Remediation of trichloroethylene-contaminated soils by star technology using vegetable oil smoldering

Remediation of Trichloroethylene-Contaminated Soils by STAR Technology using Vegetable Oil Smoldering

Madiha Salman[a], Jason I. Gerhard[a] , David W. Major[b] , Paolo Pironi[a1], and Rory Hadden[a1]

[a]Department of Civil and Environmental Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada

[b]Savron, 130 Research Lane, Guelph, Ontario, N1G 5G3, Canada

[1]Present Address: Institute for Infrastructure & Environment, University of Edinburgh, Edinburgh, EH9 3JL, UK

Corresponding Author:

Dr. Jason I. Gerhard
Dept. of Civil and Environmental Engineering
The University of Western Ontario
Spencer Engineering Building
London, Ontario, Canada N6A 5B9
Phone (519)661-4154; Fax: (519)661-3942; E-mail: jgerhard@uwo.ca

POSTPRINT (ACCEPTED MANUSCRIPT)

Published:

Abstract

Self-sustaining Treatment for Active Remediation (STAR) is an innovative soil remediation approach based on smoldering combustion that has been demonstrated to effectively destroy complex hydrocarbon nonaqueous phase liquids (NAPLs) with minimal energy input. This is the first study to explore the smoldering remediation of sand contaminated by a volatile NAPL (Trichloroethylene, TCE) and the first to consider utilizing vegetable oil as supplemental fuel for STAR. Thirty laboratory-scale experiments were conducted to evaluate the relationship between key outcomes (TCE destruction, rate of remediation) to initial conditions (vegetable oil type, oil:TCE mass ratio, neat versus emulsified oils). Several vegetable oils and emulsified vegetable oil formulations were shown to support remediation of TCE via self-sustaining smoldering. A minimum concentration of 14,000 mg/kg canola oil was found to treat sand exhibiting up to 80,000 mg/kg TCE. On average, 75% of the TCE mass was removed due to volatilization. This proof-of-concept study suggests that injection and smoldering of vegetable oil may provide a new alternative for driving volatile contaminants to traditional vapour extraction systems without supplying substantial external energy.

1. Introduction

Chlorinated volatile organic compounds (CVOCs), such as trichloroethylene (TCE) and tetrachloroethylene (PCE), are frequently encountered soil and groundwater contaminants [1, 2]. These compounds are often present as nonaqueous phase liquids (NAPLs) forming a source zone for long term groundwater contamination [3]. As known or suspected carcinogens [4], many CVOCs are high priority pollutants for clean-up.

TCE (C_2HCl_3), with a density of 1.46 g/ml at 20°C [5], is often found below the watertable. It exhibits low solubility (1450 mg/l), low boiling point (86.7 °C), and high vapour pressure (9700 Pa at 25°C) [6]. TCE concentrations between 10^3 and 10^6 µg/L in groundwater are typical at contaminated sites [7], while 5 µg/L is the typical regulatory limit [1]. Thus, a small amount of TCE DNAPL can result in contaminated groundwater for decades [8, 9]. Below the watertable, TCE can undergo anaerobic dechlorination under favorable geochemical and microbiological conditions [10, 11, 12]; biodegradation half-life values are typically from six months to one year, but rates are highly dependent on site conditions and engineering intervention [13, 14].

A remediation approach based upon smoldering NAPLs in soils was recently introduced [15,16]. Smoldering is a flameless form of combustion in which the exothermic oxidation reaction occurs on the surface of the fuel in a porous medium [17]. This reaction can be self-sustaining in the presence of sufficient fuel and oxygen (e.g., charcoal in a barbeque). Most of the studies on smoldering combustion consider porous solid fuels in the context of material synthesis [18] and fire safety [19-24]. In-situ combustion has been studied by the petroleum industry for enhanced oil recovery [25, 26]. In addition, smoldering of peat deposits has been studied due to environmental concerns [27, 28].

The first proof that a liquid distributed within an inert porous solid could be smouldered was provided by Pironi et al. [29]. Application of the process for the remediation of NAPLs within soils was first proposed by Switzer et al. [16]. NAPL smoldering was initiated by injecting air following the preheating of a local region of the soil with a one-time, short-duration energy input. The establishment and propagation of a self-sustaining smoldering front suggested that this process may have utility in subsurface remediation [16]. The process was demonstrated to be robust over a wide range of operating conditions [15]. Subsequently, it was demonstrated that smouldering NAPL could be scaled up 1000-fold from laboratory conditions [30]. Recently, several successful pilot field trials of in situ STAR have been completed beneath a former chemical manufacturing facility contaminated by coal tar [31]. These field tests demonstrated that a short, in-well ignition event (several hours) generated a self-sustaining smoldering reaction lasting more than 10 days that propagated outwards to remediate the soil within a 3.5 m radius of influence. More than 4,000 kg of coal tar were destroyed in the pilot tests conducted below the water table, revealing that groundwater is not a barrier to in situ STAR.

All of the published research and field trials on remediation using smoldering have treated heavy, complex compounds such as coal tar and crude oil (i.e., non-volatile). The high volatility of CVOC NAPLs is expected to be a barrier to self-sustaining smouldering. Switzer et al. [16], however, showed that a smoldering reaction could be initiated in TCE NAPL mixed with vegetable oil (75%:25% mass ratio of TCE:Oil) with a single proof-of-concept bench test.

Subsurface injection of vegetable oils is a well-established practice to support in-situ anaerobic biodegradation [32-35]. There is evidence that injected vegetable oil partitions into TCE NAPL in soil due to their mutual miscibility [36]. This work postulates that vegetable oil could provide a supplemental fuel for self-sustaining smoldering to remove volatile NAPLs from the subsurface.

Volatilizing and oxidizing CVOCs in situ via smoldering could provide numerous cost, energy, carbon footprint and time savings relative to existing remediation techniques; these are discussed more fully in Section 4.

The chemistry of smoldering combustion is complex. Smoldering is characterized by both pyrolysis (endothermic thermal degradation of the fuel to form a carbon-rich char) and oxidation (exothermic reaction between the char and oxygen) reactions. Self-sustaining smoldering is, however, necessarily dominated by oxidation as its exothermic nature provides the energy required for the reaction to propagate [27]. The study of the chemical reactions of smoldering is not a mature topic and in general only simple, qualitative reaction frameworks are reported; even for the most studied fuels (e.g., polyurethane foam), quantitative (stoichiometric) chemical reactions are not known [28]. Assuming that the oxidative and non-oxidative thermal decomposition products reported in the literature for TCE incineration are relevant to this study, the potential chemical by-products associated with TCE decomposition are summarized [37, 38] :

Pyrolysis

$$C_2HCl_3 \text{ (TCE)} \rightarrow C_2Cl_2 \text{ (DCA)} + C_2Cl_3 \text{ (Chlorinated vinyl radical)} + C_2Cl_4 \text{ (PCE)} + HCl \quad (1)$$

Oxidation

$$C_2HCl_3 \text{ (TCE)} + O_2 \rightarrow CO + CO_2 + Cl_2 + COCl \text{ (Carbonyl chloride)} + COCl_2 \text{ (Phosgene)} + C_2Cl_4$$

$$\text{(PCE)} \quad (2)$$

The mode of combustion (flaming or smoldering) will play a significant role in determining the products of combustion and the stoichiometry; therefore the above reactions are presented only as a basis for likely products. It is noted that these products include some of concern such as phosgene, a toxic gas [37, 38].

5

The objective of this study was to explore the conditions necessary to treat TCE NAPL-contaminated soil by smoldering combustion using vegetable oil as a supplemental fuel. Bench-scale experiments were conducted to provide a proof-of concept and to evaluate the sensitivity of the process to oil type and mass ratio of oil to TCE. Experiments were also conducted to assess if the oil could be delivered by injection of pure oil and as an oil emulsion. The smoldering characteristics, rate of remediation, and resulting concentrations of key compounds in sand and vapours were quantified to assess the fate of TCE and vegetable oil. This represents the first evaluation of the smoldering of vegetable oil and the first consideration of treating volatile NAPLs by smoldering.

