# CHARACTERIZATION OF HEAVY HYDROCARBON CONTAMINATED SOILS REMEDIATED BY THERMAL METHODS

A Thesis

by

MARCO CONCEPCION MARTINEZ

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| Chair of Committee, | Andrea Strzelec |
| Committee Members, | David Staack<br>Carmen Gomes |
| Head of Department, | Andreas Polycarpou |

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# ABSTRACT

There are numerous opportunities in the lifecycle of oil extraction, transport, and use where it can potentially contaminate the environment, in particular water and soil. Various technologies have been developed to remediate soil contamination; the techniques can be categorized as either energetic, where energy is required for treatment, or non-energetic, requiring no additional energy input. Previous studies have determined that energetic methods tend to be more effective at reducing total petroleum hydrocarbons (TPH). In particular, thermal desorption was found to remove hydrocarbons in the target molecular size range of hydrocarbon species up to $C_{40}$, while leaving beneficial carbon content, such as soil organics, intact. The goal of this study was the characterization of soil treated with energetic remediation methods. Specifically, soils treated by indirect thermal desorption (inert environment) or directly heated thermal desorption (heated by products of combustion, including oxygen) were characterized to determine their efficacy and investigate the underlying mechanisms. Temperature programmed reaction experiments (including oxidation and desorption) were used to measure the relative amounts of total, mobile, and fixed carbon content remaining on the treated soil. For the indirect thermal desorption, total carbon content was found to reduce proportionately with decreases in initial oil concentration and only marginally with increases in either treatment temperature or residence time. The minimum time and temperature values (15 minutes and 370°C, respectively) were found to adequately reduce total carbon and, by extension, TPH. Further increases in residence time or treatment temperature would increase treatment costs for insubstantial gains. Increased temperature and decreased oil concentration both decreased total carbon for the direct heated thermal desorption treatment. In contrast to the indirect treatment, total carbon reduction in the direct treatment appeared to be a stronger function of temperature, with total carbon content for the maximum temperature being a quarter of that at the minimum. Initial oil concentration appeared to be normalized to some extent by the direct treatment, with respective carbon content levels approaching each other. It was again determined that the minimum energy input treatments characterized herein would sufficiently reduce TPH.

For a 15 minute residence time and 420°C treatment temperature, the indirect treatment was found to have produced a larger carbon content reduction than the direct treatment. The Boudouard reaction is a proposed explanation for this result on the basis of entrance and exit gas flow compositions, as well as the increased fixed carbon found on the direct treated soil.

# CONTRIBUTORS AND FUNDING SOURCES

## Contributors

This work was supported by a thesis committee consisting of Professor Andrea Strzelec and Professor David Staack of the Department of Mechanical Engineering and Professor Carmen Gomes of the Department of Biological and Agricultural Engineering.

Suitable soil was sourced by Prof. Jake Mowrer and Prof. Tony Provin in the Soil Sciences Department. Artificial impaction of the soil was performed with the assistance of Prof. Staack, John LaSalle, and other members of the Plasma Engineering and Diagnostics Laboratory. Remediation was performed in a vessel provided by Hazen Research out of Golden Colorado. Technical and administrative consultation was provided by Dr. Paul Bireta and Dr. Gabriel Sabadell of Chevron Engineering Technology Company.

All other work conducted for the thesis was completed by the student independently.

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# 1. INTRODUCTION AND LITERATURE REVIEW

Applications for hydrocarbons are ubiquitous; used for everything from fuel for heating and transportation, to the base for paint and lipstick. Unfortunately, with widespread use comes a plethora of opportunities for it to interact with the environment. The opportunity for unintentional interaction of petroleum products typically happens at three points during the life cycle: extraction, transport to refinery, and regional distribution. [1] Major spills have typically been associated with the first two of these stages and produce both immediate consequences as well as damages whose effects are distributed over time. Spills, like in the Exxon Valdez case, where the hull of a tanker was torn releasing millions of gallons of oil [2]; leaks out of containment vessels [3]; and even general handling can all result in oil and its byproducts coming into contact with soil. [4] Subsequent contamination of soil and groundwater leads to diminished living conditions of the plants, animals, and humans that live in the area. [5-7] Just as the effects of these spills can persist over time, they are not isolated to the location where the spill occurred. Due to fluid mobility, which varies largely according to the specific hydrocarbon species in a given sample, this fuel/oil can spread out and sink deeper due to diffusive and gravitational effects. [8-10]

Hydrocarbon contamination has a number of negative consequences on the soil that affect its ability to support both the present and future flora and fauna in its ecosystem. Plants present at the time of contamination absorb oil through their root system, where it then travels through intercellular spaces as well as through the vascular system. These plants consequently suffer reduced rates of photosynthesis due to the oils absorbing light that would have otherwise reached the plant. Oils can also interfere with plant respiration by blocking cellular structures critical to plant respiration. [11] Contaminated soils have also been found to have lower pH values implying a higher soil acidity. [8] These factors can result in unfavorable conditions for future plant growth due to a decrease in critical nutrients. The dispersion of the hydrocarbons can also lead to leakage into the groundwater near the original spill site, contributing to various adverse health conditions associated with ingestion of a toxic substance for the humans and animals that depend on that water supply. [12]

Regulatory entities around the world have set forth various standards and guidelines requiring responsible parties to take action towards rectifying any harm to the environment they might have imposed due to soil and water contamination. One category of contamination that is frequently addressed consists of various hydrocarbon species associated with industrial production, operation, and waste. [13-15] Environmental contamination due to hydrocarbon contamination is quantified by a measure known as Total Petroleum Hydrocarbons (TPH). This value represents the mass of all hydrocarbon species with carbon numbers smaller than $C_{40}$ in a sample. That mass is then normalized by sample mass and is typically shown as a ratio of hydrocarbon mass to sample mass (mg/kg, ppm, or %). Regulatory standards vary by region but a typical upper limit of acceptable TPH is 1%. [16]

In an effort to reduce contaminant hydrocarbons to acceptable levels, several remediation methods are being utilized and they can generally be divided into two categories: non-energetic and energetic methods. Non-energetic methods include the use of dispersants, bio-remediation, land-farming, and soil vapor extraction in an effort to decontaminate without the need for energy addition. [17-19] Despite their numerous benefits, these non-energetic methods have not proven to be as effective at eliminating heavier hydrocarbons as their energetic counterparts. [20-22] Land-farming, for example, offers a low cost remediation method with relatively simple implementation. In this method, contaminated soil is spread out over a large area where the resulting aeration, in conjunction with added minerals, nutrients, and moisture all contribute to enhanced microbial activity. In addition to this increased exposed surface area encouraging evaporation of gasoline range organics ($C_6$-$C_{10}$ hydrocarbons), the microbial activity degrades diesel range organics ($C_{10}$-$C_{28}$ hydrocarbons). [21] As mentioned earlier, non-energetic methods such as land-farming have difficulty eliminating heavier hydrocarbons. In this case, the upper end of TPH range hydrocarbons are unavailable for elimination by land-farming and TPH amounting to 5% of soil mass proves challenging to the technique all together. Land-farming also requires a significant area of land for large scale treatment and treatments can last up to two years. [23]

Previous work in our lab has included the characterization of incineration, indirect-like thermal desorption, pyrolysis and electron beam remediation methods. [24, 25] For purposes of this analysis, contaminated soil can be modeled as consisting of three parts: mobile carbon, fixed carbon, and the soil matrix as seen in Figure 1. Mobile carbon content represents the volatile fraction of hydrocarbons while fixed carbon content consists of extra heavy hydrocarbons, and solid carbon char, as well as native soil organics.

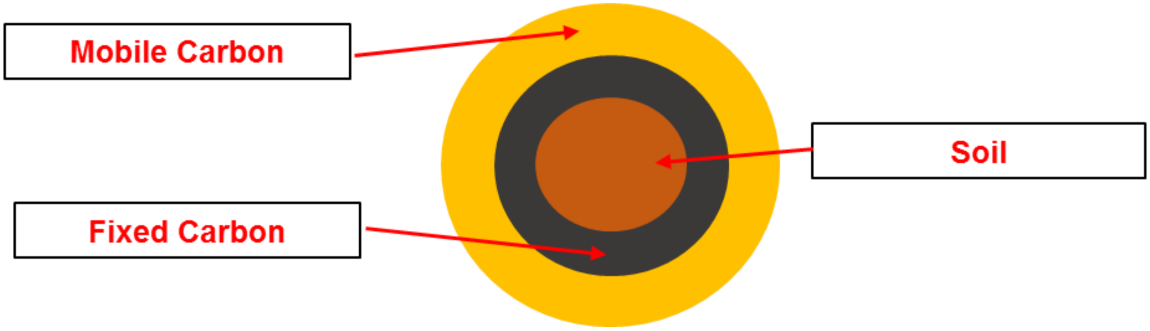

*Figure 1: Soil Model [24]*

While reduction of contaminant hydrocarbons is the goal, carbon content native to the soil and carbon char is beneficial and necessary for sustaining microbial and plant life.[26] Incineration completely eliminates not only all hydrocarbons, but any and all carbon content from the soil. Thermal desorption was found to eliminate the second most carbon content, removing the majority of the TPH range hydrocarbons, but leaving behind very heavy, waxy hydrocarbons that are a low mobility risk, as well as fixed carbon and native soil organics. [24]

The promising results from the thermal desorption work motivated further investigation into the method and how it is implemented in an industrial setting, which is the main focus of this work. Research into thermal desorption as a remediation technology for soils has been going on for decades, with studies being performed that investigate the effects of various parameters. [27-30] However, as revealed previously, not only do treatment parameters like temperature and residence time affect the results of the treatment, but even characteristics such as the physical structure of the soil can alter how a thermal desorption unit performs. For instance, a larger surface area on the soil matrix reduces onset temperature, or the temperature at which desorption begins. Porosity in the matrix, however, was found to negate that trend. [31] Time of exposure to the contaminant source has also been found to play a role in the necessary requirements for sufficiently reducing contamination. Resistance to desorption was proposed to have increased with a longer exposure time as a result of migration and more extensive adsorption. [27] These findings emphasize the idea that remediation necessitates a case specific approach. A site with a specific combination of contaminant history and soil characteristics such as that which this work aims to address, therefore, requires evaluation of relevant treatment parameters as they would apply to that site.

In industrial applications, a thermal desorption unit (TDU) can be heated either directly or indirectly. [32] Direct thermal desorption units are devices that primarily rely on convective heat transfer between the exhaust of a burner and the contaminated soil to volatilize contaminant hydrocarbons. Figure 2 shows a cutaway of a direct TDU, where a flame introduced on the left side of the containment vessel is the heat source for the device. Soil is fed into the machine which rotates to agitate the soil, helping to ensure a homogeneous treatment.

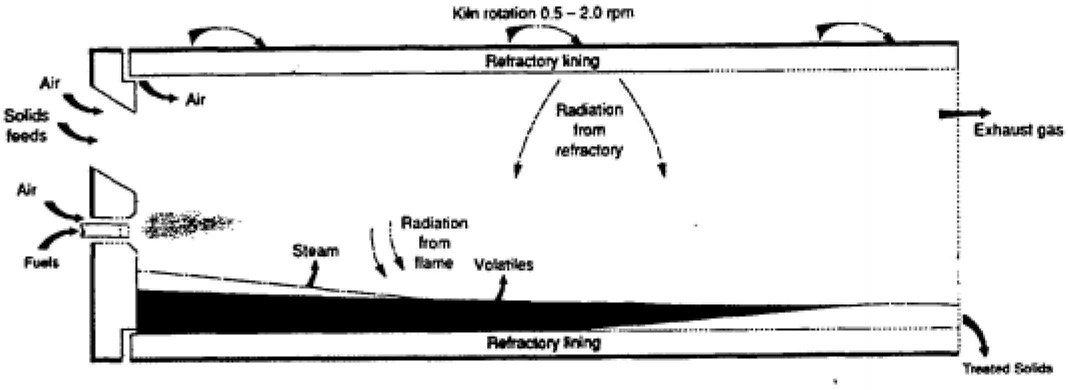

*Figure 2: Cutaway of a Direct-Heated Cocurrent Thermal Desorption Unit [33]*

In contrast, indirect thermal desorption units rely on conductive heat transfer between the soil containment vessel and the contents. Heat is supplied, either electrically or again by burners, to the containment vessel rather than directly to the soil. The configuration shown in Figure 3 utilizes a burner to supply heat to the outer shell of the containment vessel.

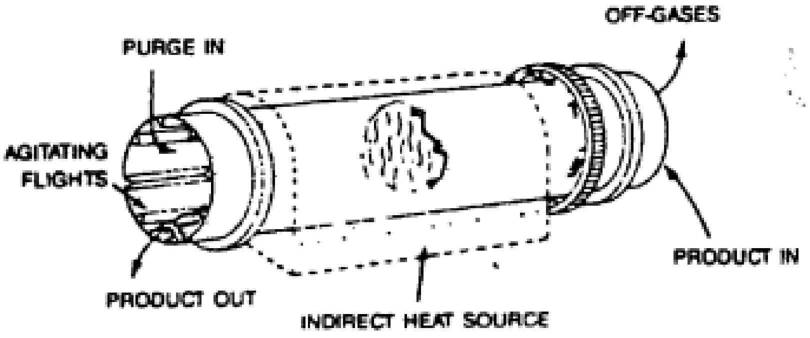

*Figure 3: Indirect-Heated Countercurrent Thermal Desorption Unit [29]*

As a result of these two variations and the differing physical and chemical changes produced in contaminated soil, treatment environment (i.e. products of combustion vs inert gas) became one parameter for investigation. Thermal desorption operates by physically separating contaminants from the soil matrix through vaporization of hydrocarbons. Different hydrocarbon species vaporize at different temperatures so it is clear that temperature should be an important factor in the effectiveness of this remediation treatment. As a result, temperature was an additional parameter under investigation. In order to determine whether time would be a limiting factor regarding effective heat transfer, or phase change completion the effect of treatment time was also studied. Finally, with impaction occurring at different rates at real contamination sites due to some areas being more prone to contamination, the effect that oil concentration in the impacted soil has on treatment results was also investigated. With relationships developed for treatment efficacy as a function of residence time, treatment temperature, extent of oil impaction, and flow-through gas composition, subsequent analysis can be used to determine optimum treatment parameters.

# 2. EXPERIMENTAL METHODS

## 2.1 Experimental Setup

### 2.1.1 Microreactor

Characterization was performed in a fixed-bed flow-through microreactor developed in the Combustion and Reaction Characterization Laboratory. This microreactor (shown in Figure 4) consists of two 0.5 inch diameter quartz u-shaped tubes (reactor 1 and reactor 2) each held in its own cylindrical ceramic radiant furnace, controlled by PID controllers whose feedback comes from a thermocouple placed alongside each reactor tube. A second thermocouple is embedded in the sample in reactor 1 to directly track sample temperature. This second, sample thermocouple is the source of all temperature data presented here. The system is fed by a bank of mass flow controllers (MKS instruments, Inc. Andover, MA) which are supplied by compressed gas bottles (Praxair). The gases are introduced into the reactor system by a gas manifold designed to combine the gases into a single mixed stream. Additionally, there are auxiliary inputs that lead directly to either of the two reactors. The effluent gases are analyzed by a Hiden quadrupole mass spectrometer that measures the partial pressures of pre-selected gases. The system described herein provides the flexibility to perform a wide variety of experiments in a single device, such as temperature programmed oxidation/desorption, BET specific surface area measurement, chemisorption, and kinetic parameter determination.

*Figure 4: Microreactor*

Sample sizes of approximately 300 mg are typically analyzed. Soil samples are placed on top of a plug of quartz wool in reactor 1. Samples are then mixed with approximately 1 gram of 600 µm diameter Y-$ZrO_2$ beads added to the sample for thermal stability and to minimize heat transfer effects. A second quartz wool plug is placed above the sample to prevent any backflow that may occur. A typical loaded sample is shown in Figure 5. Reactor 2 contains a Pt/$Al_2O_3$ oxidation catalyst to ensure that all hydrocarbons and CO reach the mass spectrometer in the form of $CO_2$.

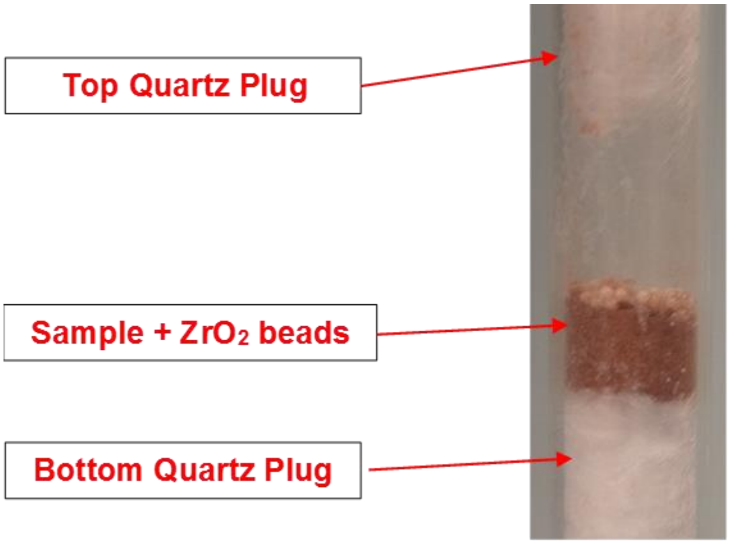

*Figure 5: Loaded Sample*

### 2.1.2 Calibration of Mass Spectrometer

The mass spectrometer is a Hiden QGA, calibrated for $CO_2$ concentration bi-monthly. In order to correlate the partial pressure measured by the mass spectrometer to the concentration of $CO_2$ in the gas stream, concentrations of 1.5%, 1.0%, 0.75%, 0.50%, 0.25%, 0.125% and 0.1% $CO_2$ in argon at 175 sccm are sent directly to the mass spectrometer and the corresponding partial pressures are recorded.

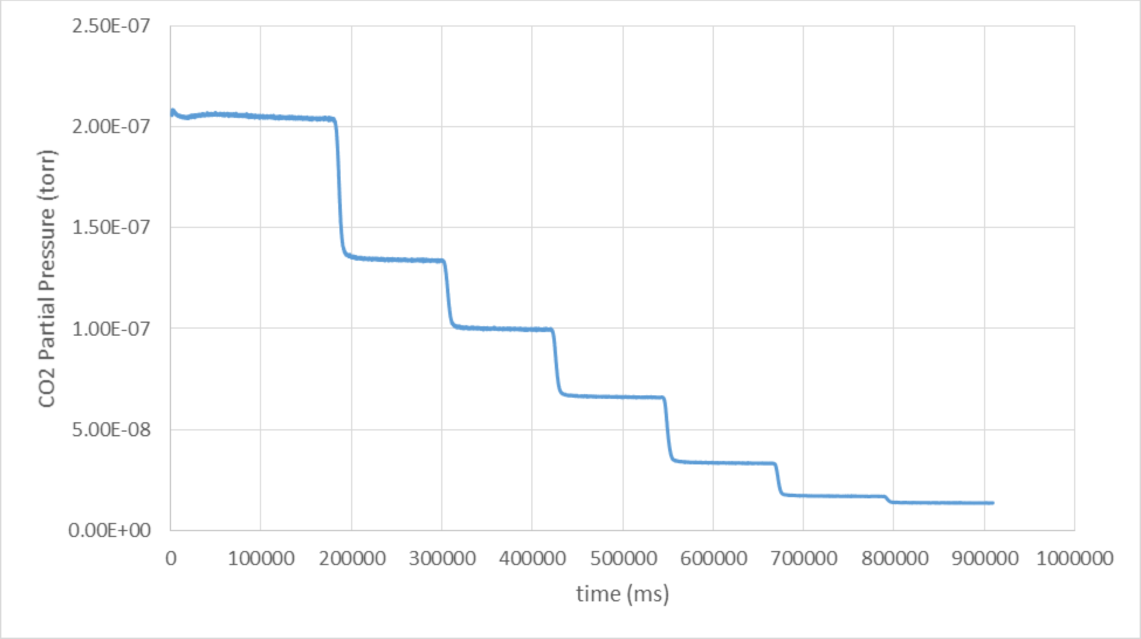

*Figure 6: CO2 Partial Pressure Data Collected by Mass Spectrometer*

Shown in Figure 6 is the $CO_2$ partial pressure as measured during a $CO_2$ calibration, where each step represents a single $CO_2$ concentration. These are used in conjunction with the corresponding argon partial pressures to produce a trendline for $CO_2$ concentration as a function of partial pressure, shown in Figure 7. This function can then be used to interpret measurements made by the mass spectrometer throughout subsequent experiments.

