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AN IR-BASED FIELD ANALYTICAL METHOD FOR TOTAL PETROLEUM HYDROCARBON MEASUREMENT- FIELD DEPLOYMENT AND BENEFIT IN SITE REMEDIATION

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ABSTRACT

Total Petroleum Hydrocarbons (TPH) in soil is often measured to determine if soils have been impacted by crude oil. PT. Chevron Pacific Indonesia (PT. CPI) operates several oil fields in Sumatra, and during site investigations and recovery, soil samples must be analyzed. Traditional laboratory methods require five days to complete, and commercial labs often take two to four weeks to release the reporting results. This could delay decision-making regarding soil delineation and site excavation as well as in determining when soil remediation has been completed. In the PT. CPI pilot studies, a portable handheld infrared (IR) instrument was pilot tested with over 500 soil samples from variable PT. CPI sites to generate site-specific models. These samples covered a wide range of soil type, oil content, and moisture content, and should, therefore, be representative of most PT. CPI sites conditions. The US EPA 8015 TPH-Gas Chromatography (GC) analytical method data of those soil samples were used to create two site-specific models with 15-20 double-blinded samples to validate the modeling work. The key advantages of this rapid IR method are that the soil samples don't use any chemicals, so no wastes are generated, and the method provides results in a few minutes. This results in saving valuable time for site-specific decision-making. After the deployment in PT. CPI fields in July 2016, continuous monitoring of incoming soil types vs. data accuracy has been set up to evaluate the performance of this instrument at variable field conditions. The post-deployment evaluation concluded a good accuracy and repeatability compared to the standard laboratory method. Potential cost savings can be more than 100,000 US$ in a scenario where 3000 samples are analyzed per month.

Keywords**:** Total Petroleum Hydrocarbon, Field Analytical Method, Infrared-based method, Site Remediation, Soil Sample

INTRODUCTION

During remediation activities of crude oil impacted soil, Total Petroleum Hydrocarbon (TPH) or C10-36 petroleum hydrocarbons is often the primary parameter to determine whether soil must be treated. This analysis is used in most of the steps from site assessment and delineation, to site excavation, and processing of the impacted soil. The common practice is to send most of the samples off-site for testing in a certified 3rd party laboratory using standard analytical methods such as USEPA method 8015. This analytical method can provide high-quality data to meet regulatory requirements. However, laboratory turn-around times for TPH measurements are about 7-14 days for USEPA method 8015. The use of USEPA method 8015 has been promulgated through SW-846 for several decades[1] and it has been recognized as the standard regulatory testing method specifically for TPH and C10-36 petroleum hydrocarbons around the world. But field crews sometimes require data generated in real time to determine the size of a source area or confirm that excavation of impacted soil is complete. In some cases, decisions need to be made quickly during a single site trip due to land access and time restrictions at remote locations, and with sample turnaround times mentioned previously, this is

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impossible. When the number of sites increase, the number of the samples sent to a laboratory also increases, which can make laboratory turn-around times even longer. PT. CPI has identified the need to be able to use a rapid test method for TPH to shorten turnaround times. With access to rapid field analysis, the field crew can work more effectively, and more data could be collected quickly to improve decision quality.

METHODS

The selection of a field method is not only based on analytical performance, but the selection process also needs to consider the following: method/instrument detection limit, ease of operation, analysis time, cost per sample, cost of the analytical device, available consumables, power supply, ruggedness of the unit, robustness and waste management requirements.

In 1997 the USEPA (Environmental Protection Agency) reviewed field analytical methods to assist in expedited site assessment.[2] Additionally, in 2000 the USEPA published the field demonstration and validation results for seven rapid TPH test kits which were evaluated under the USEPA Superfund Innovative Technology Evaluation Program.[3-7, 11] In 2013, a handheld infrared instrument demonstrated a very fast quantification capability for TPH in soil without involving a solvent extraction step. The TPH measurement takes about 15 seconds if the soil contains less than 5% soil moisture content.[8-9] The entire sample preparation and data collection process can be completed within two minutes, in most cases This technical advancement will significantly increase the amount of data that can be collected from the field and reduce the waiting time for laboratory data. In 2016, the Hawaii Department of Health recommended that this handheld IR instrument be considered as a TPH field method.[10] From 2015 to 2017, PT. CPI has evaluated the handheld IR instrument in laboratory conditions, with field samples collected from PT. CPI sites in three separate pilot studies. Deployment of this IR-based, handheld instrument began at some PT. CPI sites in 2016. Since deployment, more than 10,000 soil samples have been collected to support decision-making in the field. All data from field testing have been cross-checked against laboratory TPH data measured with USEPA method 8015 at a 5% double-blind ratio used to monitor the data accuracy monthly.

The handheld-IR instrument has been pilot tested in both the Minas and Duri fields from 2016 through 2017 with more than 500 soil samples at variable TPH concentration levels. The data from these samples were used to generate oil and soil type specific models that can be used at most sites within the oil fields. The models were developed by first air-drying all soil samples overnight and sieving them to less than 2 mm, then splitting them into two even duplicate sets using a riffle apparatus and analyzed all samples by both USEPA 8015 and the IR instrument. The IR scanning and data reduction followed the procedure reported by G. Webster, et. al, in their recent publication.[9] All the initial PLSR (Partial Least Squares Regression) models were created with about 110 samples from Minas field in 2015, 200 samples from the Duri field in 2016, and from 250 soil samples from variable sites of the Minas field during delineation sampling in 2017. The model results were validated with 10-20 double-blind samples to confirm the accuracy. The model results are then loaded into the handheld-IR instrument so that it is ready for field use.

RESULTS

During the first Minas field pilot, 110 calibration samples were used to create a PLSR model as depicted in Figure 1. Sixteen new soil samples were collected to serve as the validation check for the robustness of the model after the handheld-IR instrument had been deployed in the field for about one month. The calibration and validation results are provided in Figure 2. The data in Figure 2 show that there is a good correlation between the handheld-IR instrument values and the laboratory obtained GC-FID TPH data. This is demonstrated in Figure 2 by the red points which lie as close to the Y=X line as the blue points, except for three significant outliers (red points in the shaded gray region). Further detailed inspection of the infrared spectra of those outlying validation samples found that these outlier samples contained high concentrations of kaolinite (clay) compared with the calibration model soil types. The soil samples used to develop the model did not contain soil with high kaolinite clay content.