2. Materials and Methodology

Number 12 silica sand (Bell & Mackenzie Co. Ltd., mean grain diameter = 0.88mm, coefficient of uniformity = 1.6) was employed for all experiments. TCE (Commercial ACS grade, Alfa Aesar) was mixed manually with commercially available vegetable oil and the sand until homogeneous (precautions taken to minimize volatilization); the organic liquids were observed to coalesce into a single NAPL. In each experiment, a quartz column (Quartz Scientific Inc., 280mm high x 138mm internal diameter) was immediately packed with this synthetic contaminated sand.

The column was packed and operated according to established procedures [15,16]. Laboratory air was delivered through a stainless steel diffuser at the column's base (Figure 1). A cable heater (120V, 450W, Watlow Ltd.), connected to a variable power supply (Staco), was packed 3cm above the diffuser providing the ignition source. A 10 cm layer of the contaminated sand was then added, followed by a 3cm layer of clean sand. Thermocouples (Omega Ltd., 1.5mm x 0.5m, inconel sheath, Type K) were inserted along the centreline of the column at 1cm intervals and connected to a computer by a datalogger (34980A, Agilent). The standard ignition sequence was

followed, in which (i) power was supplied to the heater for a short period, (ii) air darcy flux of 9.15cm/s was started, (iii) immediately afterwards, the heater was turned off, (iv) air flow was maintained until the reaction had propagated the length of the column. Temperatures were recorded every 2s and the mean and variance of the smoldering front velocity was calculated following standard methods [15].

Samples of exhaust gas were collected (EPA Method 0040) for subsequent analysis (Figure 1). Exhaust gas was continuously drawn at a steady rate into the Tedlar® bag to provide a time-integrated sample for each phase: preheating, combustion, and cooling. Exhaust gases were quantified by gas chromatography–mass spectrometry (GC-MS) (Agilent with DB-624 column) using an adaptation of EPA Method 8021b. TCE and PCE were quantified since together accounting for more than 99% of the detected mass in all cases. Gas sampling for phosgene was conducted using sorbent tubes (XAD-2) that were sent to an external lab (ALS). To achieve a detection threshold of 0.1 µg/sample, a single sorbent tube was employed to collect a subsample of the continuous emission stream (pump rate of 150 cm^3/min) for two repetitions of the base case experiment. The presence of CO_2 and CO were monitored (MultiRAE IR gas analyzer) to identify the onset and duration of combustion. A sample of the contaminated sand was collected when the column was packed. Post-treatment sand was sampled at four depth intervals, for which the TCE was extracted and analyzed (EPA Method 5021).

Four sets of experiments were conducted to explore the sensitivity of NAPL smoldering to several key parameters (Table 1). The first examined the influence of oil type, with five experiments using commercially available, food grade vegetable oils - canola, corn, olive, peanut, soybean, and sunflower - and one with the biodiesel methyl soyate (Columbus Vegetable Oil® CAS no. 67784-80-9). Experiment 1, referred to as the base case, was conducted four times to assess repeatability

of smoldering behaviour (average peak temperature, velocity of the front) and sand and gas analyses (conducted on two of these four experiments).

The second set of experiments, involving 15 tests, examined the influence of the concentrations and proportions of the oil and TCE NAPL (Table 1). Six experiments in this set varied the TCE NAPL concentration for a constant canola oil concentration (Experiments 8-13) while five varied the canola oil concentration for a constant TCE NAPL concentration (Experiments 14 - 18). Four additional experiments explored the lower threshold of oil necessary to support a self-sustaining smoldering reaction for different TCE NAPL concentrations (Experiments 19 - 22).

The third set of experiments considered the use of emulsified vegetable oil (EVO) instead of neat oil. Three EVO mixtures, stable for at least 5 days, were created in a commercial mixer using canola oil, water, sodium lactate (Alfa Aesar) as an emulsifier, and span 60 (sorbitan monostearate, Alfa Aesar) as a surfactant. The three EVO solutions (termed EVO-A, EVO-B, and EVO-C) have slightly varying compositions (Table 2). Experiments involved pre-mixing the sand with only EVO (Experiments 23-25) or with a mixture of EVO and TCE NAPL (Experiments 26 and 27). Viscosity of EVO-C was measured at 1924 cP, in comparison to canola oil at 57 cP. 24% by mass water in each EVO provided approximately 4% water saturation in the sand.

The fourth set of experiments was conducted to assess the effect of oil injection on smoldering. In Experiment 28, a NAPL composed of TCE and neat canola oil (in the same proportion as the base case) was slowly injected (Watson Marlow Pump 520S) until ponding on top of the sand and then gravity drained to residual. In Experiment 29, the sand was pre-mixed with TCE NAPL then canola oil was injected into the column and drained to residual. Experiment 30 involved injecting

a mixture of TCE and EVO-C in the column packed with clean sand and then draining the column under gravity. All of these experiments were subjected to the same smoldering ignition protocol.

3. Results and Discussion

3.1 Base Cases

The temperature-time profiles for the base case (Experiment 1) illustrates that, upon initiating air flow, a temperature spike was observed that represents the onset of smoldering combustion (Figure 2). After the heater was turned off (t=44 minutes), the reaction was self-sustaining as evidenced by the succession of nearly constant peak temperatures. The figure illustrates that the smoldering front required 20 minutes to propagate the length of the column and, following the reaction's natural extinction when all the fuel was consumed, 50 minutes for the column to cool down. The average peak temperature (ignoring the first thermocouple to remove the boundary effect) was 543.0 ± 0.2°C and the average velocity of the smoldering front was 0.56 ± 0.08 cm/min. These values fall within the range of those reported for 15% to 50% saturation crude oil in medium sand [15].

All four repeats of the base case experiment produced consistent results. Calculating 95% confidence intervals assuming a logarithmic distribution of random error, the mean average peak temperature was 543 ± 15°C and the mean propagation velocity was 0.54 ± 0.10 cm/min. These estimates of uncertainty were assumed to apply to all subsequent experiments.

Experiment 14, identical except the sand was contaminated with 10% saturation TCE-NAPL alone, exhibited different behaviour. In this case, the peak temperatures successively decreased as insufficient heat was released by the smoldering reaction to allow continued propagation (Figure 3); this is not a self-sustaining reaction. In contrast, Experiment 8, which employed 15%

saturation of canola oil alone, produced a self-sustaining reaction similar to the base case (figure not shown). Thus, TCE alone was not sufficient to support a self-sustaining smoldering reaction but canola oil was with or without TCE present. This is not surprising since vegetable oil contains significantly more chemical energy than TCE (e.g., the heat of combustion of vegetable oil is about five times greater than that of TCE). Comparing Experiments 1 and 8, the average peak temperatures were similar (542°C and 552°C, respectively; i.e., within the expected error); thus, it is likely that the presence of TCE in these experiments had little effect on the self-sustaining smoldering reaction with the front propagating primarily due to the smoldering canola oil.

TCE, PCE, CO_2 and CO were found to dominate the gas emissions for these experiments. Traces of other compounds, including heptane, benzene, pentane, propenal, hexane, and octane, were observed in all experiments, including Experiment 8 with no TCE, and are consistent with known byproducts from the pyrolysis of edible oils [39]. Table 3 presents the fate of TCE for all of the experiments in which gas analysis was conducted including Experiments 1 (two repeats) and 14. First, the table illustrates the consistency of the experimental method for two repeats of the base case; for example, the total mass of TCE observed in gas and sand varied only by 2% (0.03 moles) between the repeat experiments. The table further reveals that no detectable TCE remained in the treated sand. Although post-treatment oil content was not measured, the sand in the combustion zone was observed to be clean and dry upon excavation. This matches expectations as, for self-sustaining smoldering experiments with crude oil, chemical analysis of post-treatment sand exhibited non-detect for total petroleum hydrocarbons [15].

Table 3 reveals that, averaging the two repeats of the base case, the fraction of TCE residing below the heater – due to remobilization during preheating period – was 1.7% of the initial mass, and the fraction of TCE volatilized was 75.5%. Less than 1% of the volatilized TCE was

generated during the pre-heating stage, 84% was generated during the combustion phase, and almost 16% was generated during the cooling stage. Assuming the difference between the total mass of TCE observed (in gas and post-test sand) and the initial TCE mass is due to destruction/conversion by combustion processes suggests that, in the base case, approximately 21% of the TCE mass was destroyed (i.e., primarily converted to CO and CO_2) (Table 3 final row).