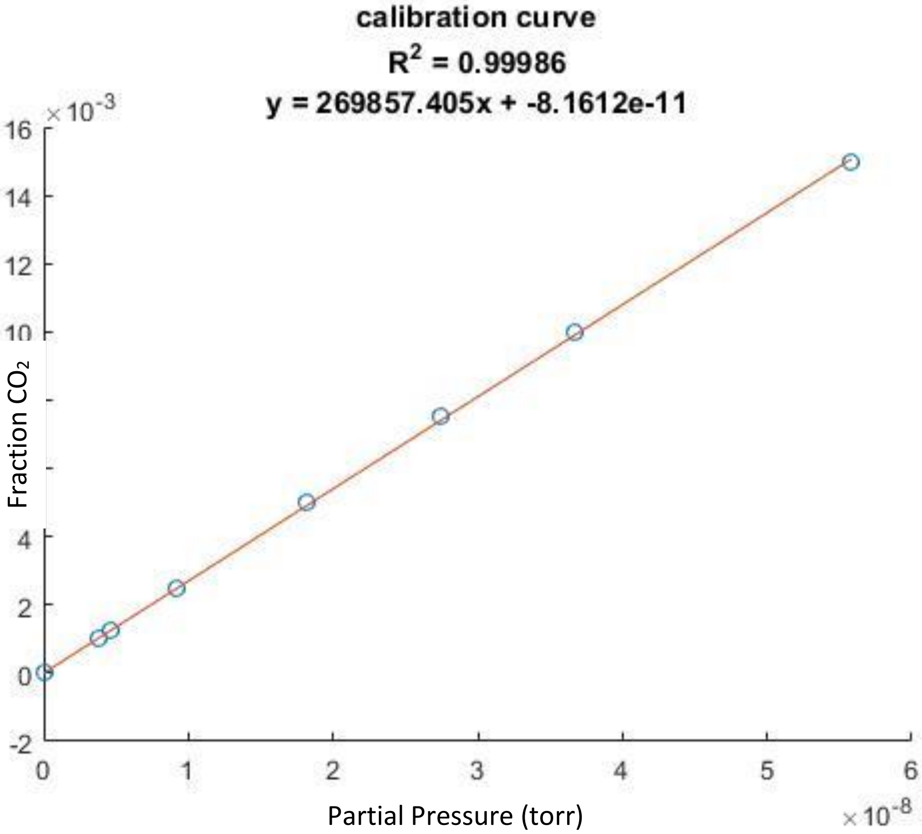

*Figure 7: CO2 Calibration Curve Example (Concentration vs Partial Pressure [torr])*

### 2.1.3 Thermal Desorption Unit

A commercial vessel provided by Hazen Research (Golden, CO) was utilized for pilot scale thermal desorption treatment of contaminated soil, a schematic for which is shown in Figure 8. Soil is fed through a hopper into a variable speed screw feeder. The screw feeder, driven by an off-board motor, conveys the soil through a rotary kiln, from right (feed end) to left (product end), at rates that ensure desired residence times. Following an 80” heated section inside the kiln, and a 30” cooling zone just after the product end of the kiln, the soil is deposited into a canister and is periodically collected. A counter-current gas stream also flows through the heated section, composed of a gas mixture corresponding to desired treatment conditions. When the counter-current gas flow reaches the feed end of the kiln, it passes through a cyclone that collects solid particles suspended in the exhaust stream. The flow then passes through two consecutive tube-and-shell condensers. The first condenser operates at approximately 150°C and primarily collects the hydrocarbon components of the exhaust stream. The second condenser operates at approximately 3°C and collects water and highly volatile hydrocarbon species that had not previously condensed out. Finally, the exhaust stream is sent to a gas flare to ensure that any remaining hydrocarbons are eliminated through combustion. The rotary kiln is positioned at an incline of 2.68° (rise of 2.25” every 4’) to improve soil mobility. The kiln is electrically heated in four independently monitored and controlled zones (see digital readouts in Figure 9 and Figure 10).

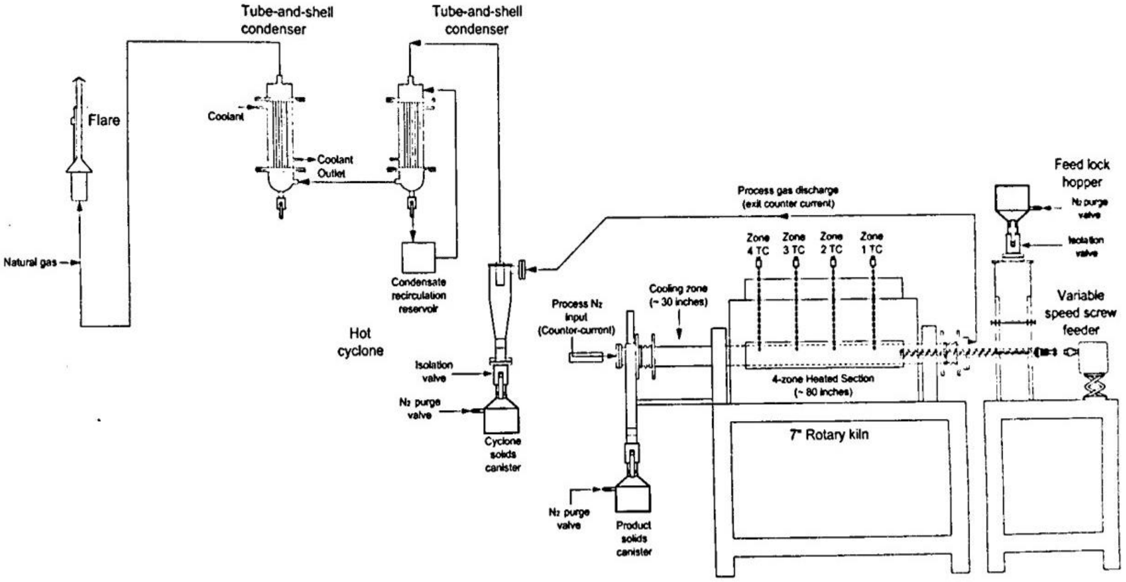

*Figure 8: Hazen Thermal Desorption Unit – Schematic (Courtesy of Hazen)*

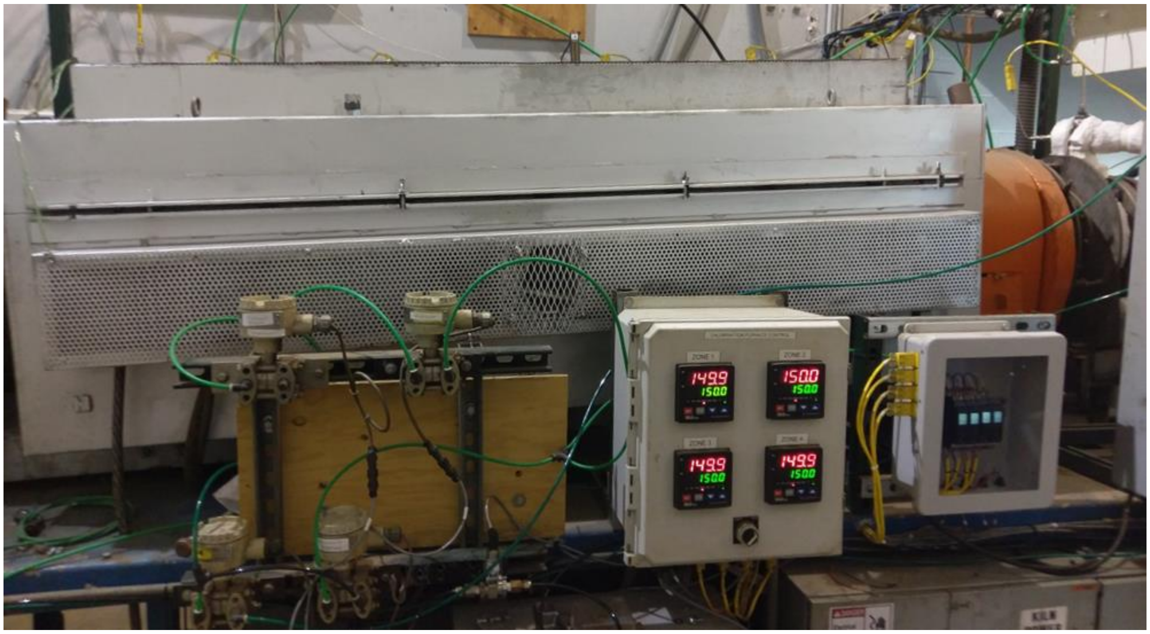

*Figure 9: Hazen Thermal Desorption Unity - Rotary Kiln*

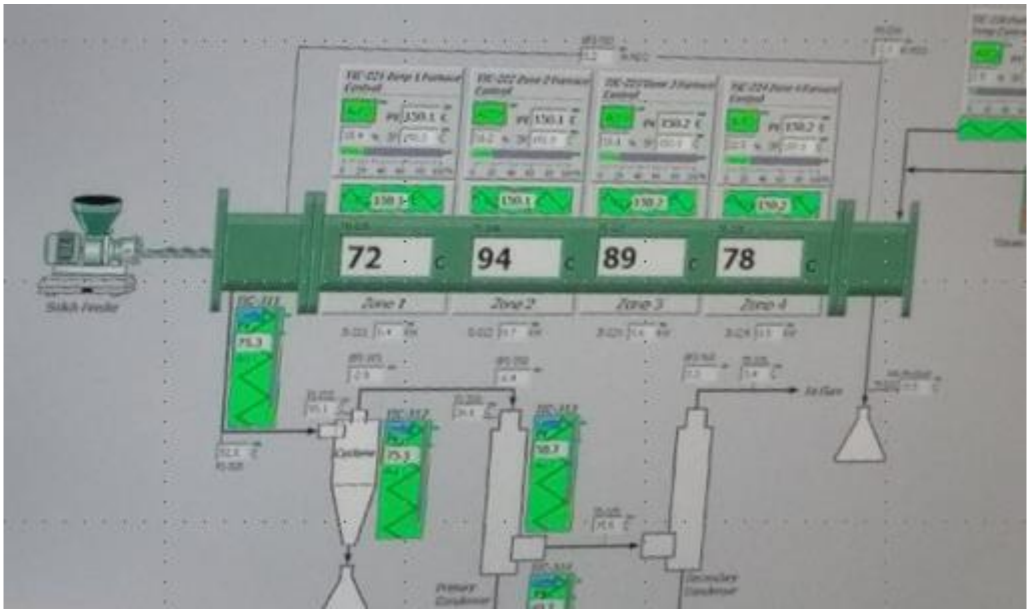

*Figure 10: Hazen Thermal Desorption Unit - Temperature Data Acquisition Module*

## 2.2 Characterization Methods

Three experiments are performed in the microreactor to study the types of carbon content used for characterization. It is important to note that each of these experiments investigates a different type of carbon. The mass spectrometer then measures the carbon evolution during each experiment which in turn provides information regarding what remained on the sample after treatment.

### 2.2.1 Temperature Programmed Oxidation (TPO)

Temperature Programmed Oxidation (TPO) quantifies the total amount of carbon present on a sample. A mixture of 10% oxygen in argon is flowed at 175 sccm through the sample as its temperature is ramped at a rate of 5°C per minute up from ambient conditions to 710°C, followed by a 15 minute hold at 710°C and then is allowed to cool, uncontrolled, down to ambient. A diagram of the flow path for a TPO experiment can be seen in Figure 11 below.

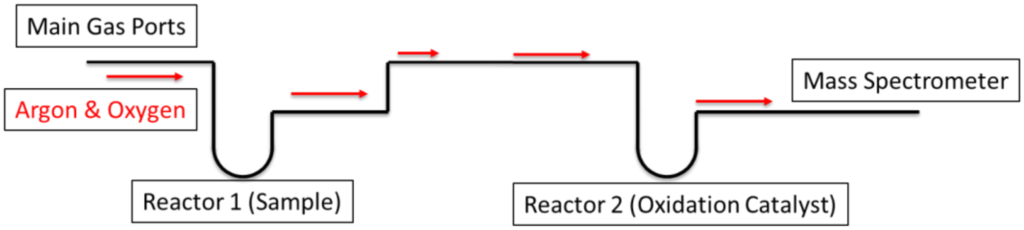

*Figure 11: TPO Flow Diagram [24]*

### 2.2.2 Temperature Programmed Desorption (TPD)

The Temperature Programmed Desorption (TPD) experiment measures the mobile carbon fraction of a sample by flowing pure argon at 175 sccm through reactor 1. Supplementary oxygen is then supplied to reactor 2 via an auxiliary port at 175 sccm as well to ensure that all carbon containing species (hydrocarbons and CO) in the gas stream are completely oxidized to $CO_2$ for measurement by the mass spectrometer. The effect of this combination is that the sample is heated in an inert environment and volatilizes only those hydrocarbon species whose boiling point is below the temperature achieved by the temperature ramp. The sample temperature is ramped at a rate of 5°C per minute up from ambient conditions to 710°C, followed by a 15 minute hold at 710°C and then is allowed to cool, uncontrolled, down to ambient. Shown in Figure 12 is a diagram of the flow path for TPD.

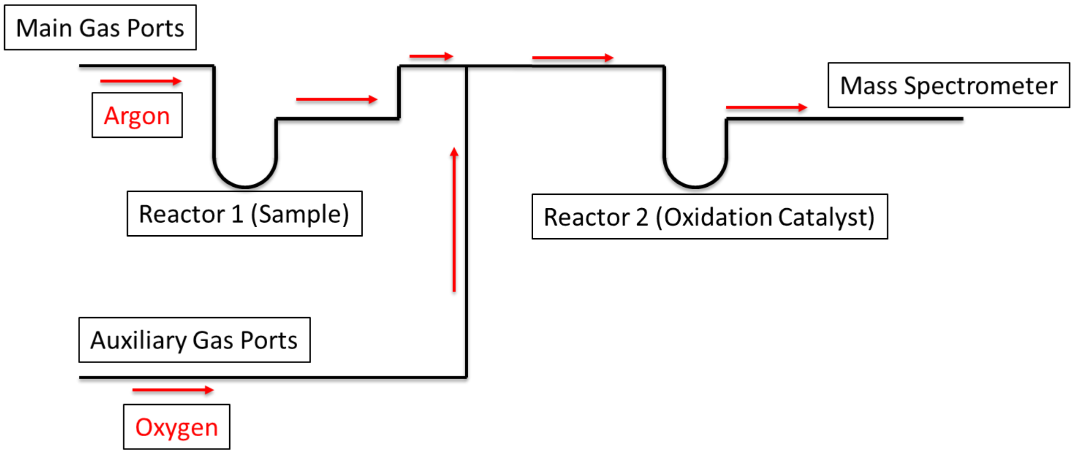

*Figure 12: TPD Flow Diagram [24]*

### 2.2.3 Temperature Programmed Oxidation – Devolatilized Sample (TPO Devol)

Temperature Programmed Oxidation performed on a Devolatilized sample (TPO Devol). A TPO Devol is identical to a TPO in procedure (as can be seen by comparing Figure 13 to Figure 11) with the exception that this is performed specifically on samples that have already been devolatilized (i.e. that have undergone a TPD). Because oxidation removes all carbon on a sample, oxidation performed on a sample that has already been devolatilized will yield the fixed and low mobility carbon content.

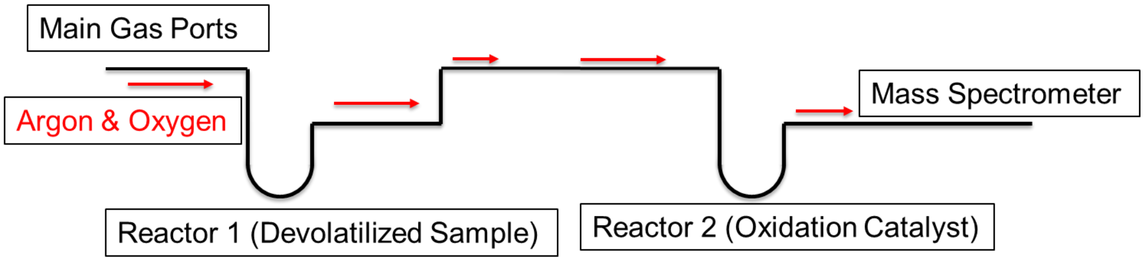

*Figure 13: TPO Devol Flow Diagram [24]*

## 2.3 Analysis

By comparing the $CO_2$ partial pressure data to a previously performed $CO_2$ calibration, the fraction of the microreactor exhaust stream that is $CO_2$ can be calculated. This can then be integrated to determine the total amount of carbon evolved from the sample. With this analysis, these temperature programmed reactions enable the observation of the volatile, fixed, and total carbon content in a soil sample. Further comparison helps determine the effects of a remediation method on carbon content. Carbon fraction comparison enables internally consistent evaluation of each remediation method. To assess treatments in a regulatory context, however, temperature programmed reaction data needs to be related to TPH.

Figure 14 shows recovery percentages for various hydrocarbon impacted soils, determined by four different measurement techniques (TPO, TPD, TPD to 525°C, and GC-FID) plotted against GC-FID. Points from each of the measurement techniques that fall on a common percent mass by GC-FID value were all taken from the same sample. TPO and

TPD data points represent recovery percentages obtained through the temperature programmed oxidation and desorption experiments previously described. TPD to 525°C recovery percentages are obtained by integrating $CO_2$ evolution curves up to the time when the temperature ramp reaches 525°C (approximately 100 minutes). This point is chosen because 525°C is the temperature at which a $C_{40}$ hydrocarbon (the largest molecular size typically included in a TPH measurement) would desorb off of the sample. Colorimetry compares a solution of impacted soil to a prepared scale to comparatively determine total hydrocarbon content. Methylene chloride (DCM) is used as the solvent for its ability to dissolve organic compounds.[34] The scale is created by mixing a known quantity of oil into DCM in incremental ratios to provide references at each concentration. The sample solutions consist of approximately 1 g soil in 10 g DCM, although proportions may vary to allow adequate distinguishability between samples. Gas Chromatography with Flame Ionization Detector (GC-FID) is the standard technique for measuring TPH.[35] Briefly, GC-FID operates by using phase interactions to separate compounds in a vaporized sample according to molecular size and boiling point. These compounds then undergo combustion in a hydrogen flame, producing ions that are collected and measured by a highly sensitive ammeter. [36, 37] All other measurement techniques were plotted against GC-FID measurements which were performed elsewhere.