This hypothesis was confirmed by the Duri pilot calibration model and validation results as shown in Figure 3. All 198 calibration and 15 validation samples were collected from one location in the Duri field which all had similar soil types (relatively high clay content). The results show excellent agreement between the handheld-IR instrument values and the laboratory GC-FID data, with no outliers. This confirms that soil type can be an important variable in developing an accurate model for site soils.

In a recently finished second pilot in the Minas field, 250 soil samples were collected during site delineation work and these samples contained a wide range of clay content. Figure 4 shows the data for all calibration and validation results versus the laboratory GC-FID TPH data. There is a very high degree of correlation between TPH values from the handheld-IR instrument and the laboratory analysis. The R^2 for the data is 0.96. The model developed during this second pilot is considered more robust than the model from the first Minas pilot, since the second model contains a wider range of soil types from across the Minas field.

In summary, the handheld-IR instrument field pilot studies demonstrate that it will provide sufficient accuracy for the measurement of TPH concentrations. In the above three pilot studies, the defined detection limit of the handheld-IR instrument for the Minas model is 170 mg/kg, while the detection limit for the Duri model is about 380 mg/kg, and the detection limit for the Minas delineation model is 196 mg/kg. The variable detection limits for different models are dependent on the number of samples collected in the low TPH concentration range. From the above three pilot studies, the results demonstrate that continuously monitoring incoming soil types will be critical for the continuous improvement and accuracy of the models. For field application, if a new soil type has not been included in the existing model, the first 20 field data points should be cross-checked with laboratory GC-FID data to ensure accuracy. If the new site soil types are significantly different from all the other sites, it is recommended that the existing model be refined to increase the tolerance or create a new site-specific model before usage of the handheld-IR instrument.

Field Deployment

Based on the results from the three pilots, PT. CPI decided to proceed with full deployment of this handheld-IR instrument in 2017 due to its reliability, repeatability, accuracy, robustness and ease of operation in field conditions. The handheld-IR instrument was first deployed in 2016 to assist with excavation of crude oil impacted soil. Technical workshops were held to inform and train the field crews on how to use the instrument. The existing Standard Operating Procedure (SOP) for field soil sampling was revised accordingly to include the new handheld-IR analytical method. Th IR instrument was used to verify that site excavation had sufficiently removed crude oil contaminated soil, before backfilling with clean soil. The method was also used to analyze the TPH in soil piles before it is hauled from the site for treatment such as bioremediation.

In September 2016, a lookback workshop was held to review the first two months' utilization of the handheld-IR instrument. The vendor, together with PT. CPI field personnel involved in day to day excavation operations, regrouped and evaluated the instruments performance. The outcome of the workshop was that the field crews were eager to use the new method. The field crews also provided critical feedback for improving field application of the method, which is discussed in more detail below. On average, 2,125 soil samples from excavation were analyzed and recorded every month.

After the method was deployed by the excavation team, then PT. CPI's site delineation crews began to study the benefit of field measurement of TPH in the middle of 2017. Due to multiple sites to be assessed in a year, PT. CPI decided to integrate the handheld-IR instrument to accelerate site delineation. Beginning in Jan. 2018, some samples coming from the delineation teams were analyzed by using this handheld IR instrument. Within one month, 1580 soil samples from the delineation team were analyzed using the handheld-IR instrument.

Due to the sizable variation in soil types within an oil field, some types of soil were possibly missed in the initial modeling work for the pilots. Consequently, a data quality monitoring program has been set up to add additional calibration samples, as needed, to increase the robustness of the predictive models. This program will check the instrument's performance by comparing the results with USEPA 8015 TPH-Gas Chromatography (GC) results monthly. The field deployment quality check data can be seen in Figure 5.

Figure 5 shows a good correlation as indicated by $R^2 > 0.8$. However, as marked by the pink circle, some of the data are outliers compared to TPH data obtained by USEPA 8015. For this reason, a monthly monitoring program is scheduled; to ensure data quality and determine if any outliers are related to new or unique site soil types, or if there may be other sampling or analytical issues. Figure 6 depicts a wide range of soil types that have been tested in the three pilot studies. The instrument vendor can provide the amount of clay and sand in a soil sample by using the specific IR spectra of the soil samples. As previously discussed, the soil type may impact the model accuracy, and it is important to make sure that the range of soil types (% sand and clay) within a field are included in the calibration model. Figure 6 illustrates that soils in the Duri model contain ~30-60% clay, while the soil types in the Minas model cover a broader range of percent clay, from a few percent to as much as 55%. Obtaining additional soil data from new sites for percentage of clay and sand will help identify whether the model needs to be updated or refined. For example, if there are sites in the Duri field which contain sandy soil, then the Duri model will need to be updated to include those soil types.

Benefits

The direct benefit of the handheld-IR instrument is obtaining TPH data rapidly in the field. Hypothetically, during site delineation, thousands of soil samples may be sent to a laboratory for TPH analysis monthly which can significantly exceed the capacity of most laboratories. The time saved due to short turnaround times and the efficiencies in labor costs and laboratory expendables are all important to cost savings.

Another benefit that can be quantified easily is the cost savings due to changing from US EPA 8015 TPH-Gas Chromatography (GC) analytical method to field analysis using the handheld-IR instrument. The laboratory method has relatively high costs, ranging from 40 – 60 USD per analysis, where the cost for the handheld-IR instrument including maintenance, consumables, manpower, and reporting is a lump sum rate. Therefore, the usage of this instrument is more efficient and effective as the number of samples analyzed increases. Figure 7 shows a hypothetical example of cost per sample versus the number of samples analyzed per month. At 338 samples analyzed per month, the cost for each sample is approximately equal to the cost of 3rd party laboratory cost for US EPA 8015 TPH-GC. Table 1 demonstrates what the potential cost savings will be with this IR instrument based on the numbers of samples measured per month. Currently, PT. CPI regularly analyzes more than 5000 soil samples every month.