Table 3 further reveals that gaseous PCE, the second largest VOC peak detected, exhibited a concentration two orders of magnitude lower than that of TCE. In addition, 3×10^{-9} moles of phosgene was found in the exhaust gas. Using the constant pumping rate attached to the sorption tube, the concentration of phosgene in the gas stream immediately above the sand surface was 0.04 mg/m^3, which is an order of magnitude below the OSHA and NIOSH regulatory limit for phosgene (0.4 mg/m^3) [40]. Given the current state of the art of smoldering chemistry, it is not possible to relate the quantity of PCE or phosgene to the amount of TCE that was burnt. While Table 3 presents a simplification of a complicated system (involving volatilization and condensation as well as pyrolysis and oxidation), since the majority of the initial TCE mass was directly observed, it is likely a reasonable approximation for engineering purposes.

3.2 Oil Type and TCE/Oil Saturation

Like canola oil, self-sustaining (SS) smoldering was exhibited by peanut oil and sunflower oil while, in contrast, methyl soyate exhibited a reaction that was not self-sustaining (NSS) (Table 1, Figure 4). Soybean oil, olive oil and corn oil exhibited behaviour that does not fit the definition of SS or NSS. Each exhibited a strong ignition followed by a sequence of peak temperatures that slowly decreased as the smoldering front propagated up the column. In all cases energy was being generated and propagated forward and the final peak temperature was well above that observed

during self-sustained smoldering for some fuels (e.g., peanut oil); for example see Figure 5. This behaviour may indicate that NAPL has mobilized due to viscosity reductions and the oil concentrations decrease with height. Alternatively, it may reveal that the column is too short for SS behaviour to be achieved before the end of the column is encountered. It is also possible that, given a longer column, the peak temperatures would continue to decline until the reaction extinguished. These types of experiments are classified in Table 1 as 'unknown' (UNK) with respect to self-sustaining smoldering. In all cases, the sand excavated from the columns appeared completely clean and dry.

The differences observed between oil types are not easily explained by thermal properties alone. While it is typical to initially consider energy content, the heats of combustion of 20 vegetable oils are nearly identical (39.5 $\pm$ 0.5% kJ/g; [41]). Thus, it is likely that the differences observed between the smoldering experiments with different vegetable oils are the result of a combination of chemical factors related either to their ability to smoulder (e.g., differing activation energy or alternative reaction pathways), or physical factors such as the initial viscosity of the oil/NAPL mixture and its dependence on temperature, which in turn dictates NAPL mobility in the heated region ahead of the front. Where thermophysical properties such as heat capacity, thermal conductivity and density vary between oils, these may also play a role.

Experiments 8 – 22 explored the sensitivity of smoldering to the concentrations of canola oil and TCE NAPL. They reveal that a minimum of 14,000 mg/kg canola oil was required for a self-sustaining combustion reaction in sands contaminated with up to 80,000 mg/kg TCE NAPL (Table 1, Figure 6). This compares to the minimum concentrations reported for coal tar at 21,300 mg/kg and crude oil at 20,800 mg/kg at the column scale [15].

The smoldering reaction was found to be self-sustaining for all the cases in which the TCE saturation did not exceed 20% of pore volume for oil saturations in the range 5%-15% (Figure 2). When TCE saturation was greater or equal to 30% and oil saturation was limited to a maximum of 15%, the smoldering front propagated in a decaying manner. A number of factors likely explain these results, including (i) lack of sufficient heat released to overcome that lost through volatilization of the TCE and preheating of fuel ahead of the front, and (ii) increased downward NAPL migration during preheating, resulting in lower fuel content in the top half of the column.

The results further reveal that the average peak temperature and the front propagation velocity for self-sustaining experiments are insensitive to the TCE/Oil ratio (Figure 6). The average peak temperature for Experiments 8-22 was observed to be 553±24°C and the average propagation velocity was 0.59±0.10 cm/min. Pironi et al. [15] observed similar values for crude oil-contaminated sand and also observed similar insensitivity to fuel content. This is likely because the increase in energy generated with additional fuel is balanced by the increase in volumetric heat capacity [15].

3.3 EVO and Oil Injection

Of the three stable EVOs used, the one formulated with methyl soyate (EVO-B, Experiments 24 and 26) did not exhibit self-sustaining smoldering. EVO-A and EVO-C, formulated with canola oil, demonstrated self-sustaining smoldering in the absence of TCE NAPL (Experiments 23 and 25) and with TCE NAPL (Experiment 27). Comparing this latter experiment (Figure 7: 10% TCE/10% canola oil/4%water) with Experiment 16 (10% TCE/10% canola oil) reveals identical propagation velocities (0.63±0.09 cm/min) and similar average peak temperatures (565 and 569±15 °C, Table 1). These similarities suggest that the water content of the EVO had a negligible effect.

When a mixture of canola oil and TCE-NAPL (in same proportions as the base case) was injected into and drained from the pre-packed sand column (Experiment 28), self-sustaining propagation was observed with an average peak temperature and an average front velocity similar to the base case (Figure 8, Table 1). However, the thermocouple profiles exhibit more variability, suggesting that the front propagated in a less uniform manner, likely due to a heterogeneous NAPL saturation distribution associated with the emplacement process. However, clearly sufficient fuel existed throughout the porous medium to support the continued propagation of the reaction. No TCE was detected in the post-treated sand above the heater (like the base case). Gas analysis indicates that the percentage of TCE volatilized was similar to that of base case (Table 3) where TCE/oil/sand were pre-mixed. Very similar results were found for Experiment 30, which was identical except that a mixture of TCE NAPL and EVO-C was employed. This suggests that injecting oil/EVO, does not impede self-sustaining propagation of the front, at least with relatively homogeneous sand.

The case in which only canola oil was injected and drained from sand that was contaminated with TCE NAPL (Experiment 29), was also found to be self-sustaining. However, the propagation velocities in the experiments where NAPL was freely drained (Experiments 28 - 30) were approximately 20% lower than those of all other self-sustaining experiments (Table 1). Pironi et al. (2011) reported a similar reduction of smoldering propagation velocity with crude oil in sand at low concentrations (approaching residual NAPL values). This is likely due to the reduced amount of heat available for transport ahead of the front (less preheating) when a minimal amount of NAPL (i.e., fuel) is available.

Table 3 indicates that the observations on TCE fate obtained from the base case apply across a range of other representative experiments including high and low initial TCE content (Experiments 12 and 17, respectively), and involving EVO-C pre-mixed in the sand and added via injection (Experiments 27 and 28, respectively). In no cases was oil observed or TCE detected in the post-treatment sand, and in all cases less than 2% of the initial TCE was found to have migrated to below the heater. The estimated fraction of TCE destroyed *in situ* during the experiments ranged from 3% to 39%.

4. Discussion on Environmental Relevance

Enhanced in situ bioremediation (EISB) of CVOC NAPL source zones has significant potential but it is slow, requiring on the order of years to decades [42]. More rapid treatment can be achieved with standard thermal remediation techniques, such as in situ thermal desorption and electrical resistance heating. However, these require continual energy input since they heat the entire site to above 100°C, a process which requires several months of electricity injection [43] leading to substantial expense and carbon footprint.

This work reveals that STAR has the potential to be an alternative in situ technology for remediating volatile NAPLs such as CVOCs. Like other thermal technologies, the primary means of remediation would be vapour stripping. The equipment for vapour capture and treatment would be identical to that used for existing thermal remediation techniques. However, the self-sustaining nature of the reaction, and the dependence on a short, one time energy input for each ignition location, means that it may provide significant savings with respect to electricity, with consequent reductions in costs and carbon footprint. It is also expected to be much faster, with a STAR reaction propagating below the water table through NAPL-occupied soil at a rate of approximately 0.5 – 1.0 m/d [31], which substantially exceeds the rate at which a boiling front will propagate due to conductive of resistive heating.