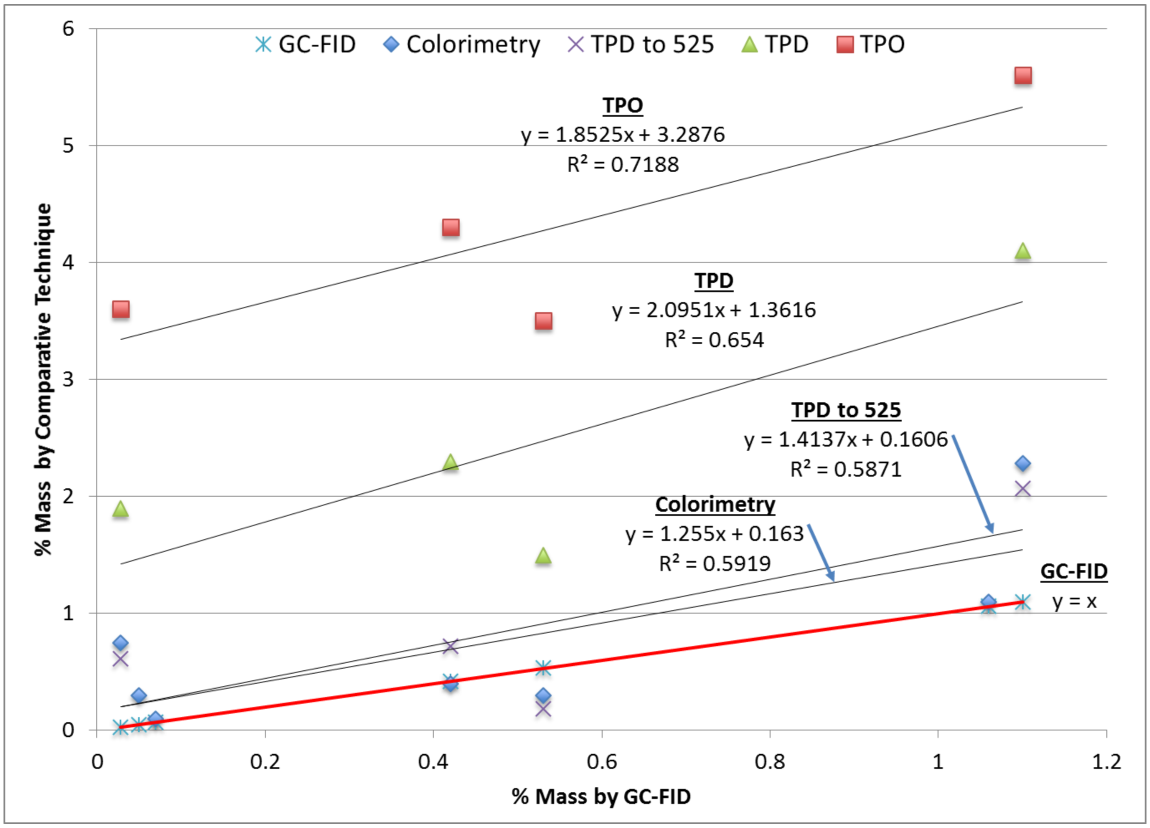

*Figure 14: Carbon Content Measurement Technique Comparison*

Although no $R^2$ value demonstrates excellent curve fit, the trendlines still serve to give in an idea of how the measurement techniques compare against each other. All hydrocarbon measuring techniques shown overestimate the values of TPH given by GC-FID represented by the red line. This can be observed for TPO and TPD in the consistently higher % mass values recorded and can be explained by noting that TPO oxidizes all hydrocarbon content and a full TPD desorbs hydrocarbons of molecular sizes in excess of $C_{90}$. Colorimetry and TPD to 525 both overestimate TPH as evidenced by the colorimetry trendline lying above that of GC-FID, albeit by significantly smaller margins than either TPO or TPD.

The relationships shown in Figure 14 demonstrate that carbon fraction measurements made in the microreactor can be used to establish an upper bound for TPH in a given sample because the temperature programmed reaction experiments consistently overestimate the amount of hydrocarbon content on the sample. Furthermore, when any of the characterization methods used measure a recovery percentage of 1% or less, TPH will certainly be within regulatory limits.

## 2.4 Remediation Methods

In order to systematically address hydrocarbon contamination, it is necessary to understand any remediation methods to be employed and the mechanisms by which they function. By understanding the relative merits of each method, soil decontamination can be tailored on a case-to-case basis.

### 2.4.1 Soil Creation

Due to transportation complications samples of contaminated soil from the site that is under immediate investigation could not be obtained. As a result, a subject soil for this study had to be synthesized. An easily obtainable soil, sufficiently similar to the previously mentioned site was identified by the Texas A&M Soils Laboratory. This soil was then artificially impacted with Doba crude oil also chosen for its similarity to the contamination site. In addition to crude oil, water was added to the soil, together in proportions representative of those found at the contamination site, namely: 3% and 5% oil with 0%, 10%, and 15% water all on a dry soil mass basis.

### 2.4.2 Incineration

Incineration is the complete oxidation of all carbon containing species in a sample. At elevated temperatures, oxygen will react with hydrocarbons and solid carbon to produce the typical combustion products of water and $CO_2$. Incineration has been shown to eliminate contamination more completely than any other energetic method previously investigated in our group. [24]

The TPO characterization experiment described in section 2.2.1 creates the conditions for incineration and, when analyzed as a remediation method, serves as a fundamental mechanism due to its relative simplicity and thoroughly understood chemistry. Incineration can, therefore, be used in the interpretation of other methods.

### 2.4.3 Thermal Desorption

Indirectly heated thermal desorption operates by elevating the temperature of the soil under inert conditions so that hydrocarbons desorb off once the sample reaches the necessary temperature. In this method, degree of contaminant removal is a direct function of the specific hydrocarbon species present, their respective boiling points, and the maximum temperature achieved. Consequently, temperature control can be used to affect what is removed from the sample. This is advantageous because much of the beneficial or inconsequential carbon content is composed of large species whose boiling points are very high and can, therefore, be avoided by limiting the peak temperature during the treatment process.

While indirect thermal desorption requires an inert environment, in an industrial setting the heat source for thermal desorption treatments is often an open flame. This open flame, or “direct” method, is produced using excess oxygen to avoid the possibility of depositing more hydrocarbons onto the soil through incomplete combustion. Consequently, the treatment is not purely thermal desorption, it has the potential for combustion, and cannot be assumed identical.

The thermal desorption unit provided by Hazen Research was used for pilot scale thermal desorption. In order to investigate relationships between relevant treatment parameters (i.e. residence time, treatment temperature, oil concentration, treatment environment, and treatment effectiveness), combinations of the following parameter settings were employed in successive runs:

*Table 1: Thermal Desorption Unit Parameter Settings*

| Oil Content (% by dry weight) | Water Content (% by dry weight) | Time (min) | Temperature (°C) | Process Gas |
|---|---|---|---|---|
| 3 | 10 | 15 | 370 | $N_2$ |
| 5 | 15 | 30 | 420 | $O_2$ |
|  |  | 60 | 470 | $CO_2$ |
|  |  |  | 550 | Water |

Oil and water concentrations were chosen to be representative of an actual contamination site to be remediated. Additionally, residence time and treatment temperature increments were prescribed by the corporate sponsor.

Process gas combinations were used to demonstrate either direct or indirect thermal desorption conditions. For indirect thermal desorption, treatment was performed in only $N_2$ flowed at approximately 37 slpm. The direct thermal desorption treatment was performed in a lean combustion products gas mixture, namely: $N_2$, $O_2$, $CO_2$, and water. $O_2$ concentration varied throughout the direct treatment to ensure that $O_2$ levels were quantifiable at the flow exit but not present in such large quantities that the treatment became incineration. $N_2$ was adjusted to compensate for less $O_2$, ensuring a constant flowrate of approximately 35 slpm. Treatment gas mixture composition is shown in Table 2.

*Table 2: Direct Thermal Desorption Gas Mixture Composition*

| | $N_2$ | $O_2$ | $CO_2$ | Water |
|---|---|---|---|---|
| Concentration | 50-60% | 15-25% | 9.5% | 15.5% |

### 2.4.4 Heat Treatment of Unimpacted Soil – Performed Elsewhere

The TX1 background soil was heated up to 550°C followed by a 12 hour hold. This heat treatment was observed to affect the physical appearance of the soil by turning it into a deeper shade of red. The heat treated soil also experienced an increase in fertility compared to the background soil.

# 3. RESULTS & DISCUSSION

Shown in Figure 15 is the temperature ramp used during each of our experiments, with hydrocarbon species boiling points plotted at the corresponding times. The ramp consists of a 5°C/min ramp from ambient up to a sample temperature of 710°C, followed by a 15 minute hold at 710°C and then an uncontrolled cool down. Special emphasis is placed on $C_{40}$ as it is the upper limit of the molecular size range described as TPH. This figure will provide a reference for what is evolving off of the sample in the $CO_2$ plots to follow.

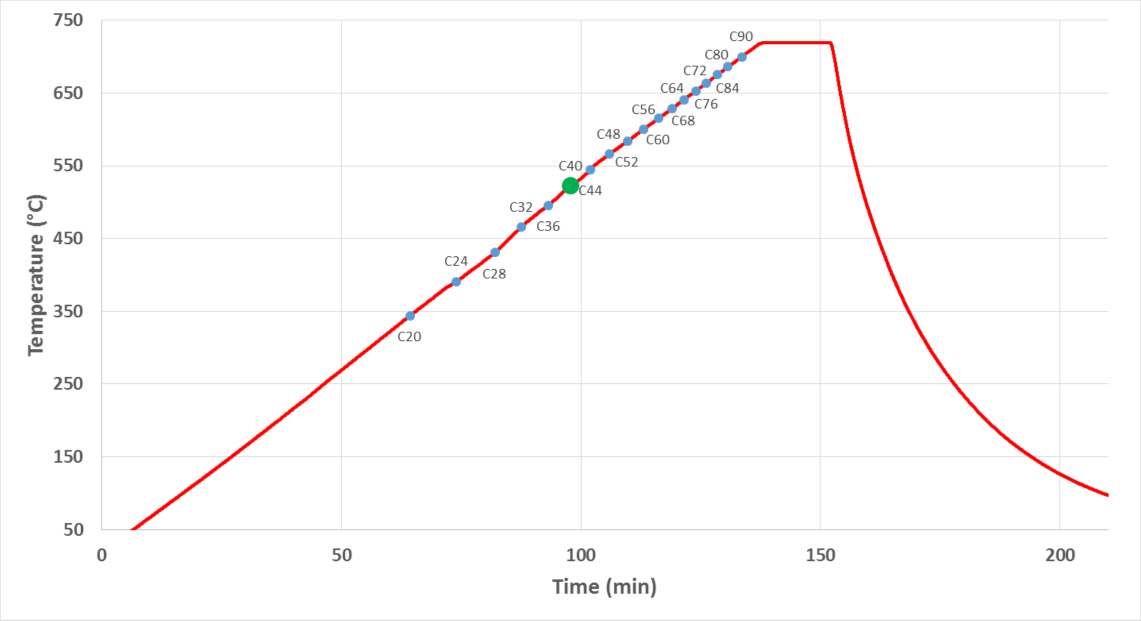

*Figure 15: Boiling points of heavy hydrocarbon alkane species overlaid onto the temperature ramp*

## 3.1 TX1 Background Soil

The TX1 background soil is the uncontaminated and untreated soil. This TX1 background is the soil that was impacted and then underwent treatment in the thermal desorption unit. Consequently, a complete characterization of this untreated, uncontaminated soil was useful for helping to put all other results into context.

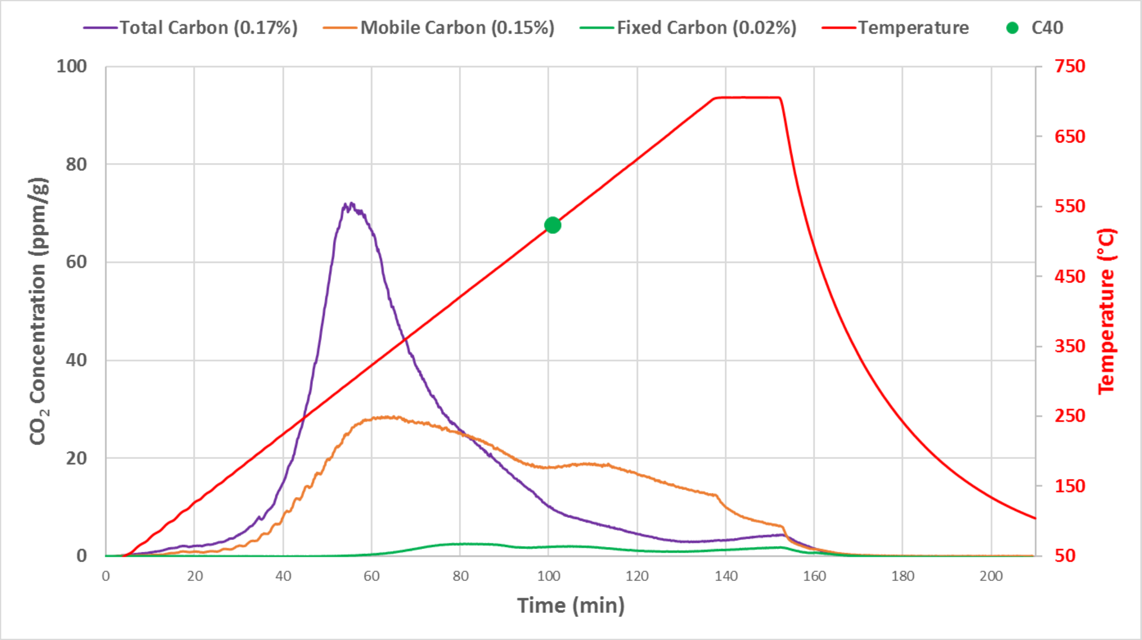

*Figure 16: $CO_2$ Evolution Plot - TX1 Background*

Figure 16 shows the $CO_2$ evolution with respect to time as a result of performing a TPO (measures total carbon), a TPD (measures mobile carbon), and a TPO Devol (measures fixed carbon) on the TX1 background soil. The shape of the total carbon curve indicates that a large portion of the carbon content present oxidizes in the lower portion of the temperature ramp, reaching a maximum at about 55 minutes into the ramp. Carbon from the soil continues to oxidize for the remainder of the experiment but in rapidly diminishing quantities. The mobile carbon curve shows a maximum carbon desorption early in the temperature ramp, similar to the total carbon curve. Mobile carbon evolution declines at slower rate than total carbon as evidenced by higher magnitude $CO_2$ concentrations starting at 80 minutes and continuing on for the remainder of the experiment. Fixed carbon evolves in very low quantities throughout the test after beginning much further into the temperature ramp than either total or mobile carbon. Finally, the sum of the mobile and fixed carbon recovery percentages add up to the total carbon recovery percentage. This indicates that all carbon is successfully accounted for between the two fractions and that the sample has been accurately characterized.

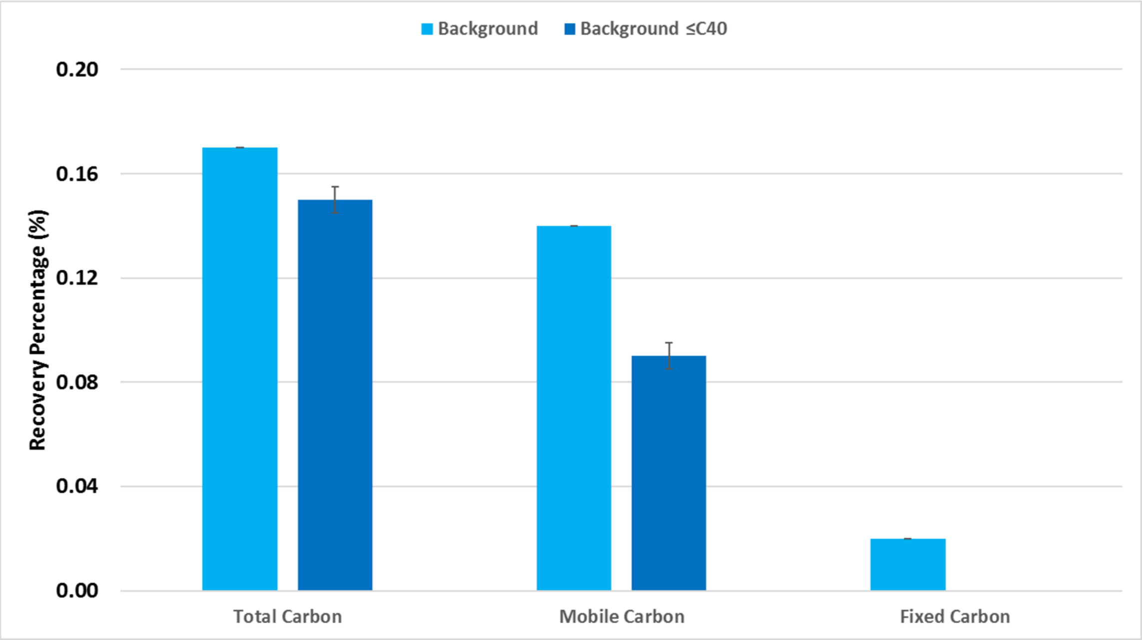

*Figure 17: Carbon Fraction Recovery Percentage Comparison - TX1 Background*

Figure 17 shows the carbon recovery percentages for each of the three carbon fractions. These numbers are the results of integrating the curves in Figure 16, both to the end of the test (complete) and up to the C40 mark (≤C40). Error bars in this and subsequent bar plots represent standard deviations of multiple replicates performed on samples of the same soil. The utility of this figure lies in its more direct comparison of the quantity of total carbon, whereas Figure 16 more clearly depicts how these amounts were distributed across the temperature ramp. These recovery percentages demonstrate that the majority of the carbon content of the TX1 background soil is in the mobile fraction. The figure reaffirms that most of the carbon in both the total and mobile fractions evolved before the C40 mark with the phenomenon being more distinct in the total carbon.

## 3.2 TX1 Heat Treated Soil

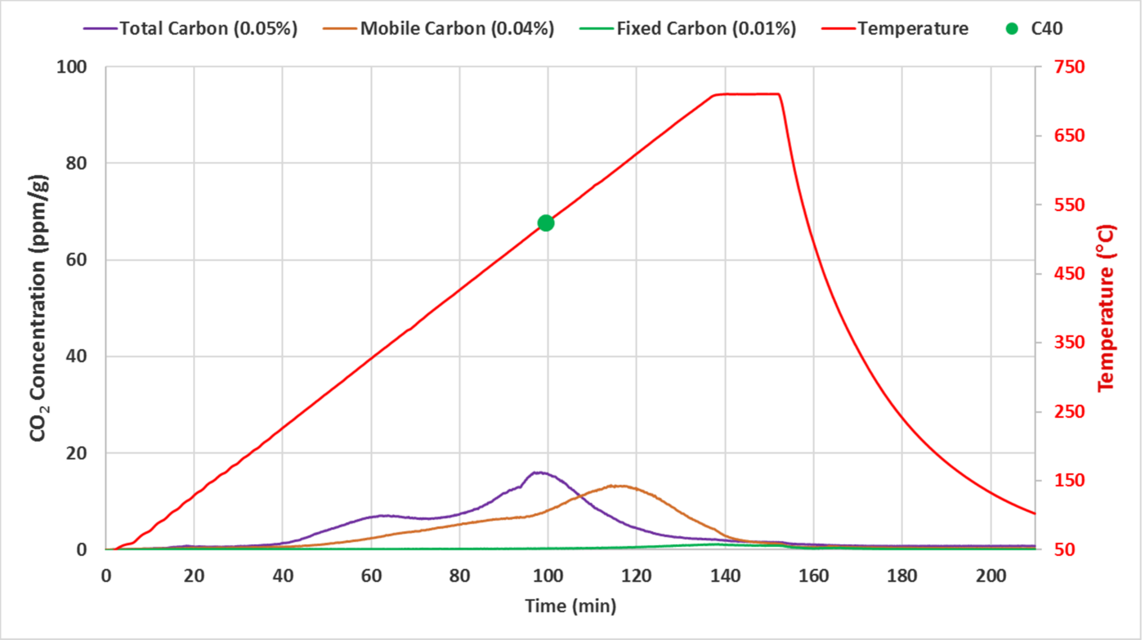

*Figure 18: $CO_2$ Evolution Plot - TX1 Heat Treated*

The total carbon curve in Figure 18 demonstrates that the carbon content evolves from the TX1 heat treated sample mostly before the C40 mark. Total carbon evolution peaks twice throughout the course of the experiment, the larger of which occurs approximately at 100 minutes. Mobile carbon evolution increases steadily, beginning very soon after total carbon and reaching a maximum after the C40 mark, at 115 minutes. The fixed fraction of the carbon content on the heat treated soil exists in very small quantities and is seen mostly near the 15 minute hold at 710°C. Figure 19 shows that there is a larger portion of total carbon content that oxidizes before the temperature ramp reaches the C40 mark. However, mobile carbon, which represents the larger carbon fraction, is more evenly split. While variations in the exact recovery percentages displayed are large relative to respective magnitudes, these variations move consistently across carbon fractions. As a result, the distribution of carbon fractions as they are shown are representative of the sample overall.