Issues and Lessons Learned

PT. CPI operates an 8,800 square kilometer area of oil in Sumatera and needs to assess soil conditions in and around the oil operating areas. Figure 8 depicts a system developed to overcome logistical challenges for analyzing soil samples. PT. CPI employs centralized hubs to serve the surrounding operational areas to greatly improve the sample throughput. With this system in place, the traveling time can be cut to approximately half an hour, and while the samples are being taken to the hub, the instrument is still taking the measurements continuously.

There is a car and driver/expediter for each instrument. Each day a car runs a “route” to pick up samples from sites and take them to the analytical hub. The field team at each site completes the sampling process, prepares and packs the sample as per the sampling SOP before the pickup time. While this process is going on, the instrument at the analytical hub may work on the available samples and begin reporting results.

The system above may not be optimal for all field conditions. For example, if sites are located within a short distance then bringing the instrument on-site might be more beneficial regarding operational simplicity and response time. Therefore, multiple utilization models can be developed based on field and site specific operating conditions.

Continuous Improvement

This handheld IR instrument can measure TPH accurately only if the moisture content, (free water within the sample) is less than 5 %. When a soil sample has moisture content more than this allowable limit, the operator has to dry the sample before taking the IR readings. For some field conditions, such as swampy or low-lying areas, the soil collected may be very wet and the time needed to dry the sample might cause delay in obtaining analytical results. Therefore, continuous improvement regarding equipment, tools, and the sample preparation methods are being developed by the vendor to improve the sample drying process.

The first generation of handheld-IR instruments came with a drying box to help prepare wet samples. The drying box is battery operated and runs with a maximum temperature of 40°C. To help with drying samples more quickly, the drying box is supplemented with a sample cradle which is made of a thin aluminum plate, wax paper and cotton. Wet samples are loaded into the sample wells, which are then put on the drying rack inside the drying box to dry the soil sample to <5% moisture. However, the drying box method can take 1 to 2 hours. To help alleviate this problem, the vendor replaced the thin plate with an aluminum alloy cradle to improve the efficiency of the drying process. By using small sample volumes and better heating material in the box, the drying time can be cut down to less than an hour, depending on the initial moisture content of the sample.

Another problem which has been encountered by field crews was the inefficiency of the exhaust fan capacity on the drying box. The moisture which is generated during the drying process could not be removed quickly from the drying box, especially for very wet samples.

With input from the field crews and further research, the vendor provided an improved drying box in October 2017. The air circulation is improved with an additional exhaust fan, and it has a bigger exhaust channel to allow quick release of moisture during heating. The sample cradle is built with tougher aluminum metal and grooved with a pattern allowing more surface area so the soil adheres better to the metal. This design allows for better heat conduction and circulation of air on top of the soil samples.

CONCLUSION

The handheld--infrared instrument is a solvent-free analytical method because no extraction step is required. Therefore, the method does not generate potentially hazardous waste in the field. The handheld-infrared instrument requires upfront modeling work that is best performed by personnel with in-depth analytical chemistry skills. However, the field operator does not need in-depth knowledge about the instrument or analytical method, and operators can be trained quickly to use the instrument to obtain good quality data. Care needs to be taken to maintain the equipment by cleaning the calibration caps and recharging the batteries daily. The handheld-infrared instrument is suitable for use in site assessment and delineation, site excavation, and monitoring the progress of soil treatment. After a year and half of usage, PT. CPI is continuously looking for improvement in accessory equipment and logistical methods to increase the effectiveness of the field handheld-IR instrument.

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REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA publication SW-846, Third Edition, Final Updates I (1993), II (1995), IIA (1994), IIB (1995), III (1997), IIIA (1999), IIIB (2005), IV (2008), and V (2015).

Expedited Site Assessment Tools for Underground Storage Tank Sites, A Guide for Regulators, Chapter VI

Field Methods for The Analysis of Petroleum Hydrocarbons; EPA 510-B-16-004, October 1997.

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil, Demonstration Plan, EPA/600/R-01/060, June 2000

Measurement Technologies for Total Petroleum Hydrocarbons in Soil, Wilks Enterprise, InfraCal TOG/TPH Analyzer, EPA/600/R-01/088, September 2001.

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil, Horiba Instruments Incorporated OCMA-350 Oil Content Analyzer, EPA/600/R-01/089, September 2001.

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil, Chemetrix, RemediAid, EPA/600/R-01/0**88**, September 2001.

Field Measurement Technologies for Total Petroleum Hydrocarbons in Soil, PetroFlag, EPA/600/R-01/088, September 2001.

S. T. Forrester, L. Janik, M. McLaughlin, J. Soriano-Disla, R. Stewart, B. Dearman, Total petroleum hydrocarbon concentration prediction in soils using diffuse reflectance infrared spectroscopy Soil Sci. Soc. Am. J. 77, (2013): 450-460.

G. Webster, J. Sorian-Disla, J. Kirk, L. Janik, S. Forester, M. McLaughlin, R. Stewart, Rapid prediction of total petroleum hydrocarbons in soil using a hand-held mid-infrared field instrument Talanta, 160, (2016): 410-416.