In situ STAR for volatile NAPLs would depend on the injection of neat or emulsified vegetable oil throughout the source zone. This is well developed technology for EISB, with the vegetable oil typically injected using temporary direct push points. Emulsifying the oil increases its mobility and distribution in the subsurface relative to neat oil, thereby reducing the number of direct push locations required. Emulsified oils have been injected at hundreds of EISB sites in North America. Due to the widespread availability of vegetable oils and the ease of emulsification the cost of EVO injection is reasonable. Contractors are familiar with the process and specialized equipment is not needed. It is expected that vegetable oil injections would be targeted at CVOC NAPL hotspots and that in situ STAR ignitions would be associated with each hotspot, eliminating the need to uniformly treat the entire site. The cost and carbon footprint implications for vegetable oil injection would need to be included in a full life cycle analysis of in situ STAR implementation for a site.

It is expected that the ignition equipment and procedures developed for in situ STAR applications at coal tar sites would work equally well for volatile NAPL source zones impregnated with vegetable oil. It is expected that, like with coal tar, the technique will work equally well above or below the water table. The peak temperatures of more than 500°C should be sufficient to drive a boiling front ahead of the reaction front while having excess energy to drive the self-sustaining reaction. The effect of water has not been examined in this initial proof-of-concept study because this is a phenomenon that needs to be studied at a much larger scale than possible in the laboratory (where boundary effects, such as the heat loss at the walls and the distance over which the heater has influence, are large). Within the smoldered region, the treated soil is expected to be sterile and devoid of organic carbon. However, it is expected that within a few weeks of the treatment, groundwater flowing back into this region will repopulate the soil with native bacteria [44].

Like air sparging, the method does rely on distributing the air effectively through the NAPL source zone. Air sparging, which relies on air bubble propagation through otherwise water saturated pores, is very sensitive to permeability contrasts. In situ STAR is less sensitive to heterogeneity because, like demonstrated in the field with coal tar, a region of preferential air flow through air-filled porosity is established between the ignition/air injection well and the propagating reaction front [31]. It is expected that the reaction will not effectively travel through clay, which in any case is unlikely to be penetrated with vegetable oil. It is expected that the smoldering reaction passing by a low permeability lens may heat that lens to above the boiling temperature and thus achieve some remediation. Overall, however, in situ STAR is not expected to substantially treat diffused CVOC mass in low permeability lenses. Rather it is envisioned as a primary treatment approach for significant amounts of NAPL at heavily contaminated sites; a follow-up, polishing technique (e.g., natural attenuation, in situ bioremediation) may be necessary.

5. Conclusions

This study demonstrated, for the first time, the ability for volatile NAPLs to be removed from soil via self-sustaining smoldering combustion of vegetable oil. While some destruction occurred, the majority of TCE mass was volatilized. The study further demonstrated that emulsified vegetable oil could equally be used instead of neat vegetable oil. In addition, it was demonstrated that the oil could be injected into previously contaminated soil. It is expected that vegetable oil or EVO could be distributed through the volatile NAPL source zone using existing technology, and self-sustaining smoldering may be a cost-effective and low-carbon-footprint method for extracting the contaminants.

There are still significant design issues that require investigation for *in situ* applications. Like already demonstrated for in situ STAR treatment of coal tar sites, it is expected that this would work equally well above or below the water table. However, field pilot testing is required to confirm this and also explore the influence of subsurface heterogeneity. Further investigation is required on the fate of volatilized CVOCs and emitted byproducts passing through moist soils above the source zone. Application of the technique as an ex situ treatment for excavated NAPL-contaminated soil avoids many of the challenges of in situ treatment and is currently being investigated for several types of contaminants (e.g,. waste oils, lagoon sludges).

Acknowledgments

References

[1]   Canadian Council of Ministers of the Environment, Canadian Soil Quality Guidelines, Trichloroethylene: Environmental and Human Health Effects; ISBN 978-1-896997-76-6 PDF, 2007.

[2]   Q. Dai, Low-Temperature Catalytic Combustion of Trichloroethylene over Cerium Oxide and Catalyst Deactivation, Applied Catalysis B: Environmental, 81 (2008) 192.

[3]   B.H. Kueper, G.P. Wealthall, J.W.N. Smith, S.A. Leharne, D. N. Lerner, An Illustrated Handbook of DNAPL Transport and Fate in the Subsurface. Prepared for the United Kingdom Environment Agency; ISBN 1844320669, R&D Publication, 2003, pp 67.

[4]   Health Canada, Guidelines for Canadian Drinking Water Quality: Supporting Documentation - Trichloroethylene. Water Quality and Health Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario, 2005.

[5]   ATSDR (Agency for Toxic Substances and Disease Registry), Toxicological Profile for Trichloroethylene, U.S. Department of Health & Human Services, 1995.

[6]   D.P.H. Hsieh, T.E. McKone, F.F. Chiao, R.C. Currie, Intermedia Transfer Factors for Contaminants Found at Hazardous Waste Sites. Trichloroethylene (TCE). Risk Science Program (RSP), Department of Environmental Toxicology, University of California, Davis, California, 1994, pp 43.

[7]   CEPA (Canadian Environmental Protection Act), Priority Substances List Assessment Report: Trichloroethylene, Environment Canada, Health Canada. 1993.

[8]   R. Cohen, J. Mercer, DNAPL Site Evaluation, EPA 600/R-93/022. Office of Research and Development, U.S. EPA, 1993.

[9]   J.F. Pankow, J.A. Cherry, Dense chlorinated solvents and other DNAPL's, in groundwater: history, behavior, and remediation, Waterloo Press, Portland, Ore, 1996, pp 522.

[10]   P.H. Howard, R.S. Boethling, W.M. Maylen, W.F. Jarvis, Handbook of environmental degradation rates, Lewis Publishers, Chelsea, MI, 1991, pp 776.

[11]   D.W. Major, M.M. McMaster, E.E. Cox, E.A. Edwards, S.M. Dworatzek, E.R. Hendrickson,, M.G. Starr, J.A. Payne, L.W. Buonamici, Field demonstration of successful bioaugmentation to achieve dechlorination of tetrachloroethene to ethane, Environmental Science & Technology, 36 (2002) 5106–5116.

[12]   U.S. Environmental Protection Agency (U.S. EPA), TCE removal from contaminated soil and ground water. EPA Ground Water Issue; EPA/540/S-92/002, Office of Solid Waste and Emergency Response, Washington, DC, 1992.

[13] U.S. Environmental Protection Agency (U.S. EPA), A Citizen's Guide to Soil Vapor Extraction and Air Sparing; EPA 542-F-01-006, Office of Solid Waste and Emergency Response, Washington, DC, 2001.

[14] I. Kouznetsova, X. Mao, C. Robinson, D.A. Barry, J.I. Gerhard, P.L. McCarty, Biological Reduction of Chlorinated Solvents: Batch-scale Geochemical Modeling, Advances in Water Resources, 33 (2010) 969–986.

[15] P. Pironi, C. Switzer, J.I. Gerhard, G. Rein, J.L. Torero, Self-Sustaining Smoldering Combustion for NAPL Remediation: Laboratory Evaluation of Process Sensitivity to Key Parameters, Environmental Science & Technology, 45 (2011) 2980-2986.

[16] C. Switzer, P. Pironi, J.I. Gerhard, G. Rein, J.L. Torero, Self-Sustaining Smoldering Combustion: A Novel Remediation Process for Non-Aqueous-Phase Liquids in Porous Media, Environmental Science & Technology, 43 (2009) 5871-5877.

[17] T.J., Ohlemiller, Smoldering Combustion, in P.J. DiNenno (Ed.), SFPE Handbook of Fire Protection Engineering, 3rd Edition, National Fire Protection Association, Massachusetts 2002, pp 1600.

[18] A.G. Merzhanov, B.I. Khaikin, Theory of Combustion Waves in Homogenous Media, Progress in Energy and Combustion Science, 14 (1998) 1-98.

[19] T.J. Ohlemiller, Modeling of smoldering propagation, Progress in Energy and Combustion Science, 11 (1985) 277-310.

[20] J.L. Torero, A.C. Fernandez-Pello, Natural convection smolder of polyurethane foam, upward propagation, Fire Safety Journal, 24 (1995) 35-52.

[21] J.L. Torero, A.C. Fernandez-Pello, Forward smolder of polyurethane foam in a forced air flow, Combustion and Flame, 106 (1996) 89-109.