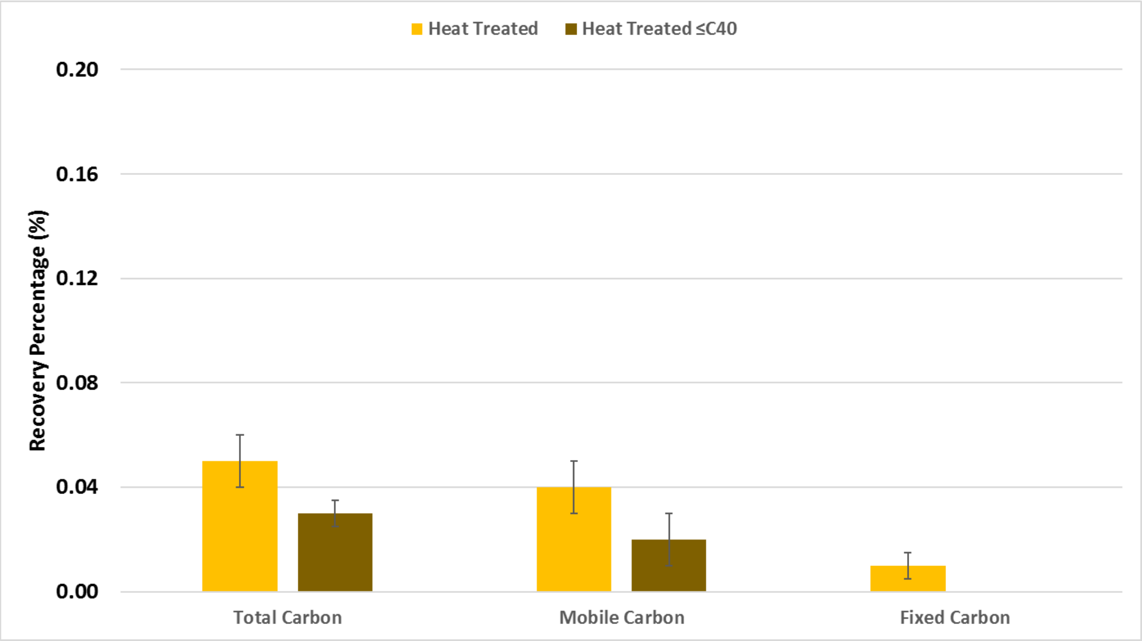

*Figure 19: Carbon Fraction Recovery Percentage Comparison - TX1 Heat Treated*

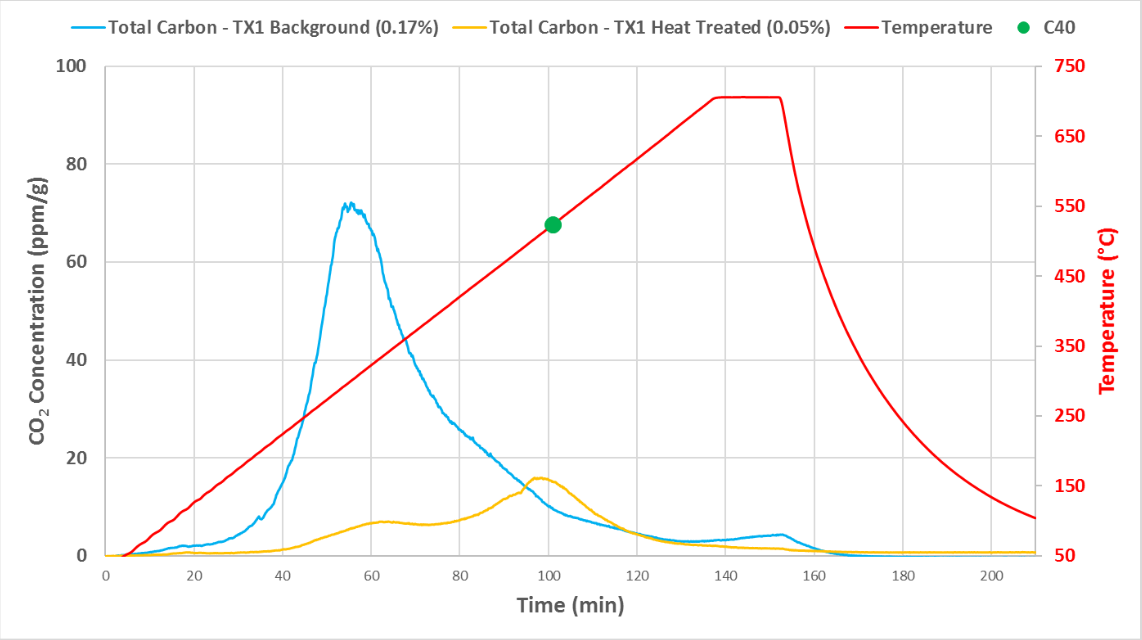

*Figure 20: $CO_2$ Evolution Plot - Total Carbon Comparison (Background vs Heat Treated)*

Apparent in both Figure 20 and Figure 21 is the dramatic reduction in carbon content from the background to the heat treated soil. More readily apparent in Figure 20 is the fact that there is a larger portion of the sample mass evolving off after the $C_{40}$ mark in the heat treated soil than there is in the background soil, with peak evolution from the heat treated soil occurring almost 60 minutes later at a temperature 200°C higher. This indicates that the size distribution of the carbon chains has shifted towards the larger end.

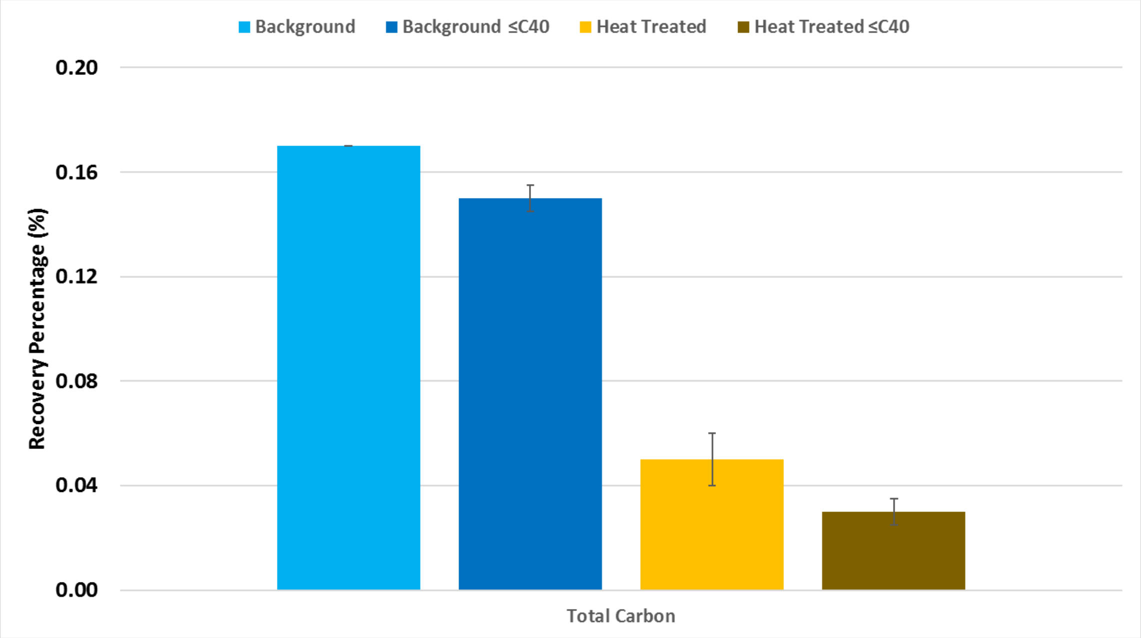

*Figure 21: Recovery Percentage Comparison (Background vs Heat Treated) - Total Carbon*

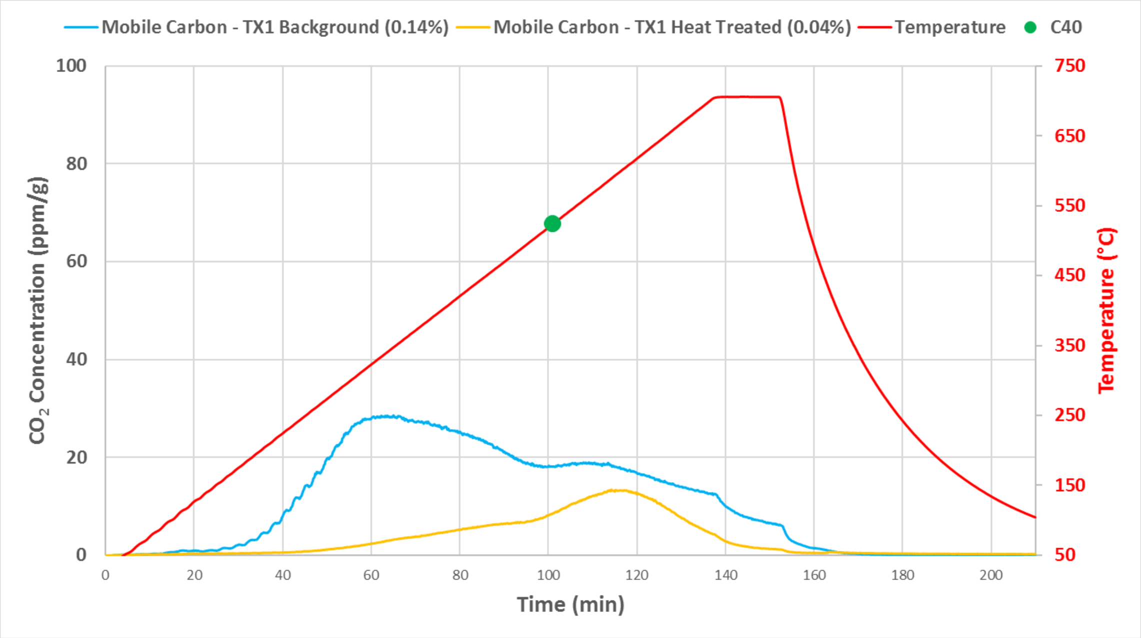

*Figure 22: $CO_2$ Evolution Plot - Mobile Carbon Comparison (Background vs Heat Treated)*

The mobile carbon continues the trend of the heat treatment reducing and shifting the distribution of evolved carbon later in the temperature ramp. Figure 22 demonstrates that, again, peak evolution from the heat treated sample occurs approximately 60 minutes after that of the background soil, implying that the largest single population of carbon species in the heat treated sample is larger than $C_{40;}$ consisting of both fixed and low mobility heavy hydrocarbons. Although most of the mobile carbon content on the background soil is lighter than $C_{40}$, Figure 23 shows that the distribution of mobile carbon in the heat treated soil is less biased.

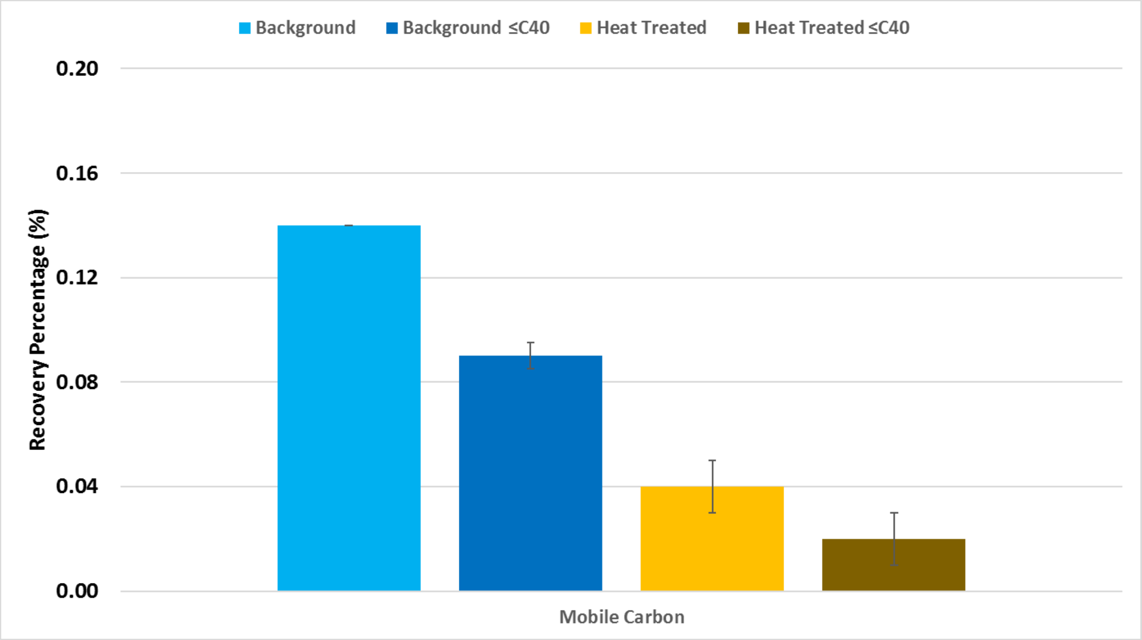

*Figure 23: Recovery Percentage Comparison (Background vs Heat Treated) - Mobile Carbon*

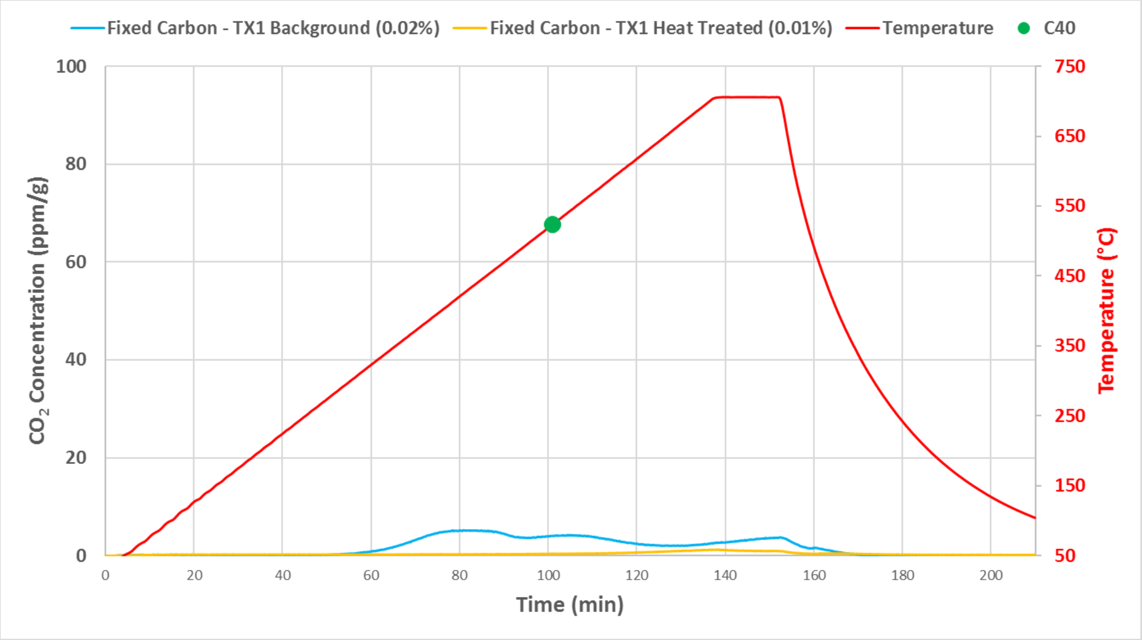

*Figure 24: $CO_2$ Evolution Plot - Fixed Carbon Comparison (Background vs Heat Treated)*

The fixed carbon data, due to its extremely low magnitudes, shows little more than that the heat treatment reduces the fixed carbon content to minute quantities. Also obvious, is that by comparing figures from total and mobile carbon to those of fixed carbon, it can be seen that the majority of the carbon present in each of the soils exists in the mobile fraction.

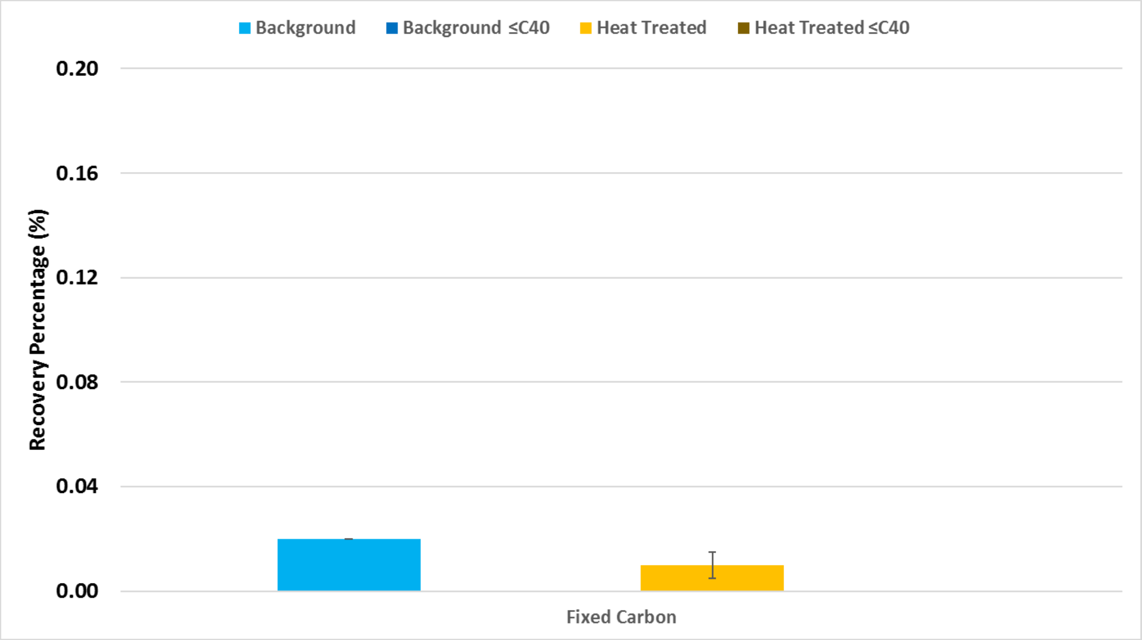

*Figure 25: Recovery Percentage Comparison (Background vs Heat Treated) - Fixed Carbon*

This analysis has shown that heat treatment diminishes and shifts the carbon content distribution in the uncontaminated soil. Mobile carbon is the dominant fraction in both samples, however, it principally consists of longer carbon chains in the heat treated soil. Important to note in Figure 16 - Figure 25 are the scales used. Each of these carbon fractions are small fractions of a single percent of the sample mass. Compared to the quantities of carbon present on the contaminated soil, this indicates that virtually all carbon content seen in the observed results is a direct consequence of the contamination and not pre-existing soil chemistry. The uncontaminated soil therefore does not make a significant contribution to the results seen after contamination.