Office of Hazard Evaluation and Emergency Response, Department of Health, Technical Guidance Manual for the implementation of the Hawaii State Contingency Plan Section 8.0 Field Screening Methods. November 12, 2009, accessed January 12, 2017.

http://www.hawaiidoh.com/TGM.aspx?p=0804a.aspx

Turbidimetric Screening Method for Total Recoverable Petroleum Hydrocarbons in Soil. EPA

Method 9074. February 2007, accessed Jan. 12, 2017.)	https://www.epa.gov/sites/production/files/2015-12/documents/9074.pdf

TABLE 1

COST SAVINGS GENERATED FOR NUMBER OF SAMPLES PER MONTH

No of Sample/Month	Cost Saving (US$)
500	6,480
1,000	26,480
1,500	46,480
2,000	66,480
2,500	86,480
3,000	106,480
3,500	126,480
4,000	146,480
4,500	166,480
5,000	186,480

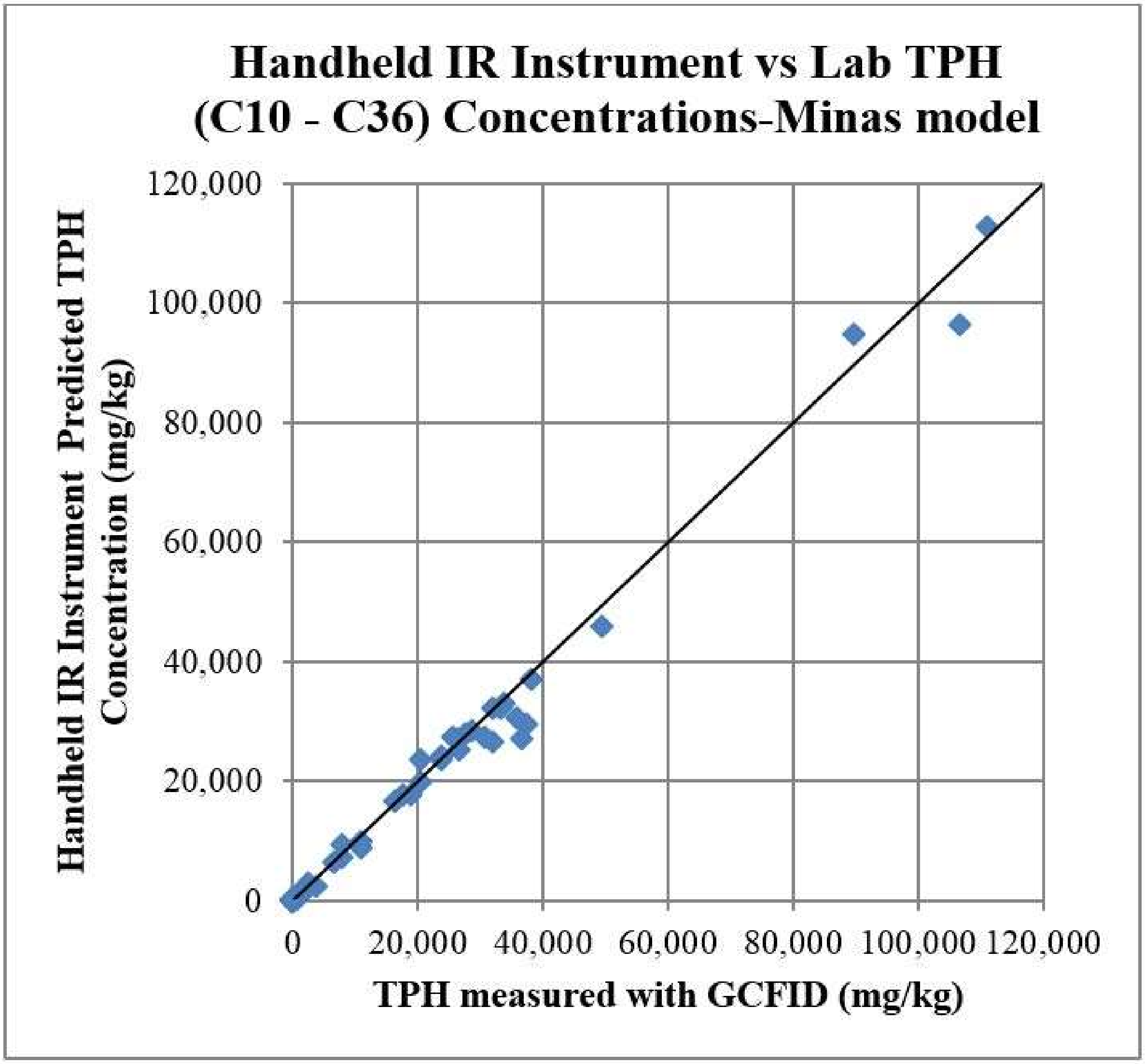

Figure 1 - Handheld IR Instrument predictions versus laboratory data for TPH C_{10} - C_{36} for calibration samples over the full TPH concentration range of 0-120,000 mg/kg of 111 soil samples from the Minas.