[22] Bar-Ilan, A. et al. Transition from forward smoldering to flaming in small polyurethane foam samples, Proceedings of the Combustion Institute, Elsevier Ltd, Chicago, IL, United states, 2005, pp 2295-2302.

[23] G. Rein, Computational model of forward and opposed smoldering combustion with improved chemical kinetics, Berkeley, University of California, 2005, pp 169.

[24] A.C. Fernandez-Pello, G. Rein, D.L. Urban, Computational model of forward and opposed smoldering combustion in micrograving, Proceedings of the Combustion Institute. 2007, pp 7.

[25] M. Greaves, T.J. Young, S. El-Usta, R.R. Rathbone, S.R. Ren, T.X. Xia, Air injection into light and medium heavy oil reservoirs: combustion tube studies on West of Shetlands clair oil and light Australian oil, Chemical Engineering Research and Design, 78 (2000) 721-730.

[26]   I.Y. Akkutlu, Y.C. Yortsos, The dynamics of in-situ combustion fronts in porous media, Combustion and Flame, 134 (2003) 229-247.

[27]   G. Rein, Smoldering combustion phenomena in science and technology, International Review of Chemical Engineering, 1 (2009) 3-18.

[28]   R.M. Hadden, G. Rein, C.M. Belcher, Study of the competing chemical reactions in the initiation and spread of smoldering combustion in peat, Proceedings of the Combustion Institute, 34 (2013) 2547–2553.

[29]   P. Pironi, C. Switzer, G. Rein, J.I. Gerhard, , J.L. Torero, A. Fuentes, Small-scale forward smouldering experiments for remediation of coal tar in inert media, Proceedings of the Combustion Institute 32 (2009) 1957–1964.

[30]   C. Switzer, P. Pironi, J.I. Gerhard, G. Rein, J.L. Torero, Volumetric scale-up of smoldering remediation of contaminated soils, Journal of Hazardous Materials, 268 (2014) 51-60.

[31]   G. Scholes, Ignition method development and first field demonstration of in situ smouldering remediation, University of Western Ontario, 2013, 146 p.

[32]   K.J. Boulicault, R.E. Hinchee, T.H. Wiedemeier, S.W. Hoxworth, T.P. Swingle, E. Carver, P.E. Haas, VEGOIL: A Novel Approach for Stimulating Reductive Dechlorination, in G.B. Wickramanayake, A.R. Gavaskar, B.C. Alleman, V.S. Magar, (Eds.), Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds, Battelle Press, Columbus, OH, 2000, pp. 1-7.

[33]   M.D. Lee, B. Borden, M.T. Lieberman, W. Beckwith, T. Crotwell, P.E. Haas, Effective distribution of edible oils – results from five field applications, in V.S. Magar, D.E. Fennell, J.J. Morse, B.C. Alleman, A. Leeson, (Eds.), Anaerobic Degradation of Chlorinated Solvents. The Sixth International In Situ and On-Site Bioremediation Symposium. San Diego, CA. June 4-7, 2001, Battelle Press, Columbus, OH, 2001, pp 249-256.

[34]   W.J. Hunter, Injection of innocuous oils to create reactive barriers for bioremediation: Laboratory studies, Journal of Contaminant Hydrology 80 (2005) 31-48.

[35]   R.C. Borden, Effective distribution of emulsified edible oil for enhanced anaerobic bioremediation, Journal of Contaminant Hydrology 94 (2007) 1-12.

[36]   Harkness et al., Results of Laboratory Column Studies to Determine the Potential for Bioremediation of Chlorinated Solvent DNAPL Source Areas, SAB3, CL:AIRE Bulletin, October 2010.

[37]   D. Bose, S.M. Senkan, On the Combustion of Chlorinated Hydrocarbons: 1. Trichloroethylene, Combustion Science and Technology, 35 (1983) 187-202.

[38] J. Dong, K. Yoon, Thermal Decomposition Mechanism of Chlorinated Volatile Organics at Pyrolytic and Oxidative Conditions, Korean Journal of Chemical Engineering, 16 (1999) 501-504.

[39] P.G. Shields, G.X. Xu, W.J. Blot, J.F. Fraumeni, G.E. Trivers, E.D. Pellizzari, Y.H. Qu, Y.T. Gao, C.C. Harris, Mutagens from heated Chinese and US cooking oils, Journal of the National Cancer Institute, 87 (1995) 836–41.

[40] U.S. Environmental Protection Agency, Health Assessment Document for Phosgene; EPA/600/8-86/022A. Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Research Triangle Park, NC, 1986.

[41] A. Demirbas, Fuel properties and calculation of higher heating values of vegetable oils, Fuel, 77 (1998) 1117-1120.

[42] H.F. Stroo, M.R. West, B.H. Kueper, R.C. Borden, D.W. Major, C.H. Ward, In situ bioremediation of chlorinated solvent source zones in B.H. Kueper, H.F. Stroo, C.M. Vogel, C.H. Ward (Eds.), Chlorinated Solvent Source Zone Remediation, Springer, New York, 2014, 713 p.

[43] J.L. Triplett, Kingston, P.C. Johnson, B.H. Kueper, K.G. Mumford, In situ thermal treatment of chlorinated solvent source zones, in B.H. Kueper, H.F. Stroo, C.M. Vogel, C.H. Ward (Eds.), Chlorinated Solvent Source Zone Remediation, Springer, New York, 2014, 713 p.