## 3.3 Untreated Impacted Soil

Characterization of the soil once it was mixed with specified amounts of oil and water (chosen for relevance to an actual contamination site) allowed for the establishment of an upper limit to carbon content seen in the soil. Comparison of all treatment iterations to these results provides a reference frame for how effectively a given set of treatment parameters performed.

### 3.3.1 Untreated Impacted – 3% oil

While most parameters being investigated were related to treatment settings, oil concentration was one that had to be accounted for beginning with the soil creation. As a result, there were two separate untreated impacted soils to be characterized; one soil containing 3% oil by dry soil mass, and another containing 5% oil.

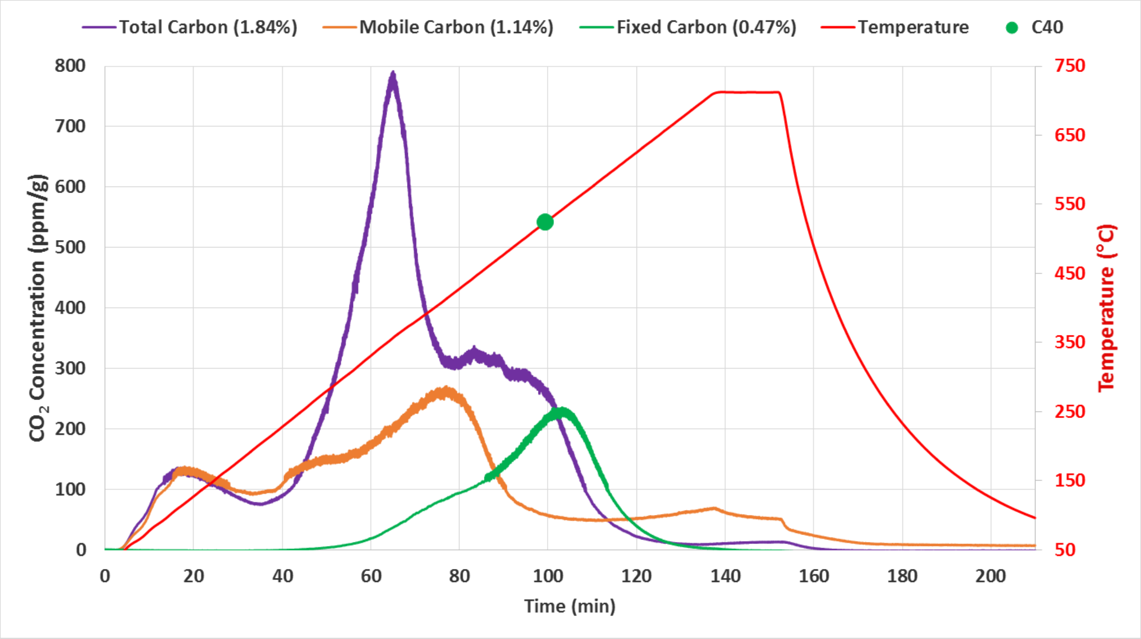

*Figure 26: $CO_2$ Evolution Plot - Untreated Impacted (10% Water 3% Oil)*

The first notable aspect of Figure 26 is the significant increase in magnitude of the left-hand y-axis, compared to previous figures. Where $CO_2$ concentration never exceeds 80 ppm/g for the background soil, peak evolution is now a full order of magnitude higher at

800 ppm/g. This difference confirms that the background soil chemistry plays a minor role in the carbon content seen after soil impaction. Total carbon shows a slight maxima in carbon evolution very soon after the beginning of the experiment cresting at 15 minutes before dropping slightly. Peak evolution in the total carbon curve occurs fairly early in the temperature ramp at about 65 minutes, rising well above the rest of the curve. The total carbon curve then falls to a brief plateau before decreasing to minute amounts just past the C40 mark. Mobile carbon evolves in a manner almost identical to total carbon up until 40 minutes where the two plots begin to diverge. Similar to total carbon, the mobile evolution curve reaches a maximum before the C40 point although about 10 minutes later and with a more gradual growth leading up to it. Again, similar to total carbon, the mobile curve falls to a plateau following the peak but this is held much longer. Fixed carbon evolution is virtually non-existent until 55 minutes when it begins a gradual climb to a peak occurring at approximately the same time as the C40 mark. The curve then drops back to zero at a slightly faster rate than it rose, resulting in a much lower recovery percentage than the mobile carbon curve reaches as shown in the recovery percentage comparison in Figure 27. The distributions of the total and mobile curves indicate that contaminant hydrocarbons lie predominantly on the lighter end of the spectrum, with total carbon content evolving almost entirely before the C40 mark.

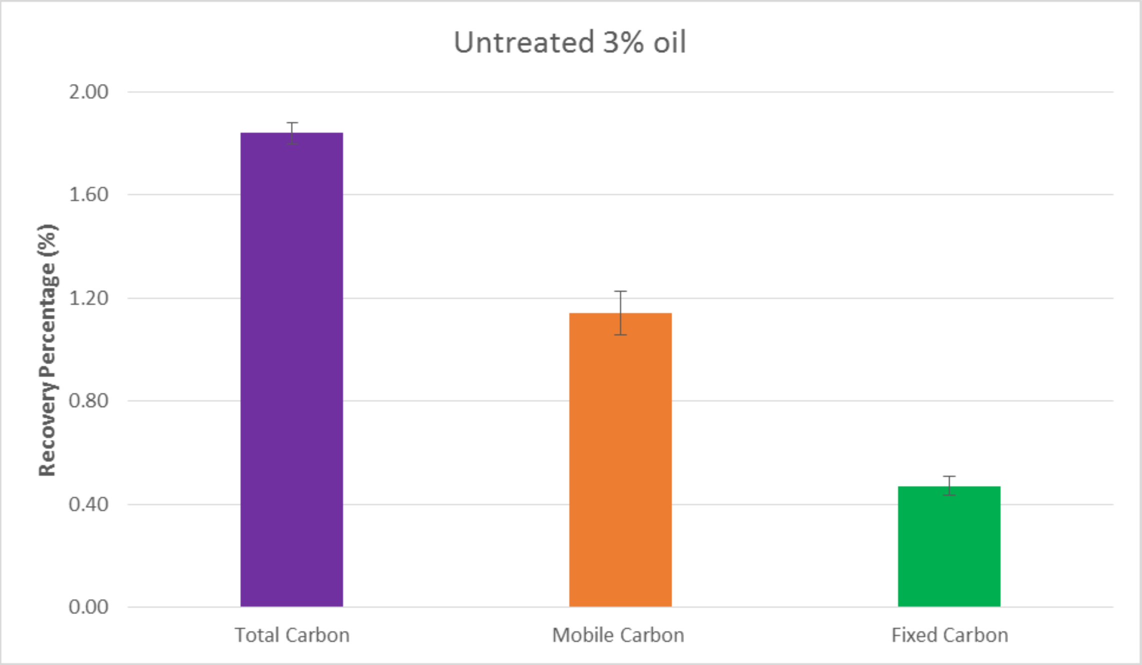

*Figure 27: Carbon Fraction Recovery Percentage Comparison – Untreated 3% Oil Concentration*

Worthy of note is the apparent discrepancy between the nominal 3% oil by dry soil mass and the 1.84% carbon by as-received sample mass. The concentration of 3% oil becomes 2.65% after accounting for the weight of oil and 10% water mixed into the soil. Furthermore, simulated distillation performed on the crude oil used to impact the soil revealed that carbon makes up 86.5% of the mass of the oil resulting in carbon making up 2.3% of the as-received soil mass. Other factors contributing to the disparity include evaporation of extremely volatile compounds during transportation or sample loading, local inhomogeneities, and differing instrument precision limitations between bulk impaction and sample measurement.

### 3.3.2 Untreated Impacted – 5% oil

As mentioned previously, there was also an untreated impacted soil with 5% oil by dry soil mass created. This soil was also characterized to ensure that treated soils could be compared to corresponding untreated samples.

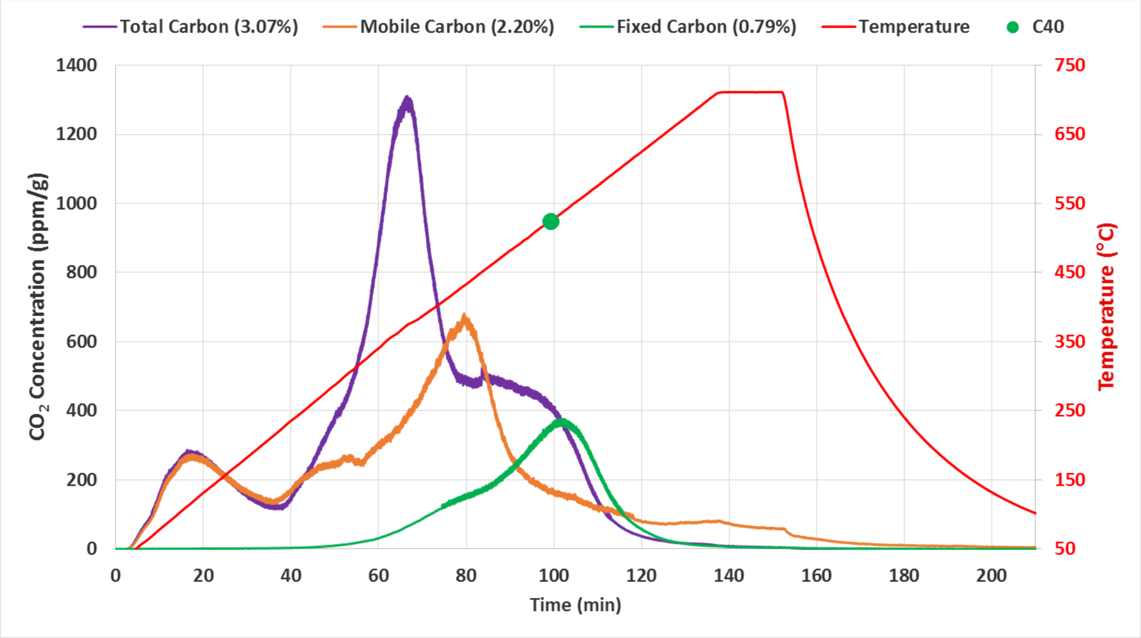

*Figure 28: $CO_2$ Evolution Plot - Untreated Impacted (10% Water 5% Oil)*

The total carbon curve in Figure 28 again shows a small maxima very early in the temperature ramp followed by a slight decrease in carbon evolution. Next is a sharp total carbon peak occurring at 65 minutes to a magnitude of 1300 ppm/g. This peak is followed by a steep drop and a subsequent plateau which drops quickly to zero just past the C40 point. The mobile carbon curve matches the total carbon curve almost exactly until 40 minutes into the experiment. Evolution then dips before increasing steadily to a peak at 80 minutes. Mobile carbon then drops to a plateau which it maintains until the temperature ramp reaches the uncontrolled cooldown. Fixed carbon evolution begins at approximately 55 minutes where it increases at a steady rate to a maximum of about 380 ppm/g at approximately 100 minutes. The curve then drops to zero at a slightly faster rate than it rose where it stays for the remainder of the experiment.

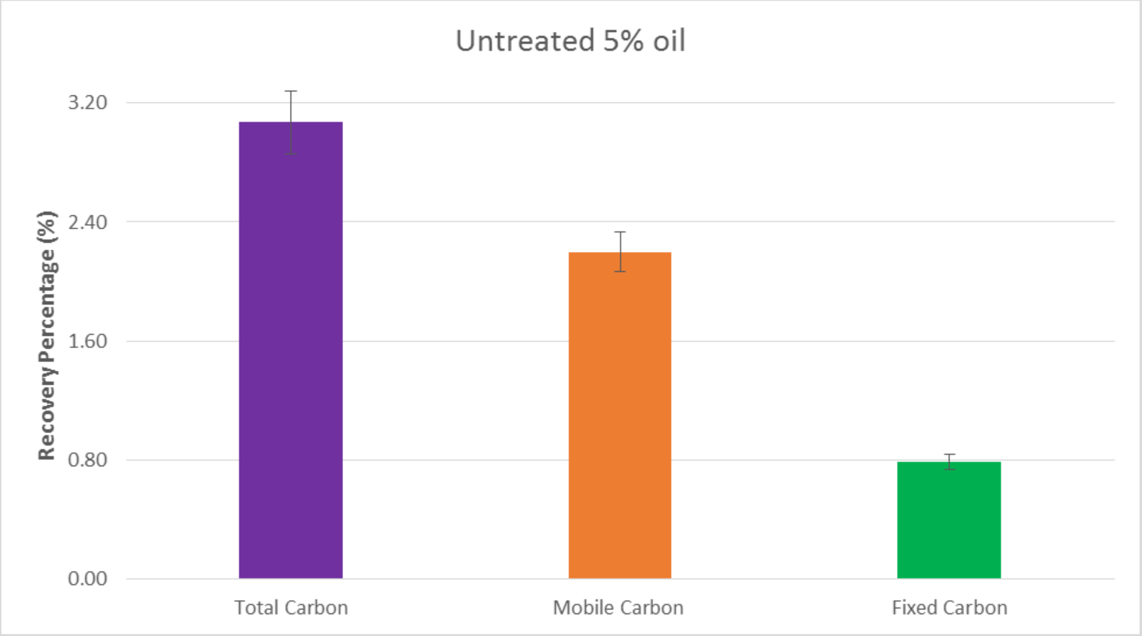

*Figure 29: Carbon Fraction Recovery Percentage Comparison – Untreated 5% Oil Concentration*

The recovery percentages in Figure 29 demonstrate a similar trend to Figure 27. Mobile carbon represents the majority of the total carbon content on the untreated soil sample. Fixed carbon, in comparison, is just over a third of the magnitude of mobile carbon.

## 3.4 Treatment Parameter: Oil Concentration

The effect of the oil concentration treatment parameter can be seen in three directly comparable cases: untreated soil, indirectly treated soil, and directly treated soil. For each of these cases, samples were chosen for comparison such that all other treatment parameters were identical.

The legend of each of the $CO_2$ evolution plots shows the soils used with the following naming convention: XwYo. Where X is the amount of water mixed into the soil upon creation, shown as a percentage of the dry soil mass. Y, similarly, shows the amount of oil mixed into the soil, shown as a percentage of the dry soil mass (i.e. 10w3o indicating 10% water and 3% oil). For the samples that underwent treatments, time (A) and temperature (B) of the treatment will be indicated as: A@B (i.e. 15@420 indicating a residence time of 15 minutes at a treatment temperature of 420°C).

As described previously, the objective of soil remediation technologies is to reduce TPH levels below regulatory limits. Figure 14 and the subsequent discussion demonstrates that by performing TPO experiments, a measurement of all carbon content and a consistent overestimation of the TPH level can be made. Consequently, by conducting a series of TPO experiments on treatment runs that had significant combinations of treatment parameters, trends of remediation effectiveness for each parameter could be developed and estimations of regulatory satisfaction could be made. The following results were, therefore, compiled using TPO data.

### 3.4.1 Oil Concentration - Untreated Soil

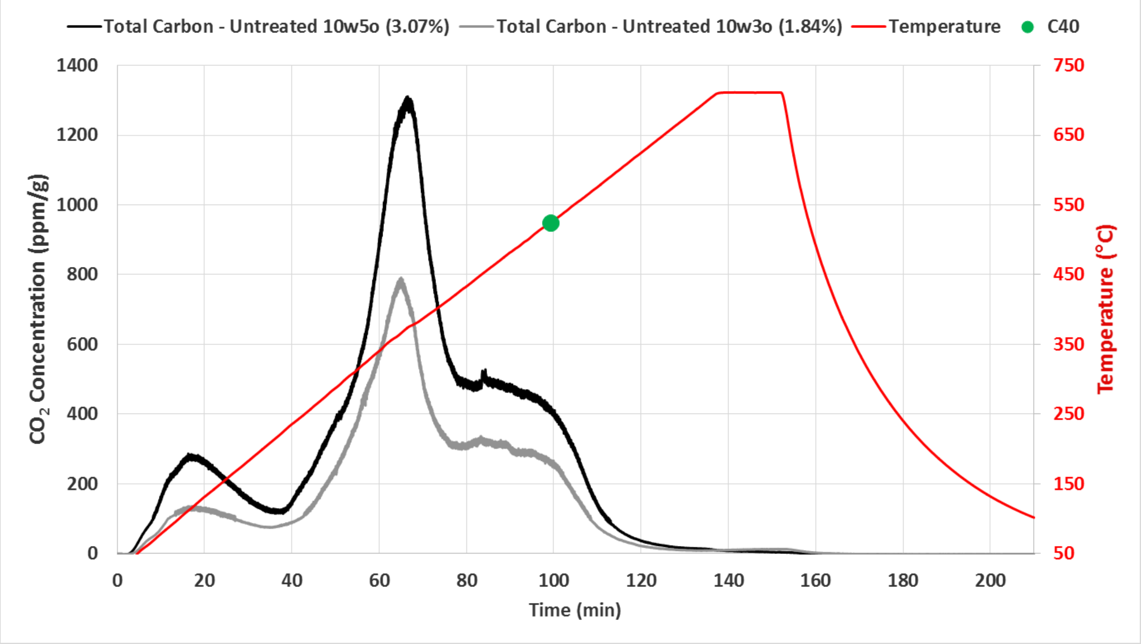

*Figure 30: $CO_2$ Evolution Plot - Total Carbon – Untreated Soil (3% Oil vs 5% Oil)*

As described in the untreated impacted sections, both the 3% oil (10w3o) soil and 5% oil (10w5o) soil have small peaks early on in the temperature ramp with a sharp spike to a global maximum at approximately 65 minutes. These are followed by plateaus and finally drops occurring shortly after the C40 mark. Where the two plots differ is the overall magnitude of the curves. The soil impacted with 3% oil has a correspondingly lower carbon recovery percentage than the soil with 5% oil – a difference of well over 1%, as Figure 31 clearly shows. As was expected by using an identical source of impaction, the distribution of carbon content is nearly identical between the two oil concentrations.