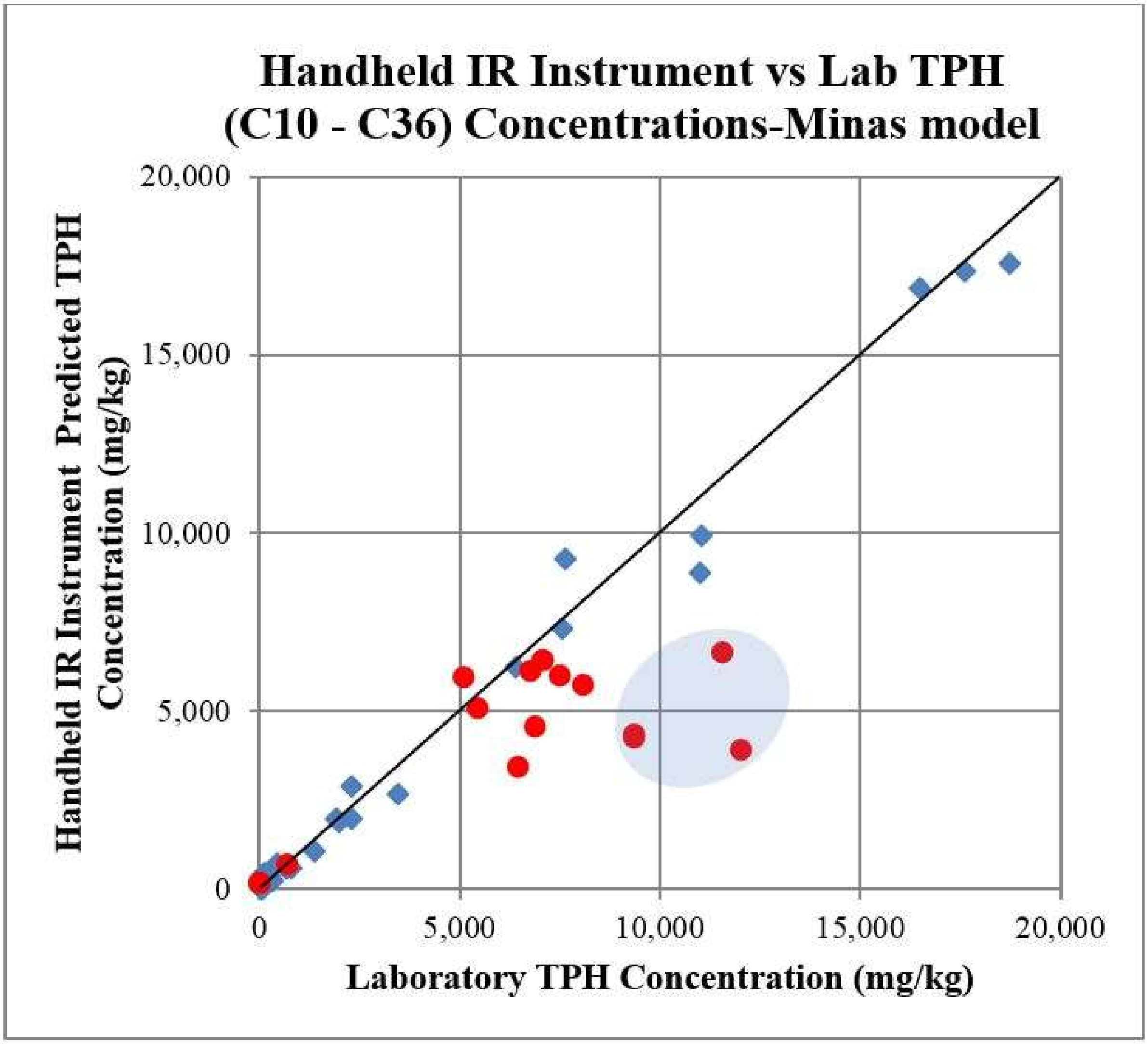

Figure 2 - Handheld IR Instrument predictions using Minas calibration model vs. GCFID data validation Samples (•) & Calibration Samples (◆) over the TPH concentration range of 0-20,000 mg/kg.

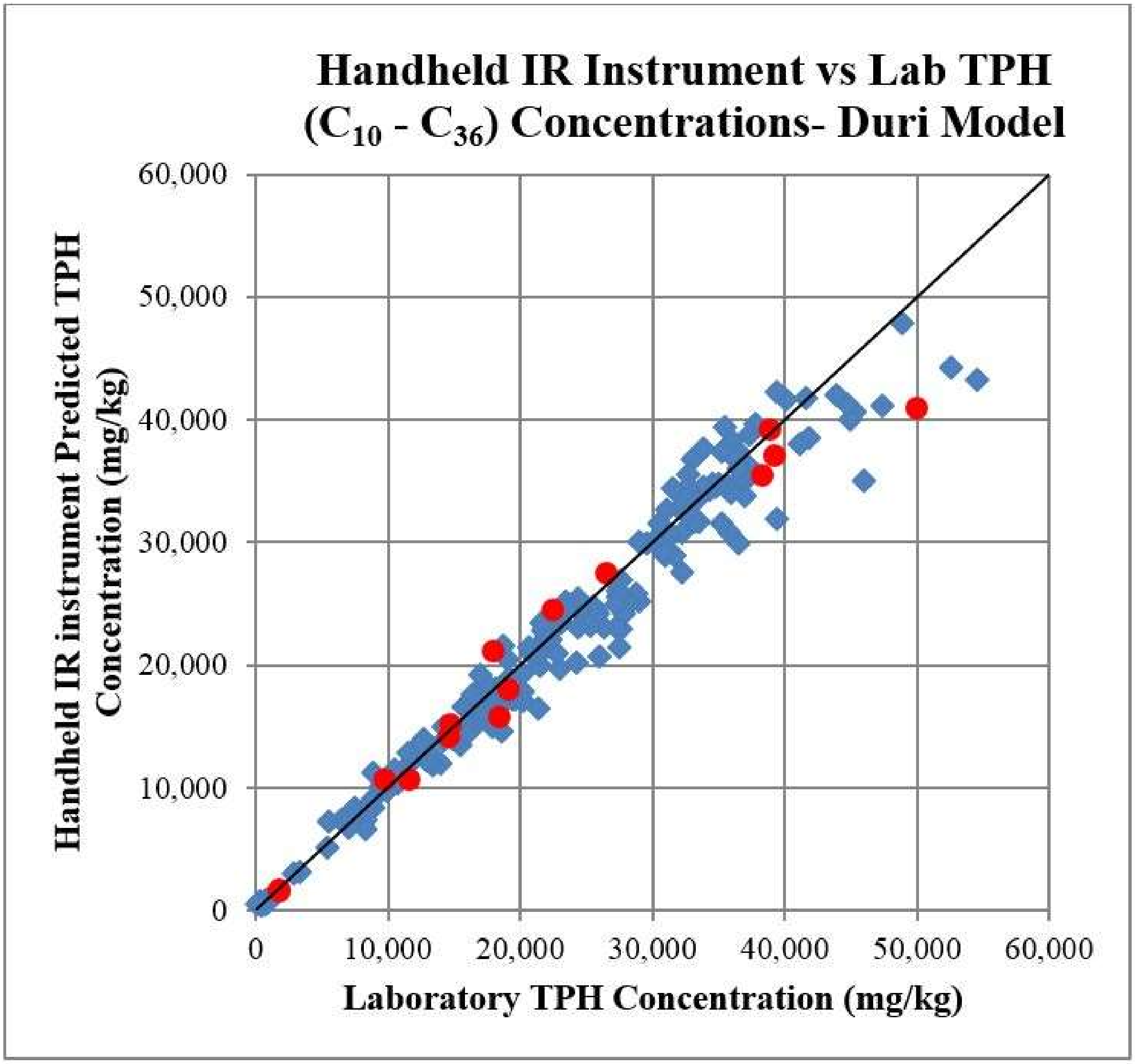

Figure 3 - Handheld infrared instrument predictions using the Duri calibration model vs. GCFID Data Validation Samples (•) & Calibration Samples (◆) over the TPH concentration range of 0-60,000 mg/kg.