[44] J. Abu-ashour, D.M. Joy, H. Lee, H.R. Whiteley, S. Zelin, Transport of microorganisms through soil, Water, Air, and Soil Pollution, 75 (1994) 141-158.
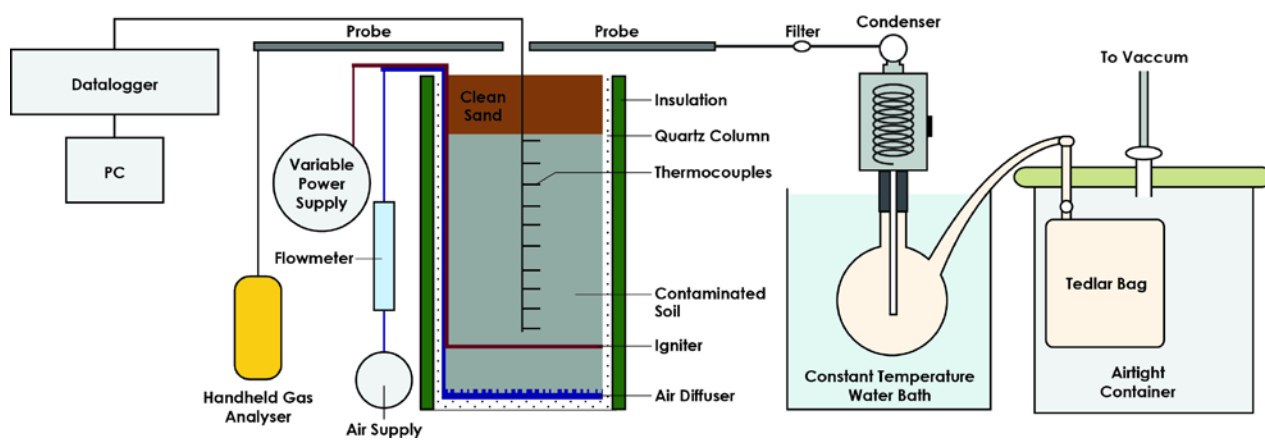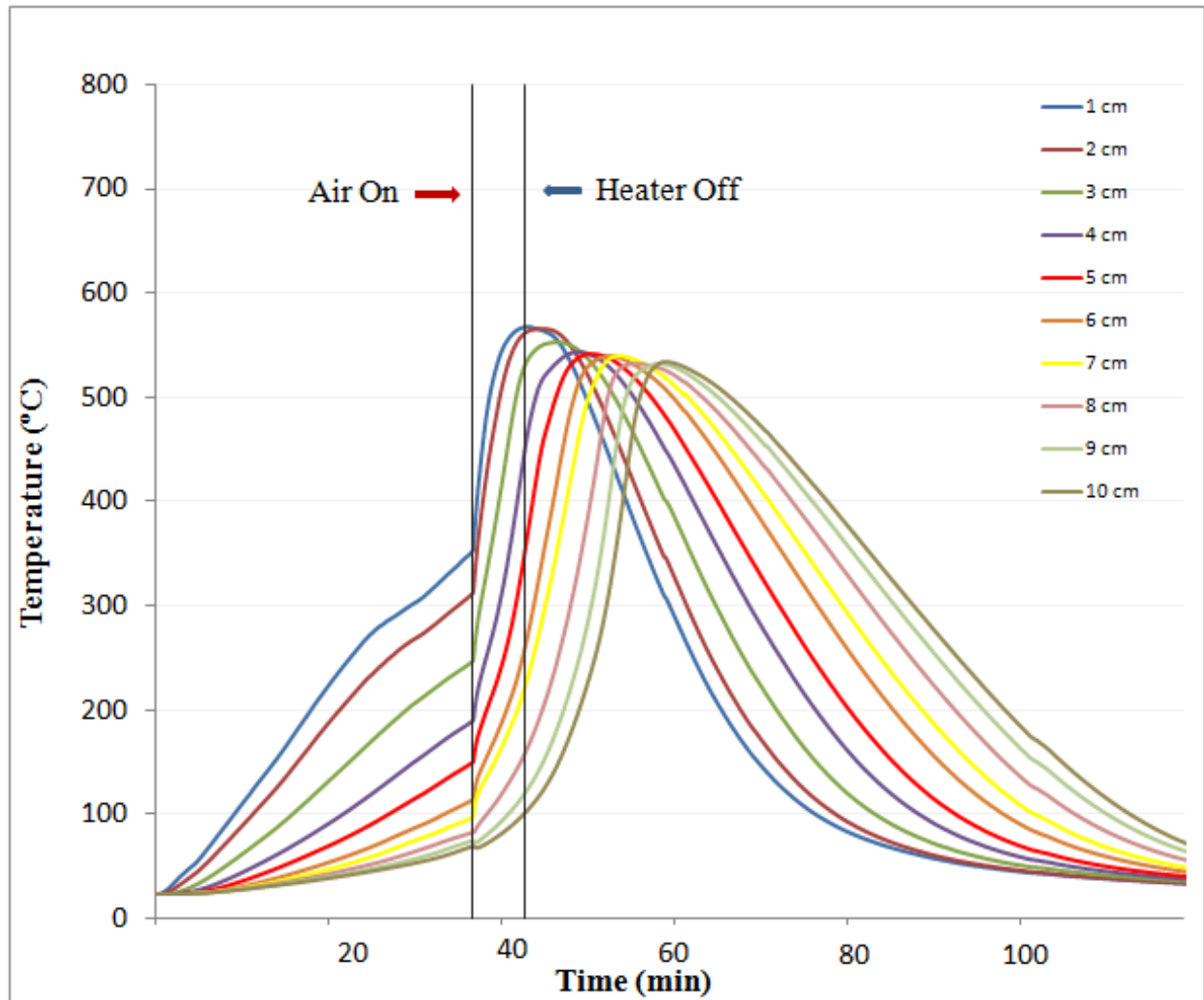
Figure 1: Experimental set-up.