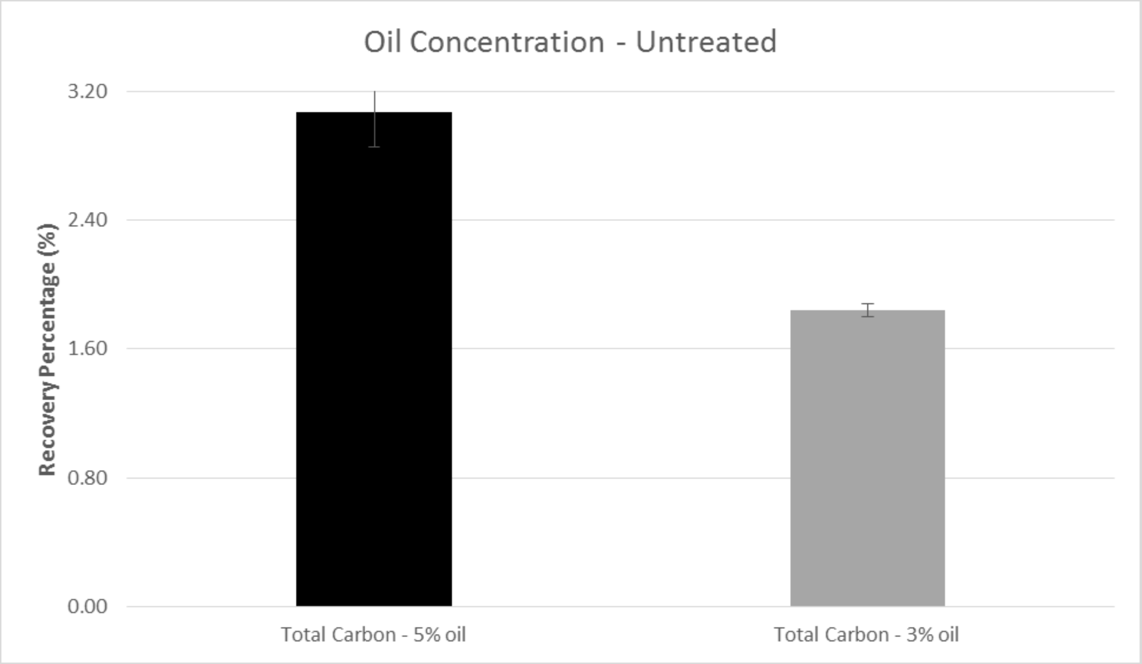

*Figure 31: Recovery Percentage Comparison - Total Carbon – Untreated Soil (3% Oil vs 5% Oil)*

### 3.4.2 Oil Concentration - Indirect Treated

To discuss treatment results in the proper context, all treatment data will be shown in comparison to corresponding untreated soils. This will provide an accurate visualization of what benefit each treatment iteration provided.

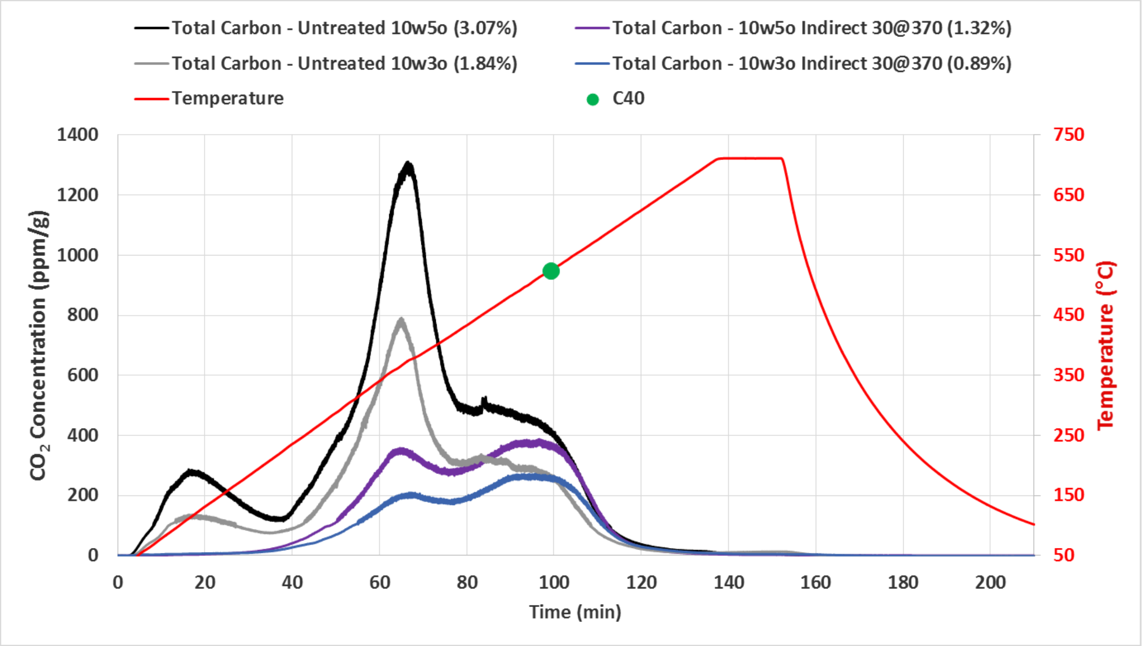

*Figure 32: $CO_2$ Evolution Plot - Total Carbon – Indirect Treated Soil (3% Oil vs 5% Oil – 30 minutes at 370°C)*

The indirect treated soils demonstrate similar disparities to the untreated soils in carbon content. Total carbon content distributions in both treated soils are shifted later into the temperature ramp with evolution beginning at approximately 35 minutes compared to the 5 minute starting point in the untreated soils. Each treated soil experiences two peaks in carbon evolution of similar magnitudes, the first and lesser of which happens at the same time as the maximum peak in the untreated soil. There is a second broader peak in each treated curve that occurs just before 100 minutes which appears to be the remainder of the last plateau in the untreated soils. Altogether, Figure 32 reveals that the treatment most effectively reduced the lighter hydrocarbon content in the untreated soils.

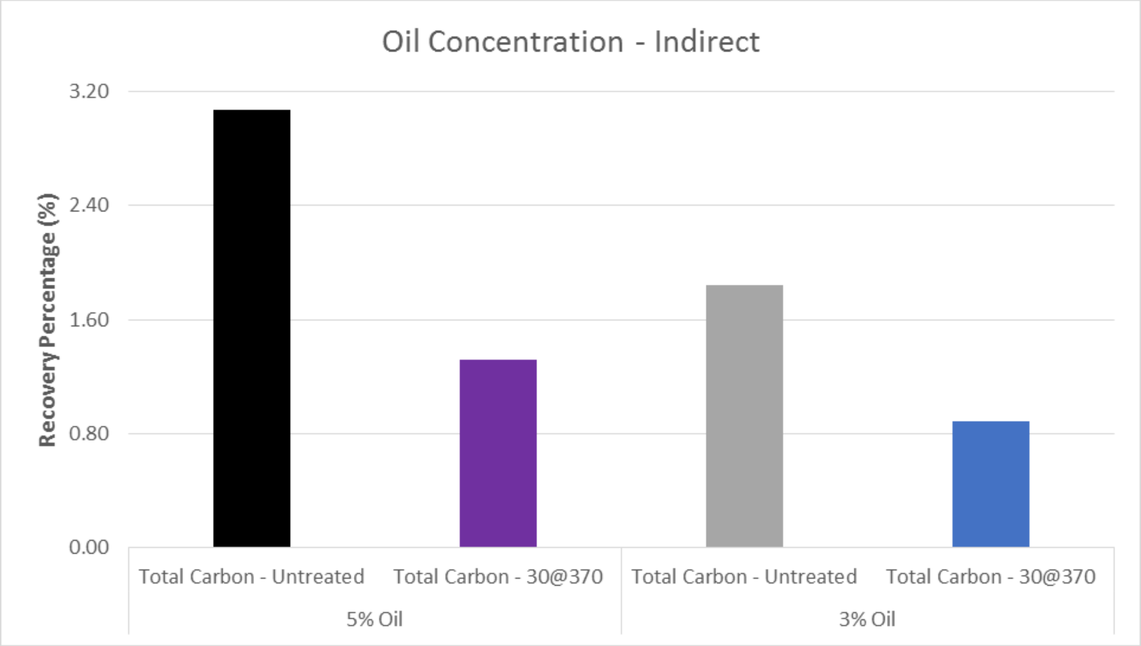

*Figure 33: Recovery Percentage Comparison - Total Carbon – Indirect Treated Soil (3% Oil vs 5% Oil – 30 minutes at 370°C)*

The indirect heated treatment serves to reduce the recovery percentage for both oil concentrations by more than half, although the 5% oil soil underwent a slightly larger reduction both in absolute carbon content as well as relative to the untreated sample. A possible explanation for this is the contribution of heat during treatment of the 5% soil from combustion of larger amounts of oil. Absent from Figure 33 as well as subsequent recovery percentage comparison plots are error bars. Based on repeatability of untreated soil characterization results and the enhanced homogeneity that comes as a result of treatment, replicates for some of the results presented have yet to be performed. A statistically relevant number of replicate characterization experiments will be performed as follow up work, in preparation for publication of the findings presented here. These replicates will, however, largely only account for procedural variability in the characterization experiments. Restricted available sample size limits investigation of spatial and temporal variations associated with any individual treatment run.

### 3.4.3 Oil Concentration - Direct Treated

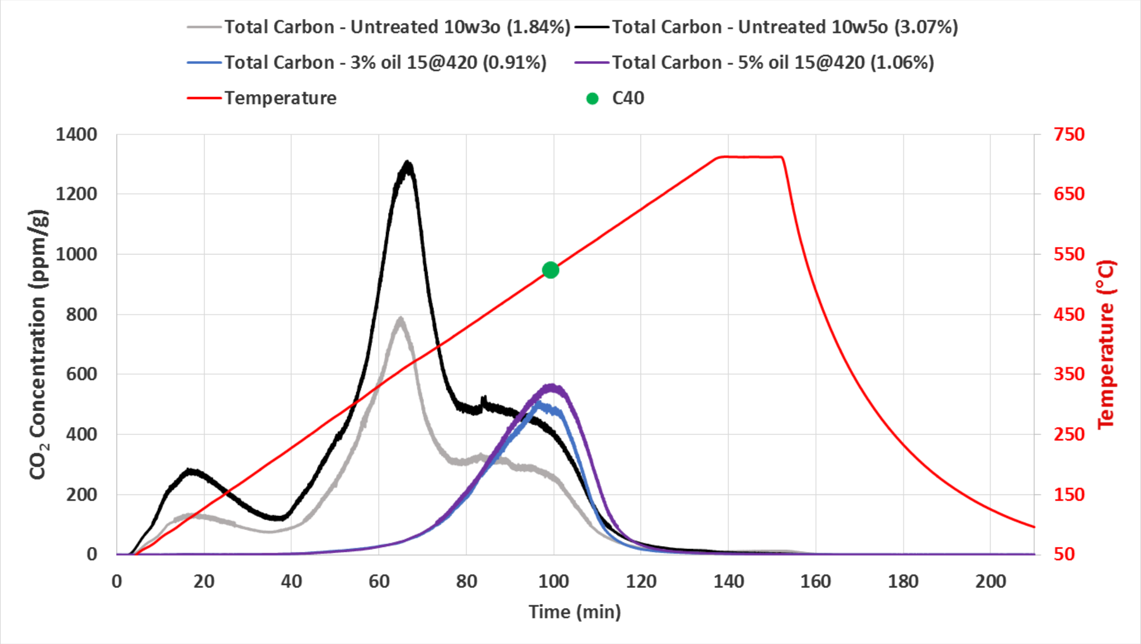

*Figure 34: $CO_2$ Evolution Plot - Total Carbon – Indirect Treated Soil (3% Oil vs 5% Oil – 15 minutes at 420°C)*

Like the untreated and indirect treated soils, both 3% and 5% soils were affected similarly by the direct treatment. Both carbon distributions are rearranged and shifted into single bell curves, cresting at the C40 point.

Where the direct treatment differs in behavior from previous results is in the relative proximity of recovery percentages between the two oil concentrations. The treatment resulted in a drastically larger reduction in total carbon for the 5% oil sample. While still greater, the 5% soil appears to have been brought down to a recovery percentage approximately equivalent to the 3% soil.

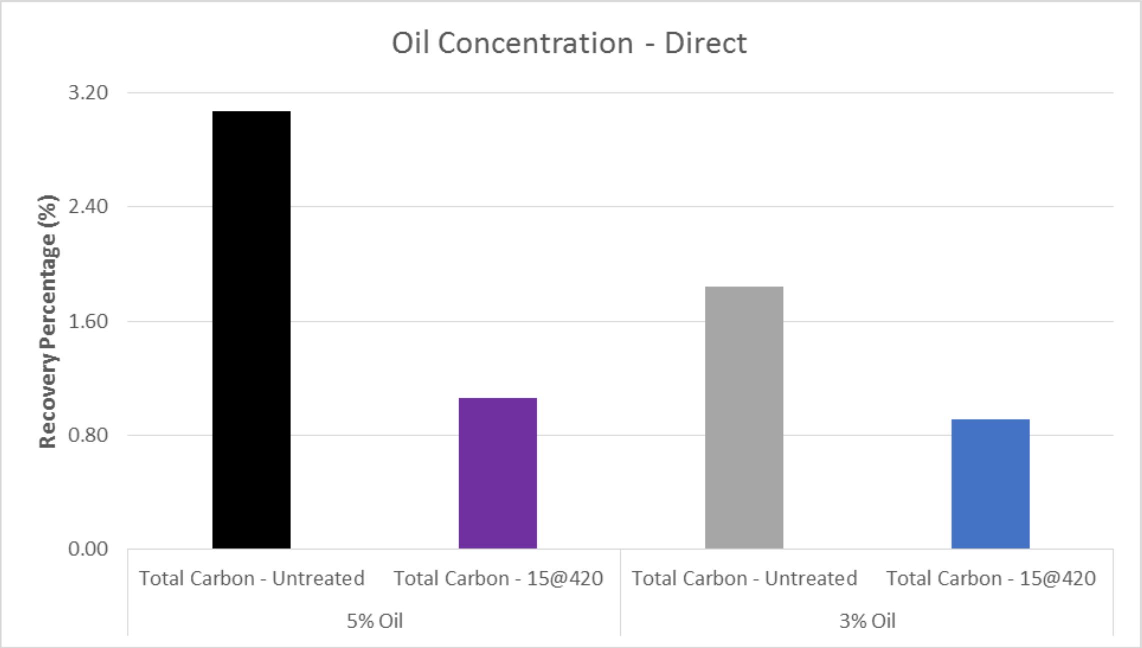

*Figure 35: Recovery Percentage Comparison - Total Carbon – Direct Treated Soil (3% Oil vs 5% Oil – 15 minutes at 420°C)*

## 3.5 Treatment Parameter: Treatment Temperature

The principal mechanism for thermal desorption is devolatilization of contaminant hydrocarbons. With regulations focused on TPH range hydrocarbons and devolatilization being a function of species boiling point, treatment temperature is a critical parameter.

### 3.5.1 Temperature - Indirect Treated

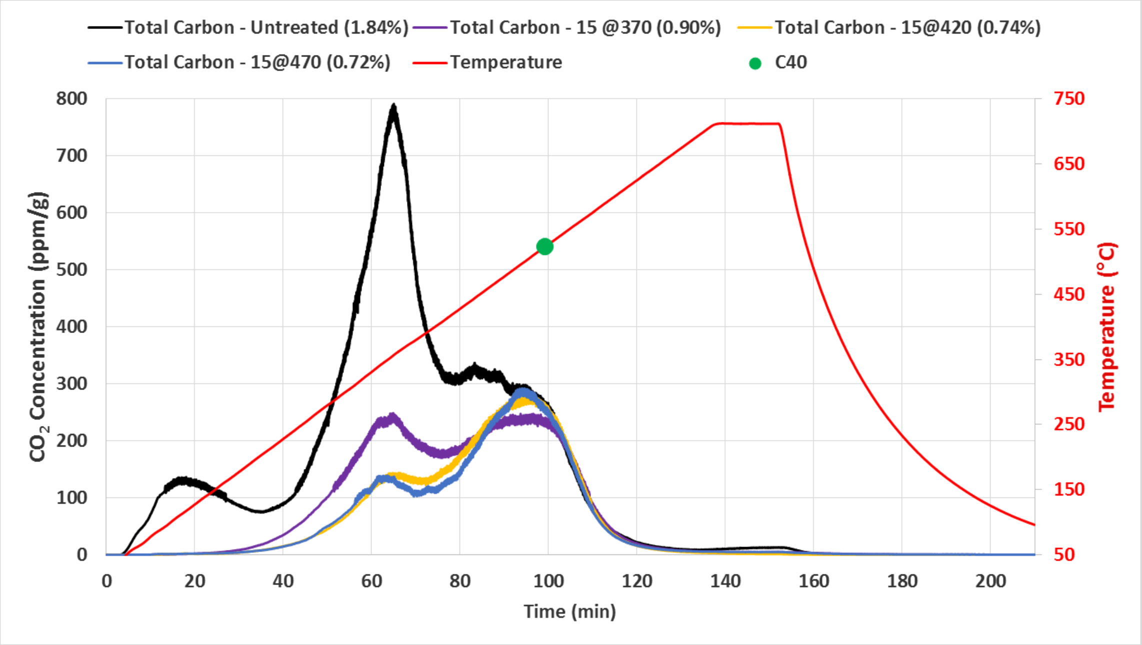

*Figure 36: $CO_2$ Evolution Plot - Total Carbon – Indirect Treated Soil, 3% Oil (15 minutes at 370°C, 420°C, & 470°C)*

As with previous parameter sets, the small peak early in the untreated curve is completely absent, with carbon evolution beginning at 30 minutes for each of the three treatments shown in Figure 36. Carbon content appears for each sample in bimodal distributions, with the first maxima in each curve occurring 65 minutes with the maximum peak in the untreated sample. This first peak in the 370°C treatment is the largest of the three treatment temperatures, with a magnitude approximately 100 ppm/g larger, while the other two samples peak at approximately the same concentration. Evolution peaks for a second time in all three curves at approximately 95 minutes before dropping back to zero in a manner almost identical to the untreated sample. The behavior of this second set of maxima is opposite of the first. The sample that was treated at

370°C is 50 ppm/g lower than the other two, with 420°C and 470°C reaching similar magnitudes of approximately 290 ppm/g.