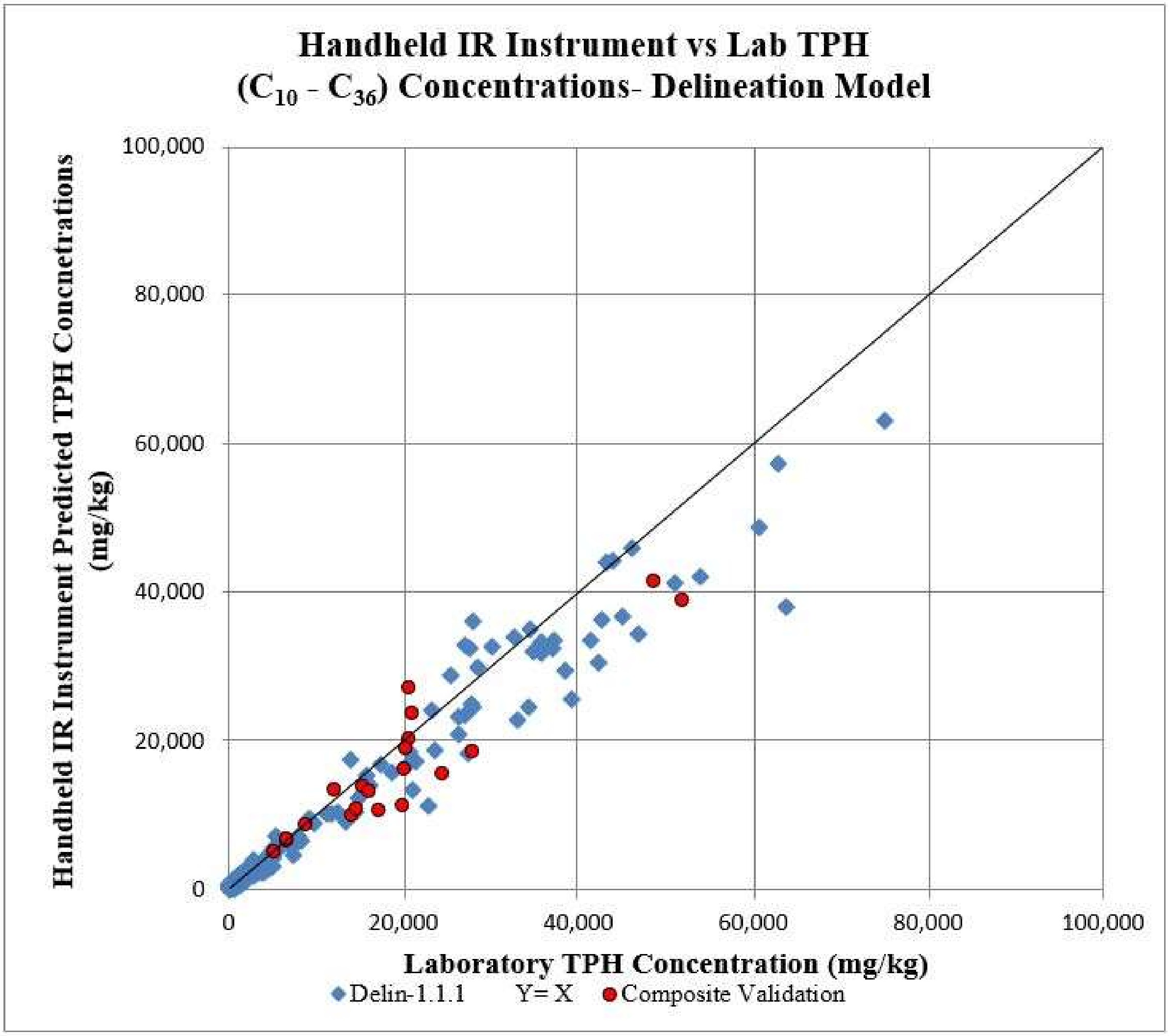

Figure 4 - Handheld infrared instrument predictions using the delineation calibration model vs. GCFID Data. Validation Samples (•) & Calibration Samples (◆) over the TPH concentration range of 0-80,000 mg/kg.