Figure 2: Thermocouple profiles (labeled by distance above base) for sand with 10% TCE and 15% canola oil saturations (Experiment 1).
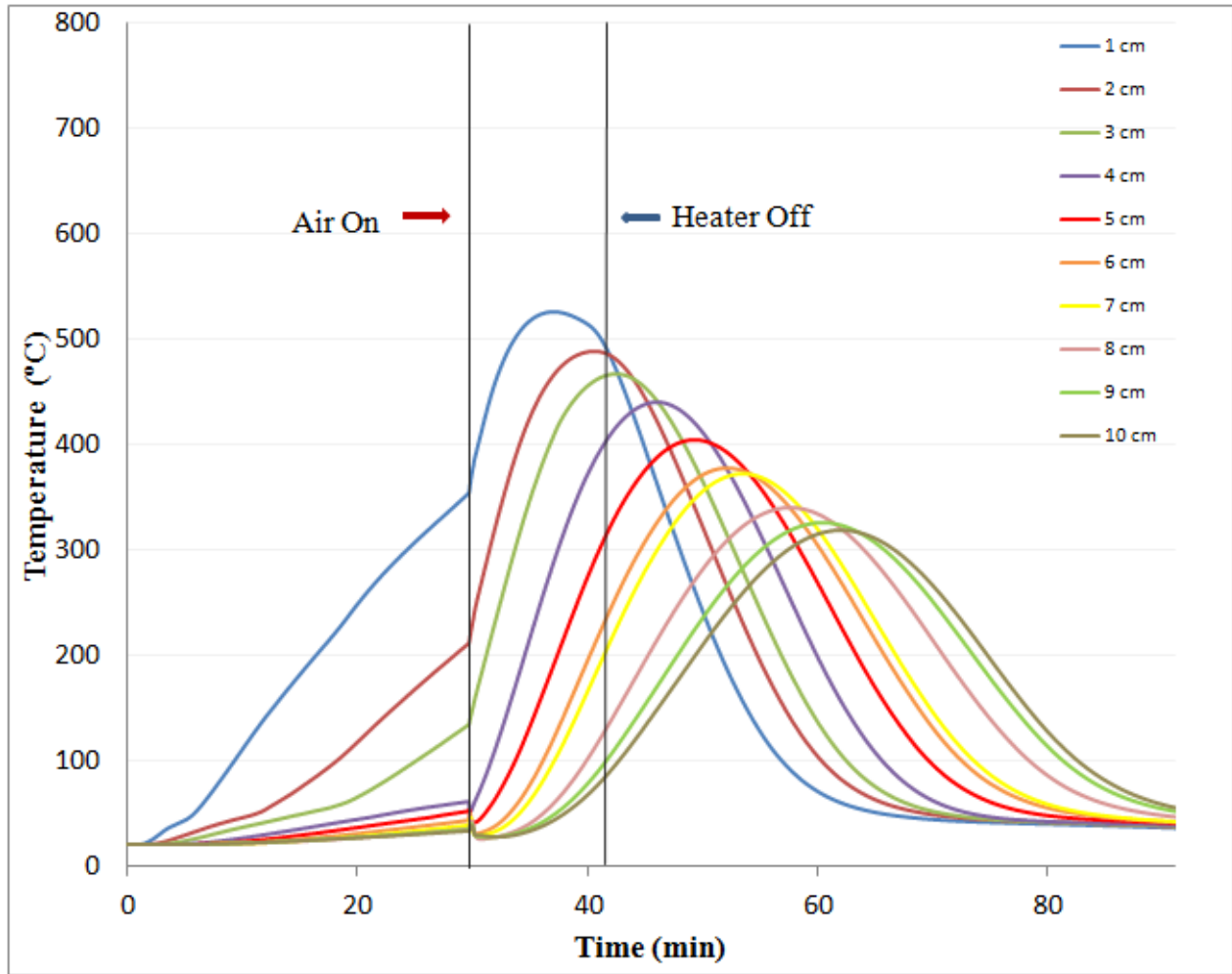
Figure 3: Thermocouple profiles for sand with 10% saturation TCE NAPL only (Experiment 14).
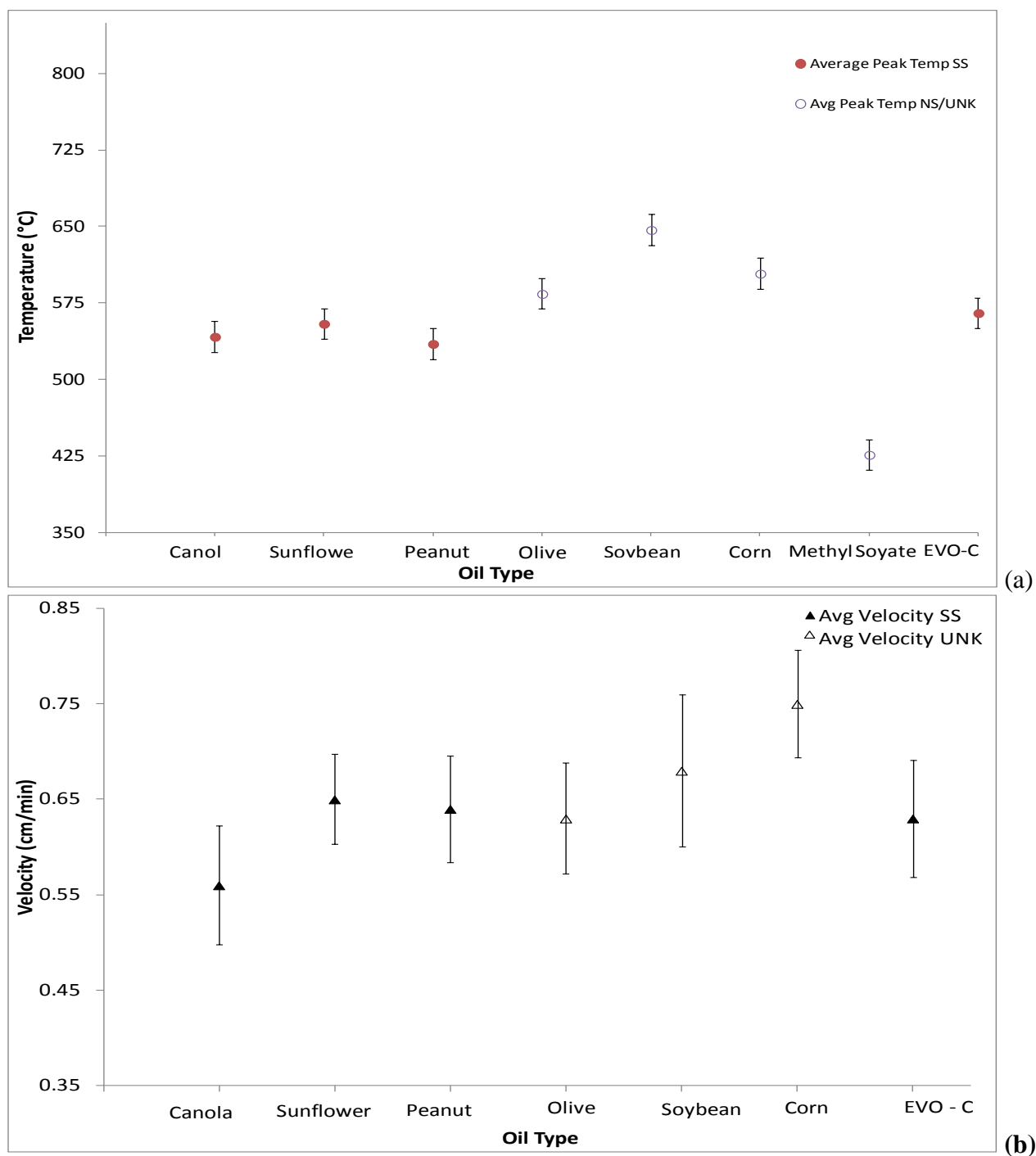
Figure 4: (a) Average peak smoldering temperatures, and (b) average velocity of the reaction for different oil types (Experiments 1-7, 28). SS = steady, self-sustaining, NS = non-self-sustaining, UNK = unknown (UNK). Uncertainty is represented by 95% confidence intervals.
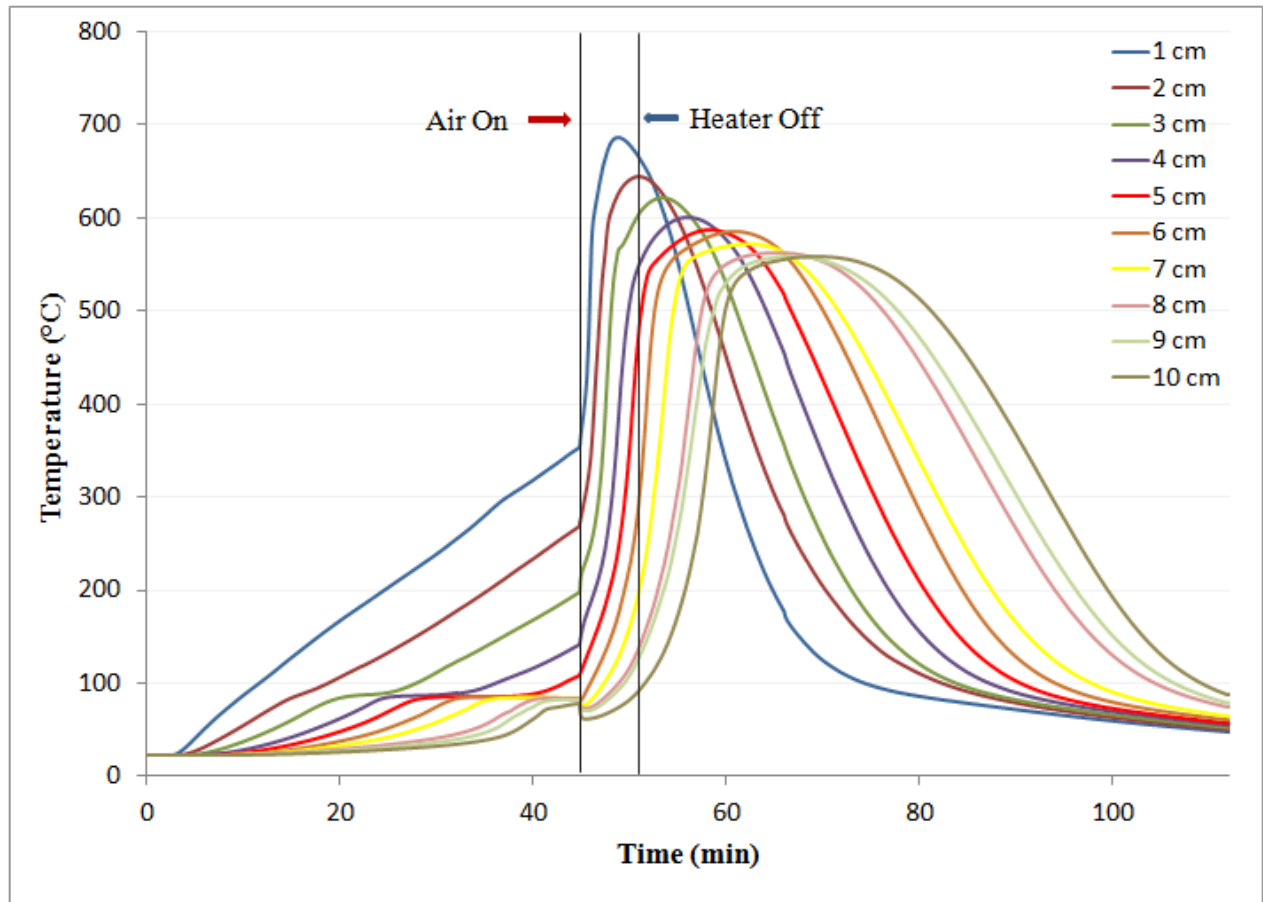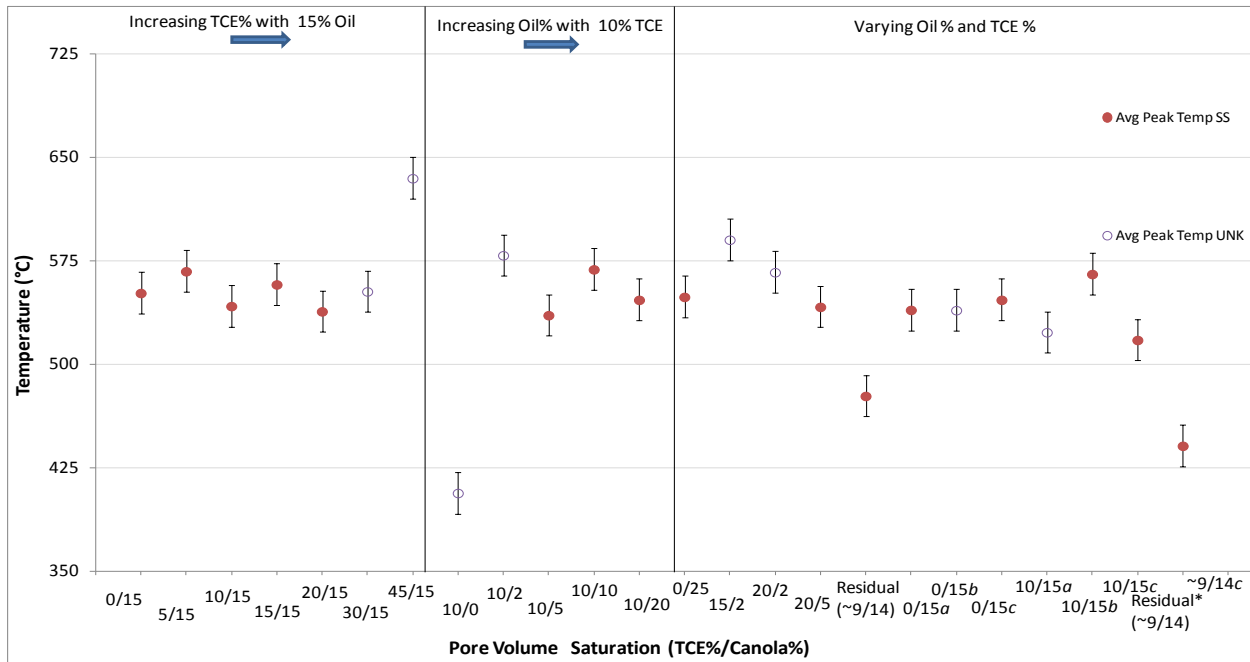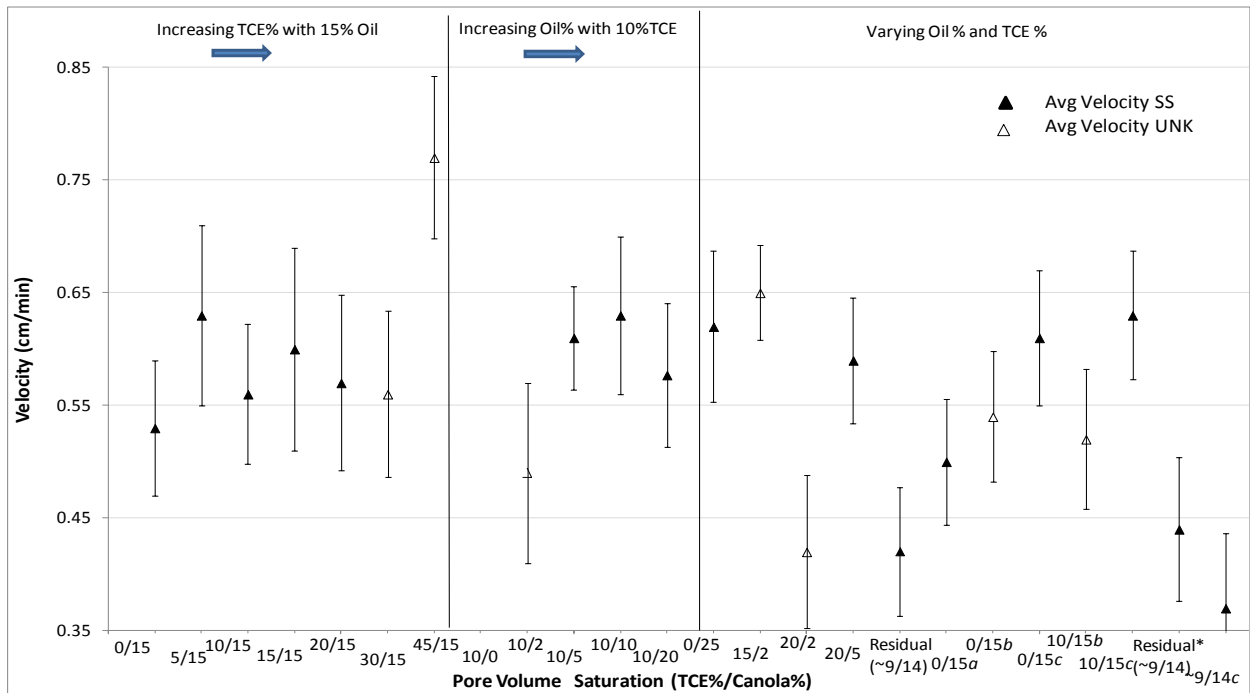
Figure 5: Thermocouple profiles for sand with 10% TCE and 15% olive oil saturations (Experiment 6).