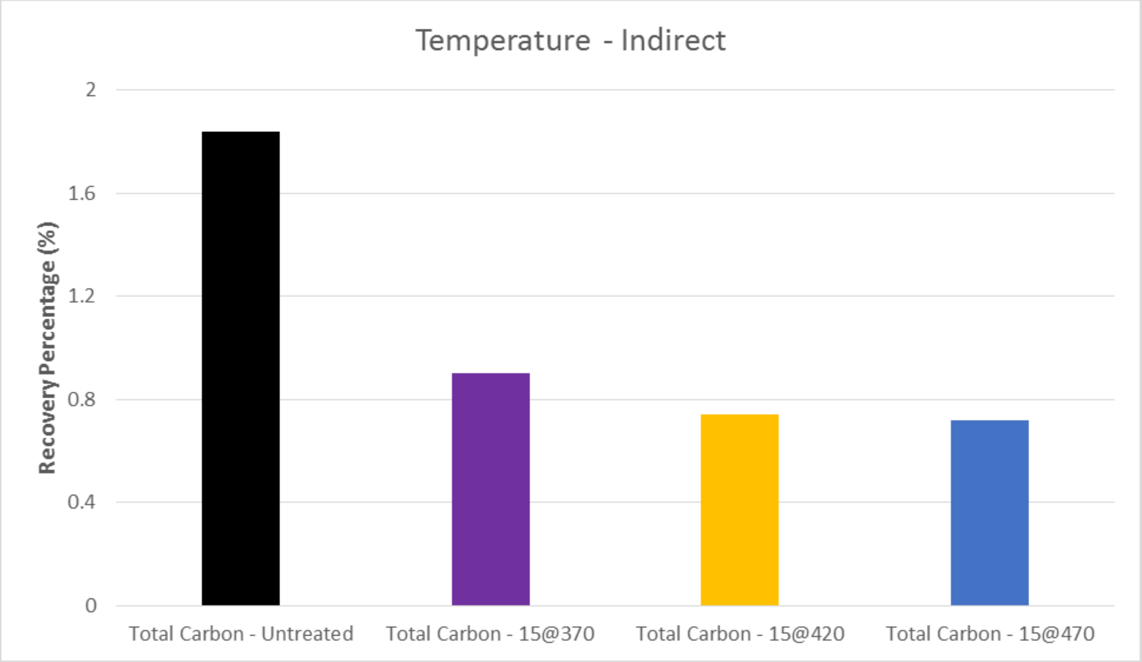

*Figure 37: Recovery Percentage Comparison - Total Carbon – Indirect Treated Soil, 3% Oil (15 minutes at 370°C, 420°C, & 470°C)*

### 3.5.2 Temperature - Direct Treated

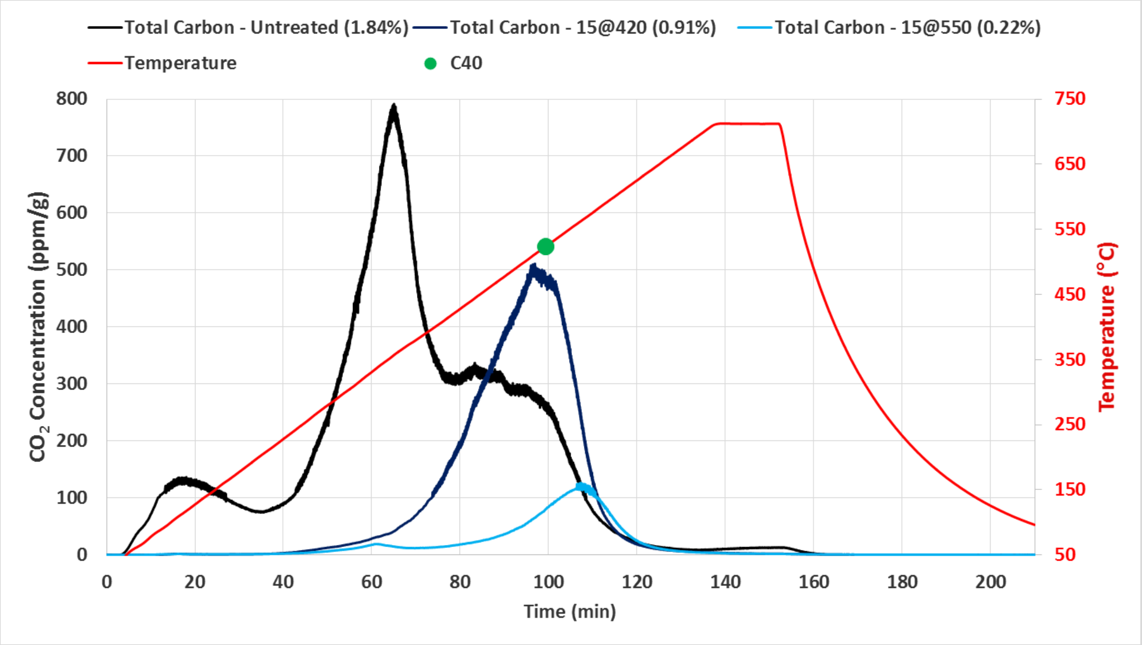

*Figure 38: $CO_2$ Evolution Plot - Total Carbon – Direct Treated Soil, 3% Oil (15 minutes at 420°C vs 550°C)*

The curves in Figure 38 are similar to those in Figure 34 in that they indicate the distributions of carbon content have been transformed primarily into single peaks by the treatment. The soil treated at 420°C evolves in a bell curve that begins showing carbon at 40 minutes. The peak occurs at 100 minutes with a $CO_2$ concentration of 500 ppm/g. After a slight bump at 60 minutes, the 550°C soil exhibits the same behavior, reaching a maximum of roughly 120 ppm/g at approximately 110 minutes.

Although the form of each curve is similar, there is a large difference in size. The sample that underwent treatment at 420°C reaches both a maximum and a corresponding recovery percentage quadruple the magnitude of the 550°C sample. This is in addition to the fact that the recovery percentage of the 420°C treated soil is already half that of the untreated sample.

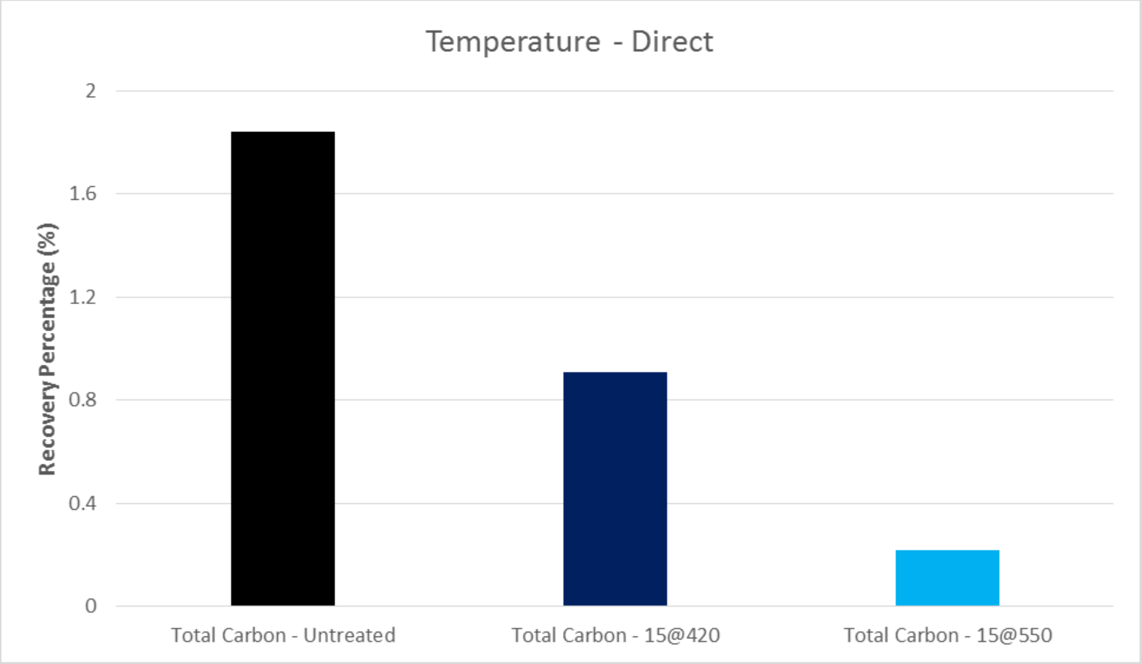

*Figure 39: Recovery Percentage Comparison - Total Carbon – Direct Treated Soil, 3% Oil (15 minutes at 420°C vs 550°C)*

### 3.6 Treatment Parameter: Residence Time

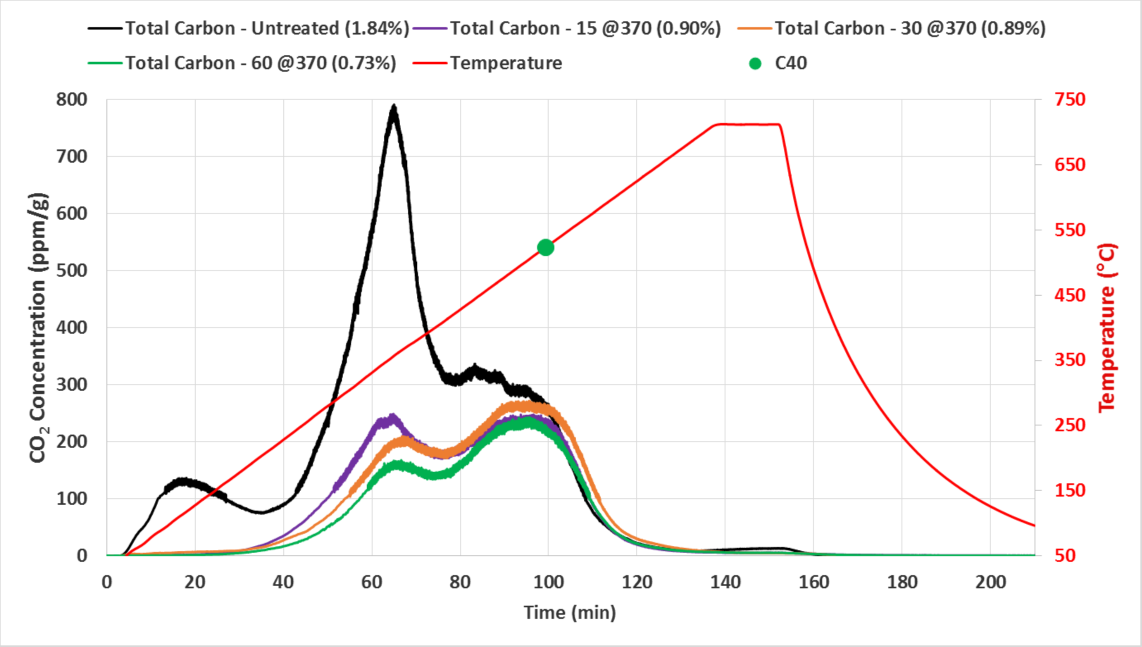

*Figure 40: CO$_2$ Evolution Plot - Total Carbon – Indirect Treated Soil, 3% Oil (15 min vs 30 min vs 60 min at 370°C)*

The direct heated treatments were all performed with a 15 minute residence time, as a result, the effect of residence time is solely investigated for the indirect heated treatments. For each of the three residence times investigated, the resultant carbon distribution is bimodal in nature. The first peak in each curve occurs approximately at the same time as the maximum peak of the untreated sample while the second peak appears at 95 minutes. While the second peak remains fairly constant in time and magnitude between each of the three runs shown in Figure 40, the first peak decreases with each increase in residence time. The recovery percentages also follow this trend of dropping with increase in residence time; although this drop relatively minor, as made obvious by Figure 41.

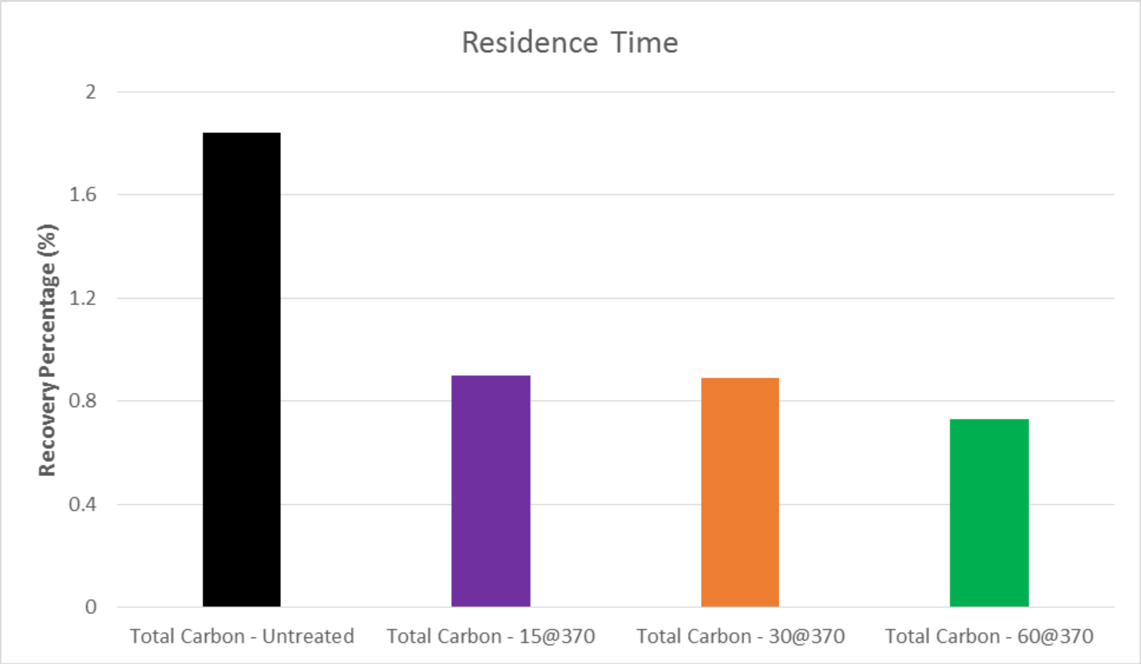

*Figure 41: Recovery Percentage Comparison - Total Carbon – Indirect Treated Soil, 3% Oil (15 min vs 30 min vs 60 min at 370°C)*

Using a multiple regression for the data presented up to here, a simple model for approximate total carbon recovery percentage (RP) as a function of oil concentration (OC), residence time (t), and treatment temperature (T) was developed for the indirect heated treatment:

$$RP = .372 * OC - .00521 * t - .00293 * T + .955 \qquad R^2_{adj} = 0.938$$

## 3.7 Treatment Parameter: Indirect vs Direct

Flow-through gas composition distinguishes the indirect from the direct treatment. With purely $N_2$ in the process gas, the indirect treatment primarily relies on the phase change of hydrocarbon species. In contrast, the direct treatment additionally uses $O_2$ which oxidizes a portion of the contaminant hydrocarbons. As a result of these different mechanisms, the two treatment variations produce different products.

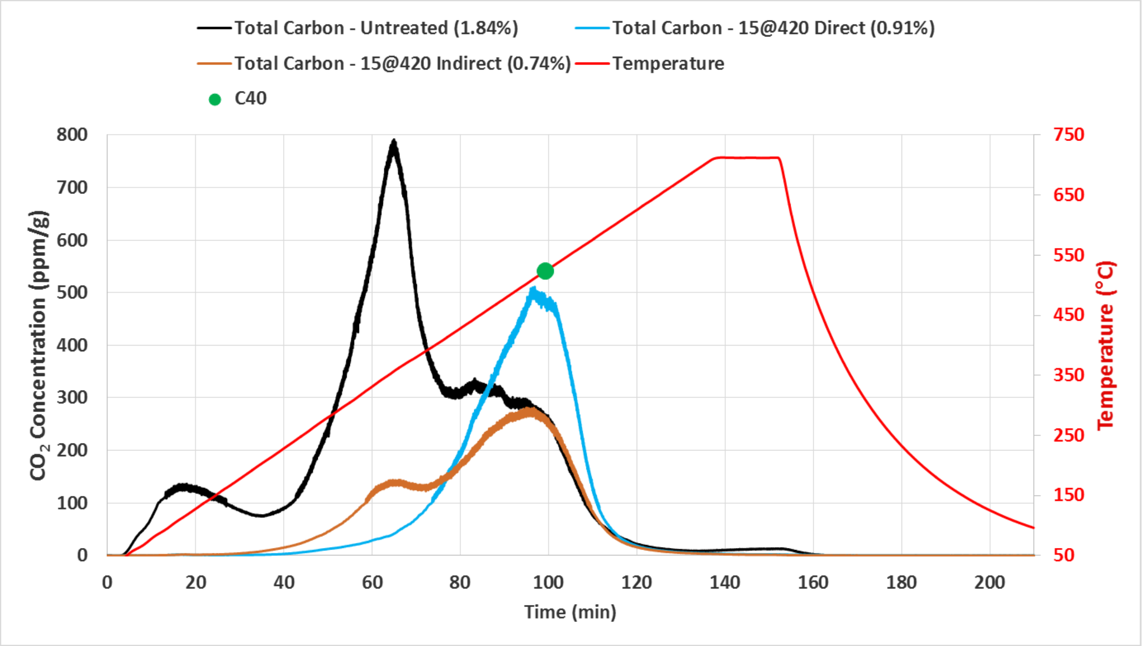

*Figure 42: $CO_2$ Evolution Plot - Total Carbon – Indirect vs Direct, 3% Oil (15 min at 420°C)*

The carbon distributions in Figure 42 are drastically different, with resulting differences in recovery percentages to match despite having identical treatment temperatures and residence times. The indirect treated curve consists of a small peak of 120 ppm/g at approximately 65 minutes and a larger peak of 280 ppm/g at 95 minutes. The direct treated curve has a single peak of 500 ppm/g at 95 minutes with evolution rising and falling at similar rates before and after the peak respectively. As mentioned previously, the direct treatment takes advantage of both devolatilization of hydrocarbons due to increased temperature, but also oxidation. Despite this, the recovery percentage for the direct treated soil is actually higher than that of the indirect treated soil.

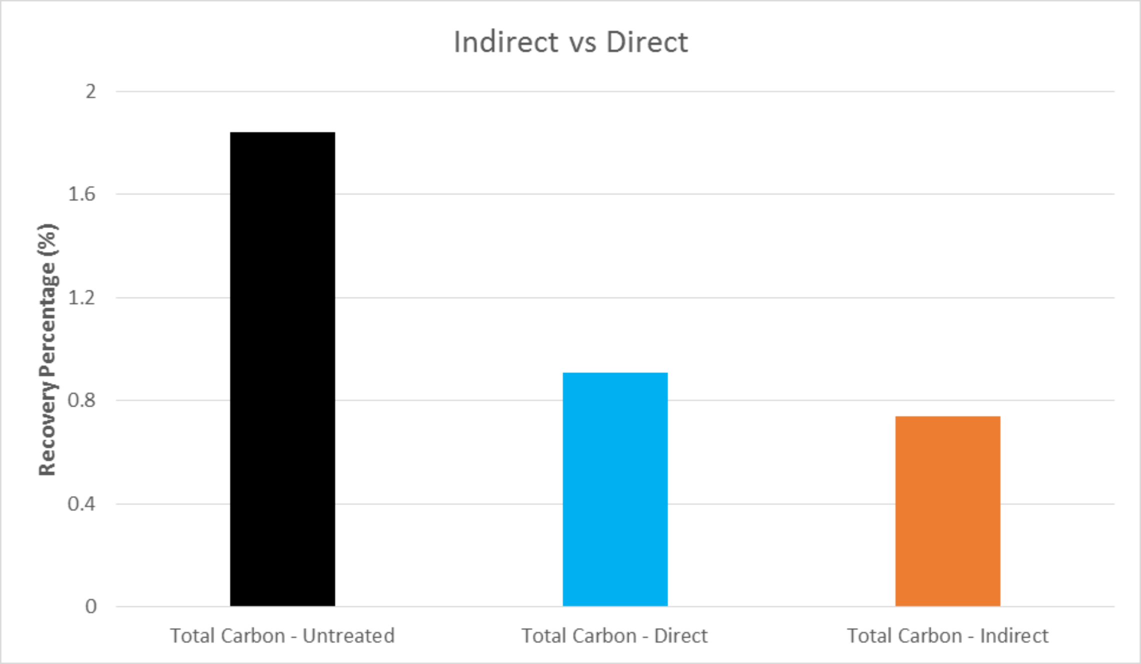

*Figure 43: Recovery Percentage Comparison - Total Carbon – Indirect vs Direct, 3% Oil (15 min at 420°C)*

The increased recovery percentage in the direct treated soil appears counter-intuitive. With two separate mechanisms at work removing hydrocarbons, it would seem obvious that the direct heated case would be capable of removing more contamination. Inspection of Figure 44 offers an explanation.

The plot shows concentrations of four different species present in the gas exiting the TDU: $CH_4$, $CO$, $CO_2$, and $H_2$. Each of four separate runs is demarcated by a vertical dashed red line. All four runs were direct heated treatments, with the remaining treatment parameters shown in Table 3.

*Table 3: Direct Heated Treatment Run Descriptions*

| Run | Oil Concentration | Treatment Temperature | Residence Time |
|---|---|---|---|
| 16 | 5 | 550 | 15 |
| 17 | 5 | 420 | 15 |
| 18 | 3 | 420 | 15 |
| 19 | 3 | 550 | 15 |

Throughout the direct treatment runs, $CO_2$ into the TDU was held constant so variations of $CO_2$ in the off-gas are solely results of processes taking place during treatment. Figure 44 shows a drop in $CO_2$ and CO concentrations starting at run 17 which continues throughout run 18. Because run 17 used a soil with 5% oil and run 18 used 3% oil, initial oil concentration can be eliminated as the cause of this imbalance between carbon containing species entering the TDU and those leaving the TDU.

