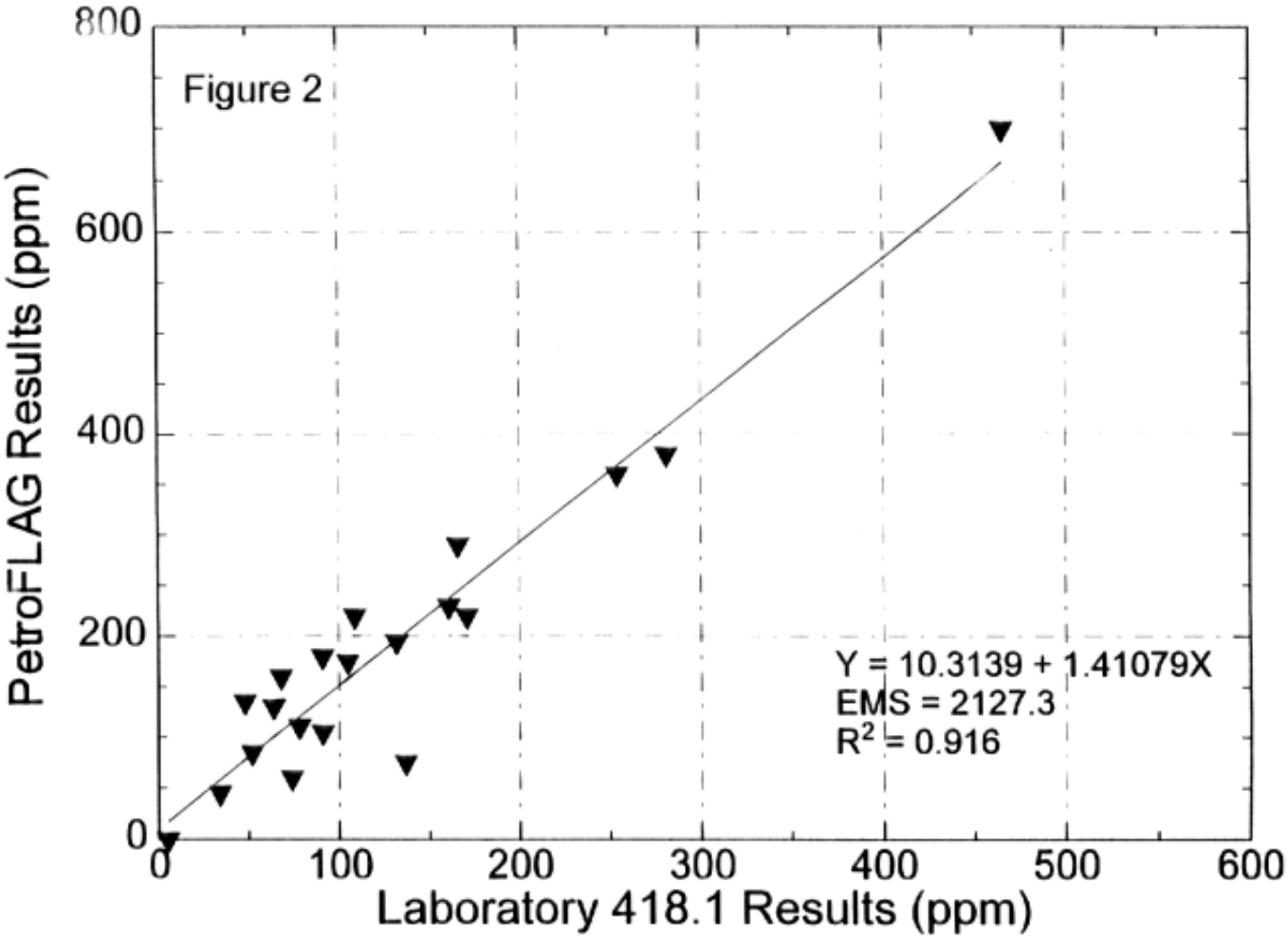
Figure 2
PetroFLAG Results (ppm)
800
600
400
200
0
0
100
200
300
400
500
600
Laboratory 418.1 Results (ppm)
Y = 10.3139 + 1.41079X
EMS = 2127.3
R² = 0.916