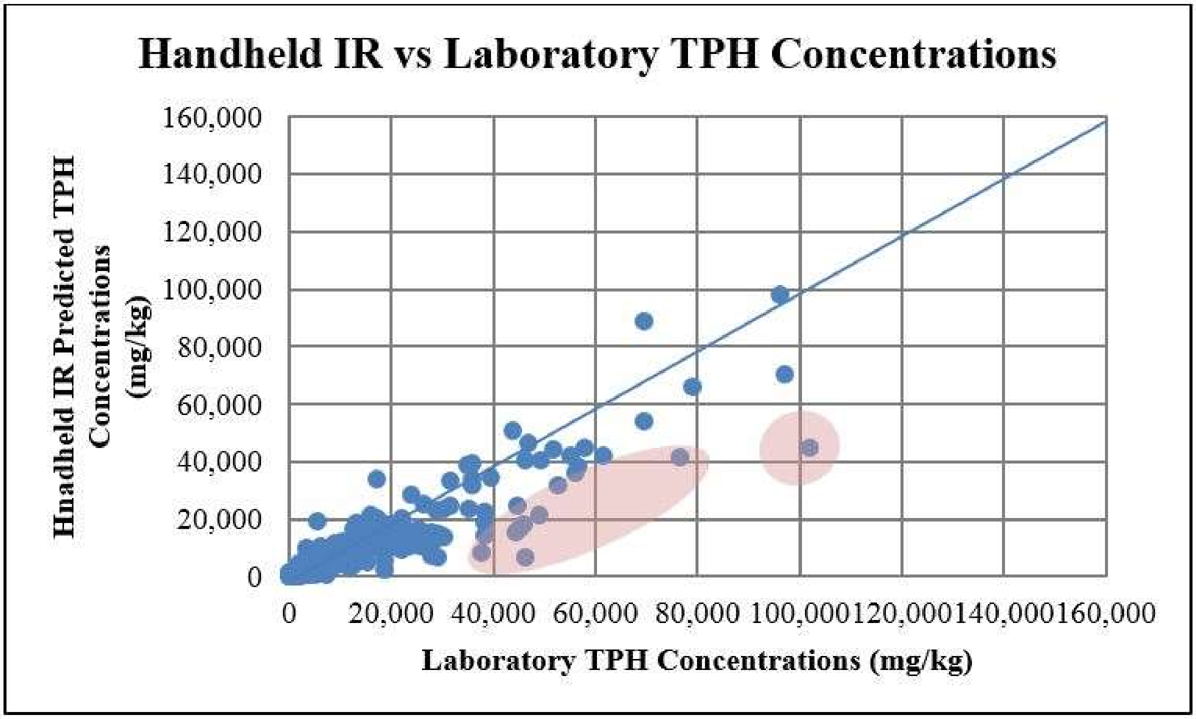

Figure 5 - Field deployment monthly monitoring results through October 2017.

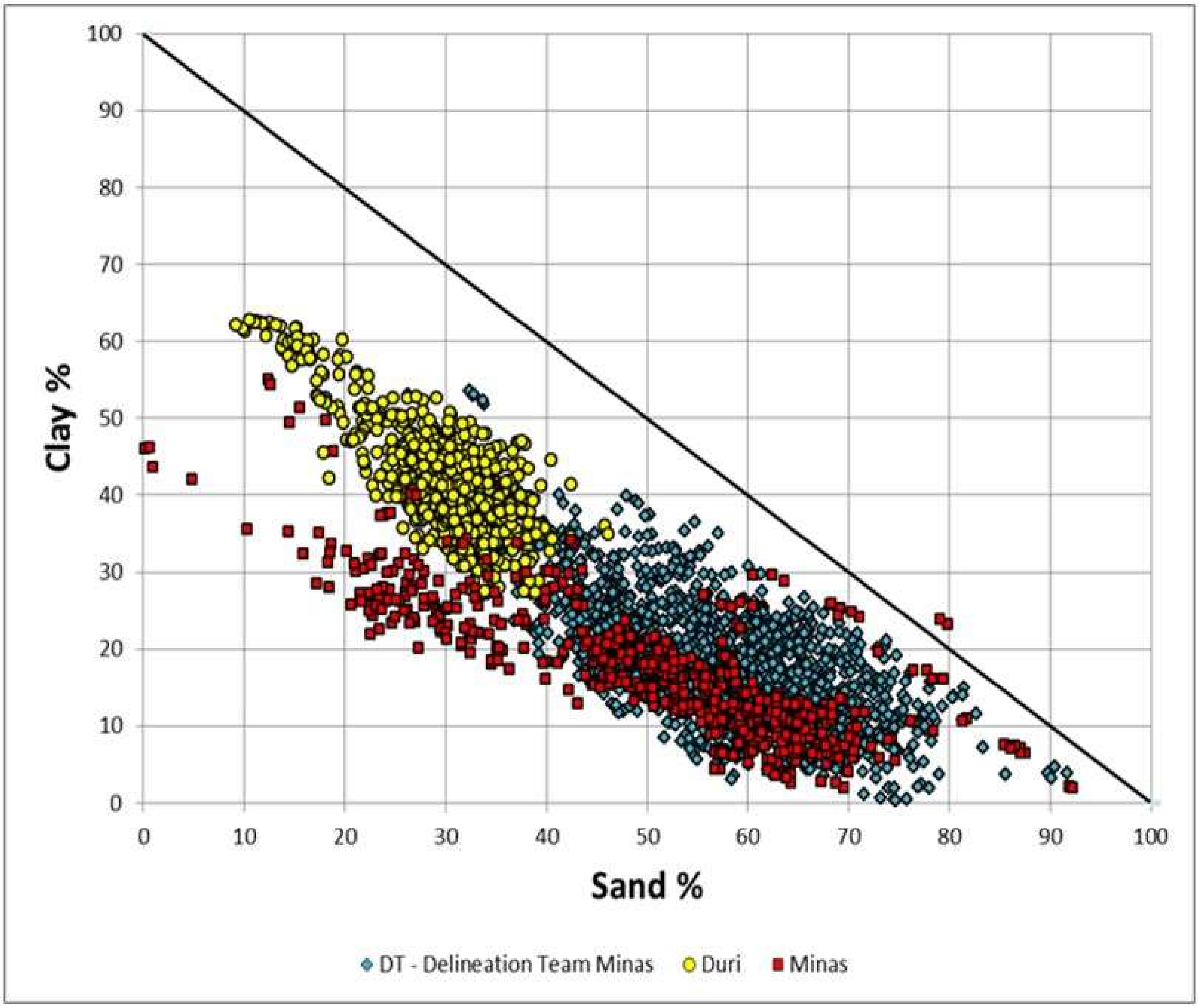

Figure 6 - Comparison of soil types in samples used in the three models from the Minas, Duri and Minas Delineation pilots (red squares- Minas Model, Yellow dots- Duri Model, blue rhombus- Minas Delineation model).