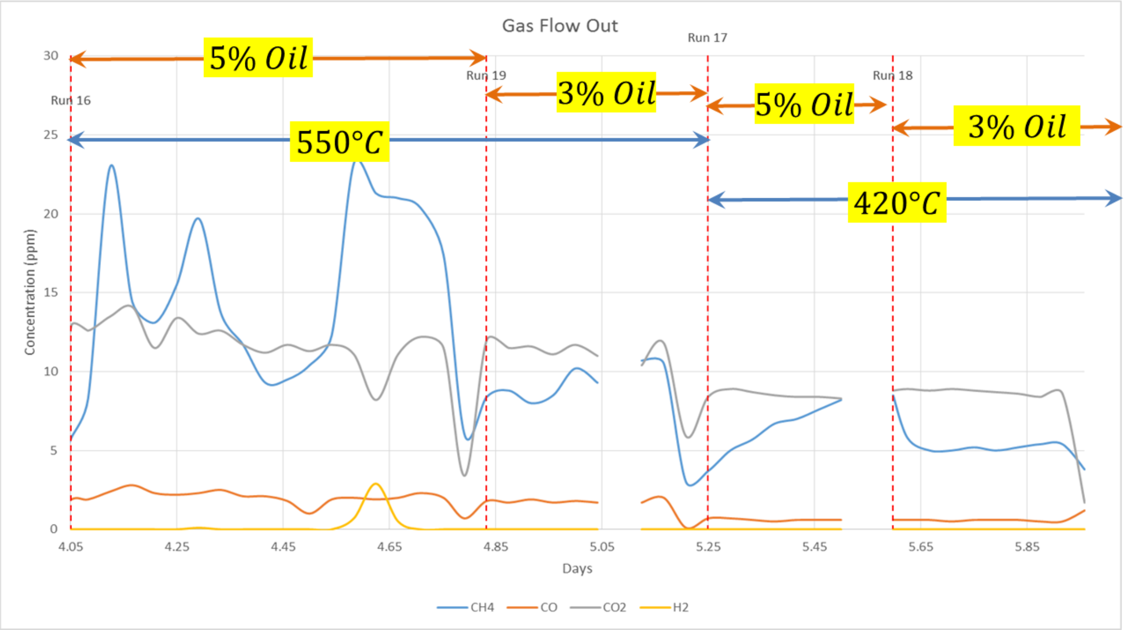

*Figure 44: Thermal Desorption Unit - Off-Gas Component Concentrations*

The difference between carbon entering and leaving the TDU can be explained by a Boudouard reaction, especially considering that the treatment was performed in an iron refractory furnace; a prime environment for such a phenomenon, this type of reaction is described as:

$$2CO \rightleftharpoons CO_2 + C$$

Where the forward direction becomes more favorable as temperatures decrease. [38]

The implication of this reaction is that the CO that resulted from incomplete oxidation of hydrocarbons as well as dissociation of $CO_2$ was converted into graphitic carbon which was then deposited onto the soil. In addition to the proximity of iron to the treatment process, this phenomenon occurring at the lower temperature of 420°C in runs 17 and 18 appears to contribute to evidence of this reaction. Additionally, the greater amount of fixed carbon in the direct treated soil compared to the indirect shown in Figure 45 could be the result of the graphitic carbon deposition mentioned previously.

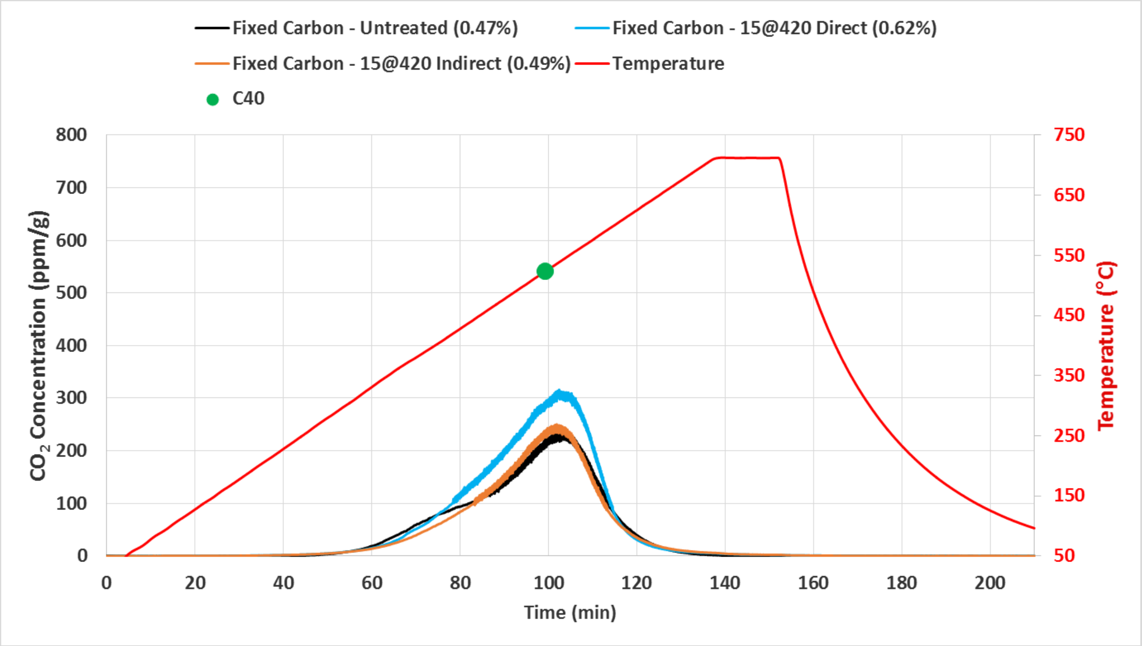

*Figure 45: $CO_2$ Evolution Plot - Fixed Carbon – Indirect vs Direct, 3% Oil (15 min at 420°C)*

The larger peak in fixed carbon of the direct heated soil as well as the larger recovery percentage of fixed carbon both indicate the presence either of more solid carbon or of more extra heavy hydrocarbons. The former would coincide with the Boudouard reaction hypothesis, however, further investigation would be needed to confirm.

# 4. CONCLUSIONS

## 4.1 Summary

The background soil analysis demonstrated that most of the carbon content on the unimpacted soil consisted of lighter hydrocarbon species that were primarily in the mobile carbon fraction. Comparing the background soil to the impacted, untreated soil, however, revealed the relative insignificance of the total carbon native to the background soil. This was due to an order of magnitude shift in the overall quantity of carbon present on the sample as seen in the sweep of temperature programmed reaction experiments. The untreated soil contains carbon content primarily consisting of lighter hydrocarbons, with almost the entirety of carbon evolution occurring prior to the C40 mark. This indicates that a large portion of contaminant hydrocarbons will have TPH range molecular sizes. The degree of contamination (i.e. oil concentration) has a fairly predictable effect on total carbon results, where soils impacted with 5% oil consistently produced results that were similar in form but larger in magnitude compared to 3% oil samples. This is especially true in the comparison of the untreated and indirect comparisons. The direct treatment, however, appears to have a normalizing effect on total carbon, perhaps as a result of combustion that is made possible by the presence of oxygen. The result was the recovery percentage of the 5% oil soil approaching and very nearly matching that of the 3% oil sample.

Temperature performed in a manner consistent with expectations as well although the degree to which it affected results varied greatly between the indirect and direct treatment variations. An increase in temperature produced a decrease in recovery percentage for the indirect heated soils, however extensive temperature increases produced diminishing returns on recovery percentage decreases. Furthermore, the minimum temperature (i.e. 370°C) resulted in a total carbon recovery percentage of less than 1%, indicating that the extra energy needed to increase treatment temperature is unnecessary from a regulatory perspective. These findings of satisfactory carbon content reduction were repeated with the direct treated soil (albeit at 420°C rather than 370°C), however temperature has a much more dramatic effect in those samples.

Similar to temperature, increased residence time resulted in decreases in recovery percentage. Extending the similarities, the added benefit of decreased carbon content is miniscule in comparison to the additional energy costs associated with longer treatment times. This is especially true considering that, again, the minimum value (15 minutes) provided a reduction in carbon well within the necessary limit.

Results for the indirect heated treatment were found to be given approximately by

$$RP = .372 * OC - .00521 * t - .00293 * T + .955$$

Where RP, OC, t, and T represent total carbon recovery percentage, initial oil concentration, residence time, and treatment temperature, respectively.

Finally, comparison of the indirect to the direct heated treatment yielding unexpected results. While both successfully reduced total carbon content below 1%, the indirect treatment actually provided a larger reduction. This difference is hypothesized to be a result of the Boudouard reaction in conjunction with an incomplete carbon balance in the gas flow entering and leaving the TDU. The disproportionation of carbon monoxide could have resulted in the deposition of solid carbon onto the direct treated soil, resulting in greater fixed carbon content and, consequently, a larger total carbon recovery.

## 4.2 Conclusions

This study has demonstrated that the minimum analyzed residence time and treatment temperature (15 minutes at 370°C for indirect heated thermal desorption and 15 minutes at 420°C for direct heated thermal desorption) are the best combination of thermal desorption treatment parameters for remediation of the subject contaminated soil. This was determined through comparison of treated soil carbon content with a TPH limit of 1%, as well as consideration of the costs associated with additional energy requirements. Furthermore, soil treated by direct heated thermal desorption was found to have additional nutritional benefits in the form of greater fixed and low mobility carbon compared to the indirect heated treatment performed at the same residence time and treatment temperature (15 minutes at 420°C). This was determined to be potentially attributable to the Boudouard reaction.

## 4.3 Future Work

Proceeding from this work, the first step should be ensuring the statistical significance of the results presented here. This will be followed by the further development of a conversion between results obtained through temperature programmed reactions and the exact TPH value associated with known samples. Subsequent results can then be viewed more accurately from the perspective of regulatory entities.

With the TPH conversion established, the necessary temperature programmed reaction experiments should then be conducted in order to determine exact TPH values for treated soils. Additional analysis should be performed regarding soil fertility and other ecologically valuable parameters. Using trends in TPH values as indicators, parameter effects can be extrapolated and used to optimize treatment conditions for both cost and effectiveness.

After the pilot scale treatments are performed and analyzed at the prescribed parameters, full scale testing can be carried out on a trial basis. Pending satisfactory performance, the ideal treatment conditions can be utilized for wide scale remediation application.

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# APPENDIX

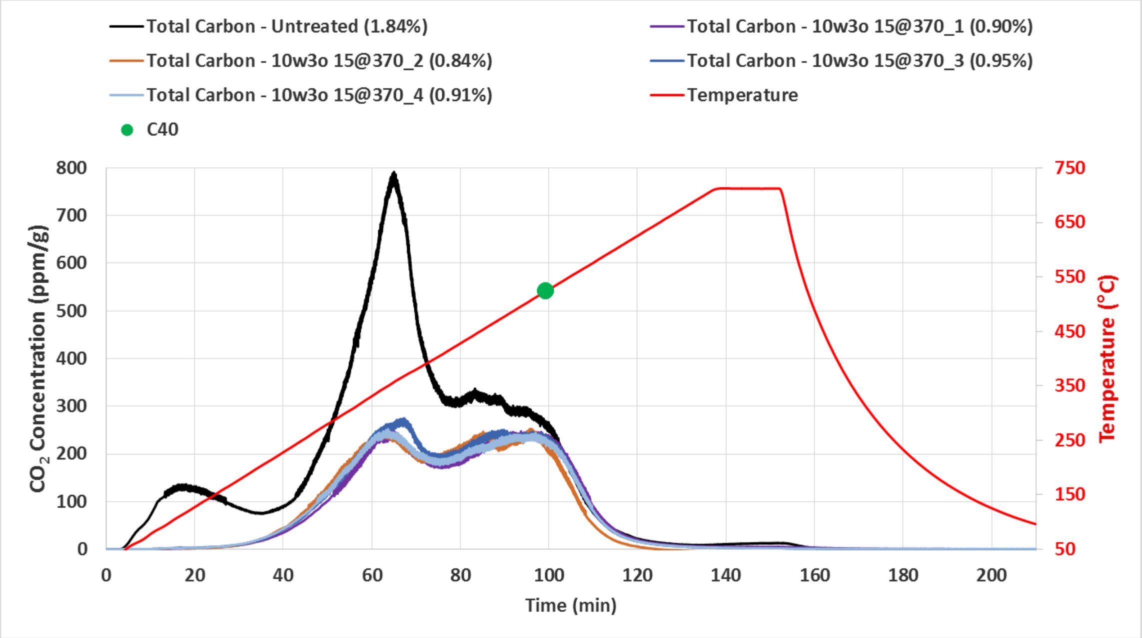

*Figure 46: Replicates of TPO - Indirect Treated 15 Minutes at 370°C*

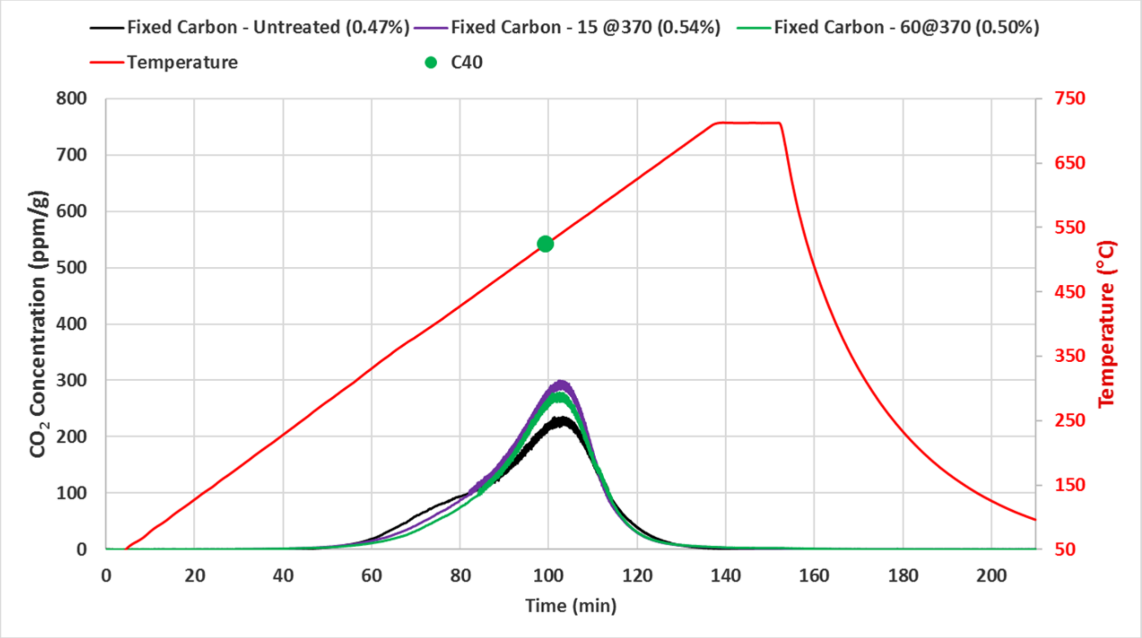

*Figure 47: Fixed Carbon vs Residence Time – Indirect*

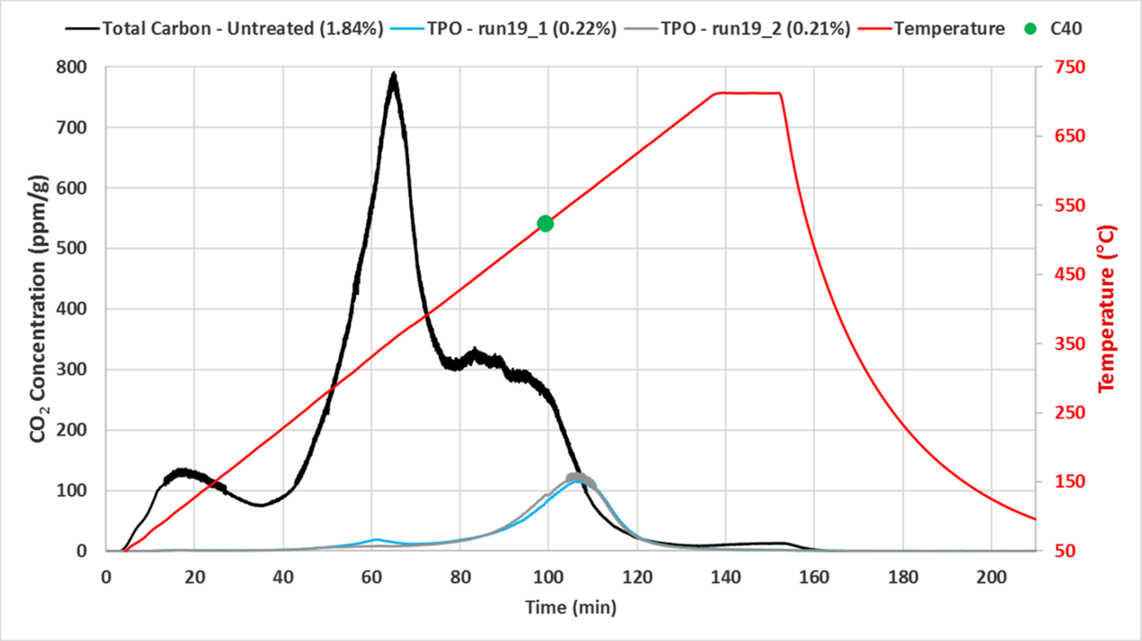

*Figure 48: Replicates of TPO - Direct Treated 15 Minutes at 550°C*

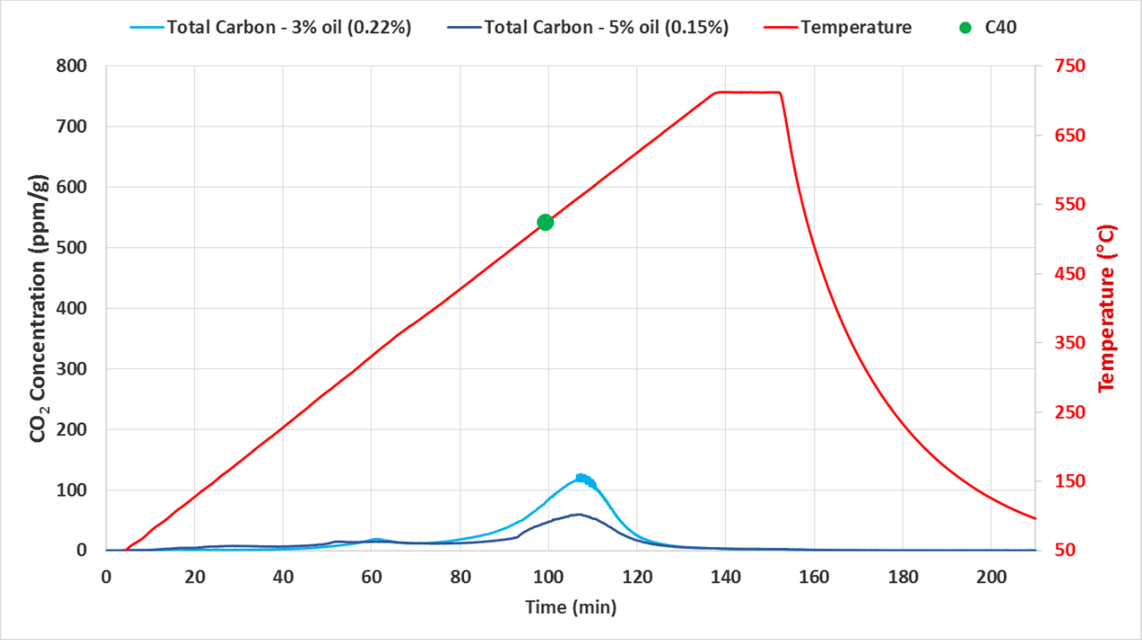

*Figure 49: Oil Concentration Comparison - Direct - 15 Minutes at 550°C*