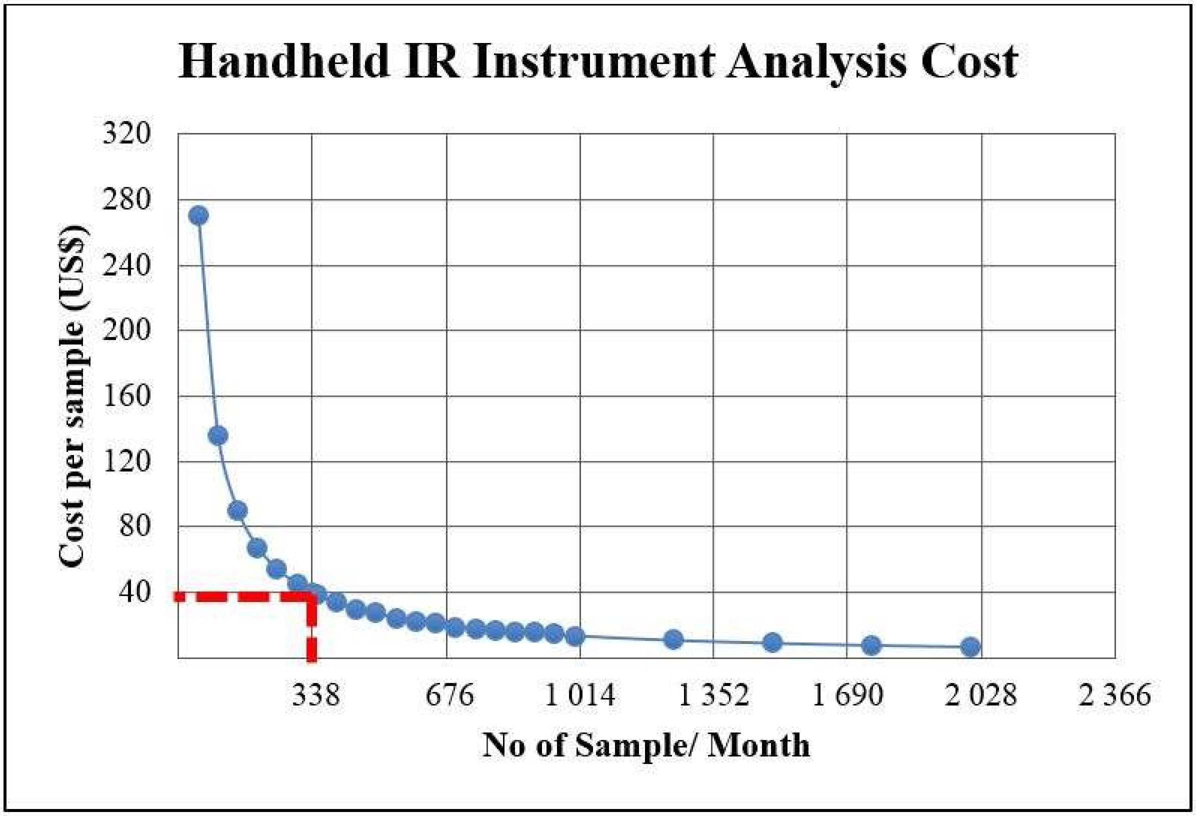

Figure 7 - Cost analysis per sample vs number of samples per month.

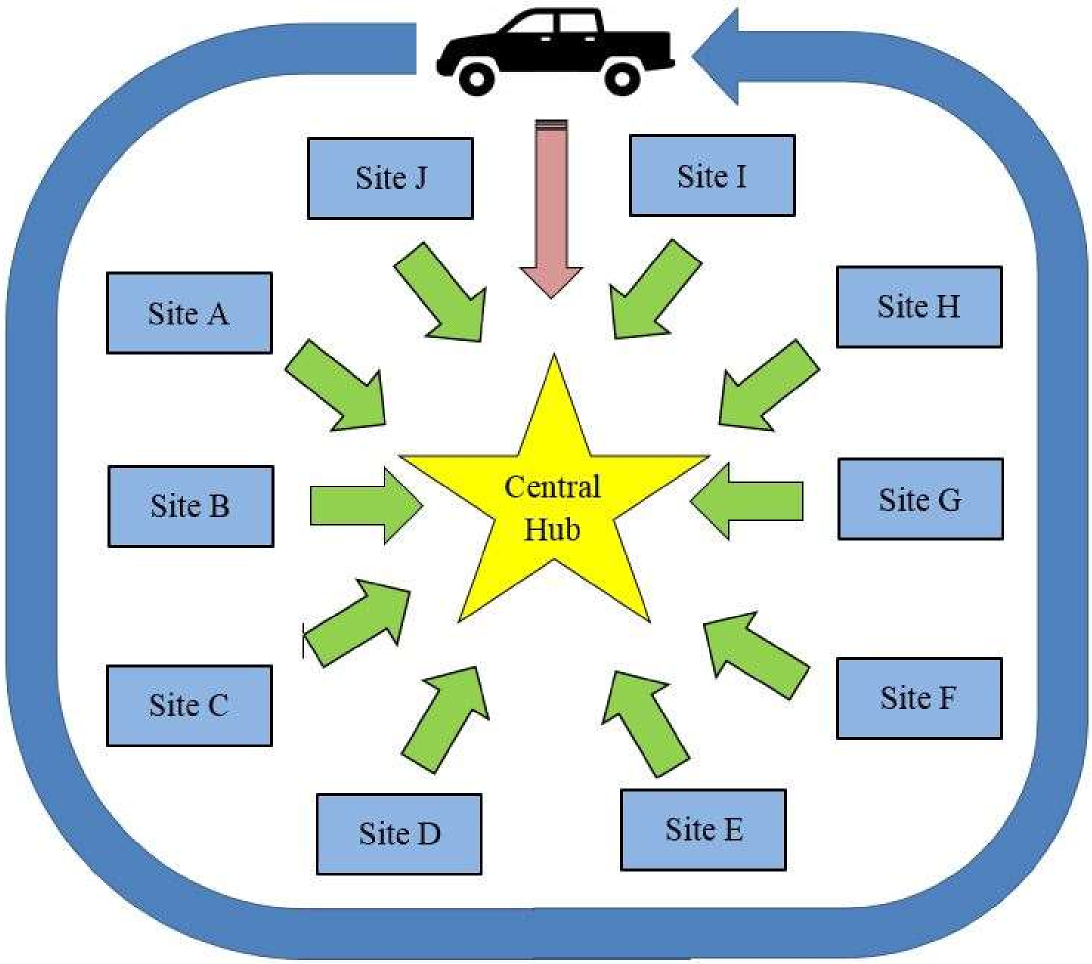

Figure 8 - System/model utilizing a centralized hub to serve multiple areas.