(a)

(b)

Figure 6: (a) Average smoldering temperatures and (b) average reaction velocity for TCE/ canola oil ratios (Experiments 1, 8-30). Uncertainty is represented by 95% confidence intervals. *a, b,* **and** *c* **represent EVO-A, EVO-B, and EVO-C, Residual* represents residual TCE and injected canola oil in sand.**
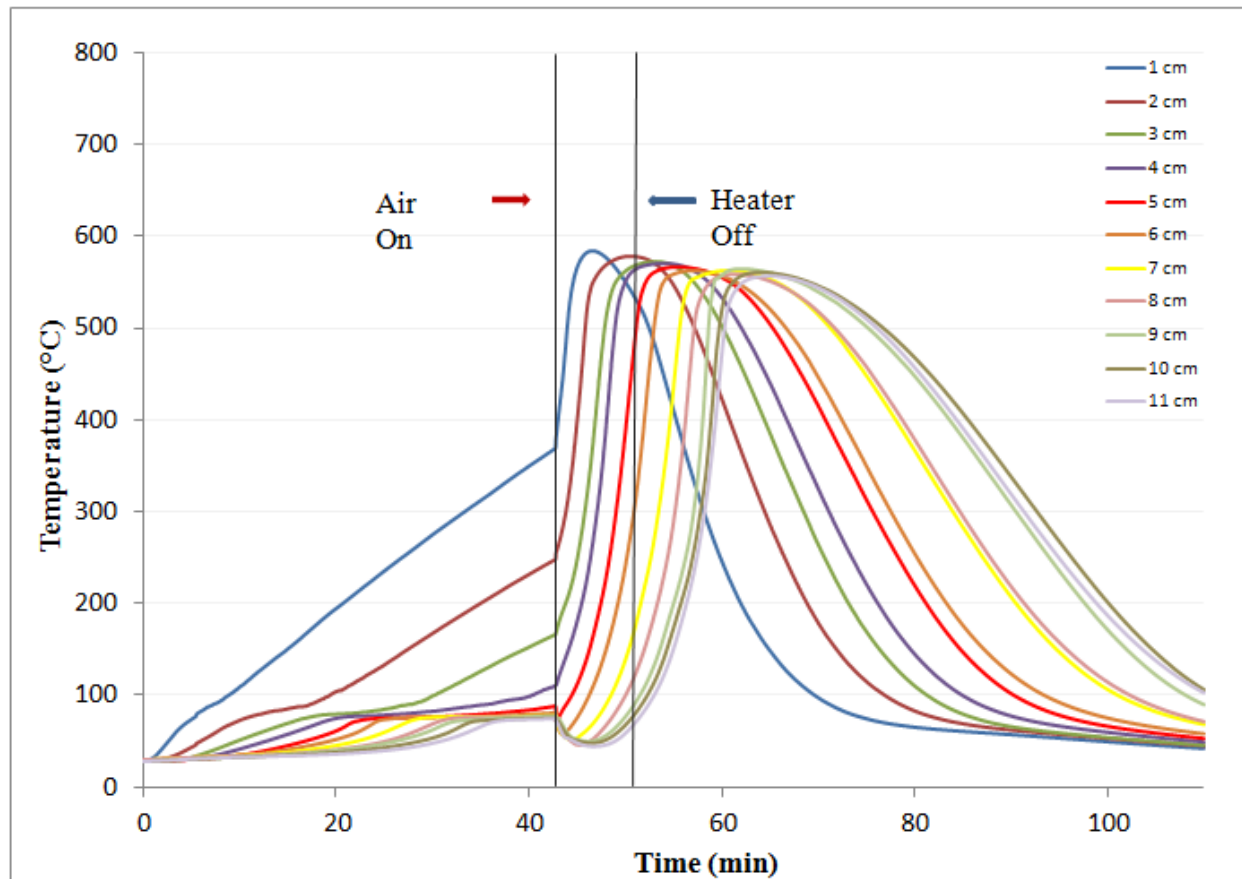
Figure 7: Thermocouple profiles for sand pre-mixed with 10% TCE NAPL saturation and 15% EVO-C saturation (Experiment 27).
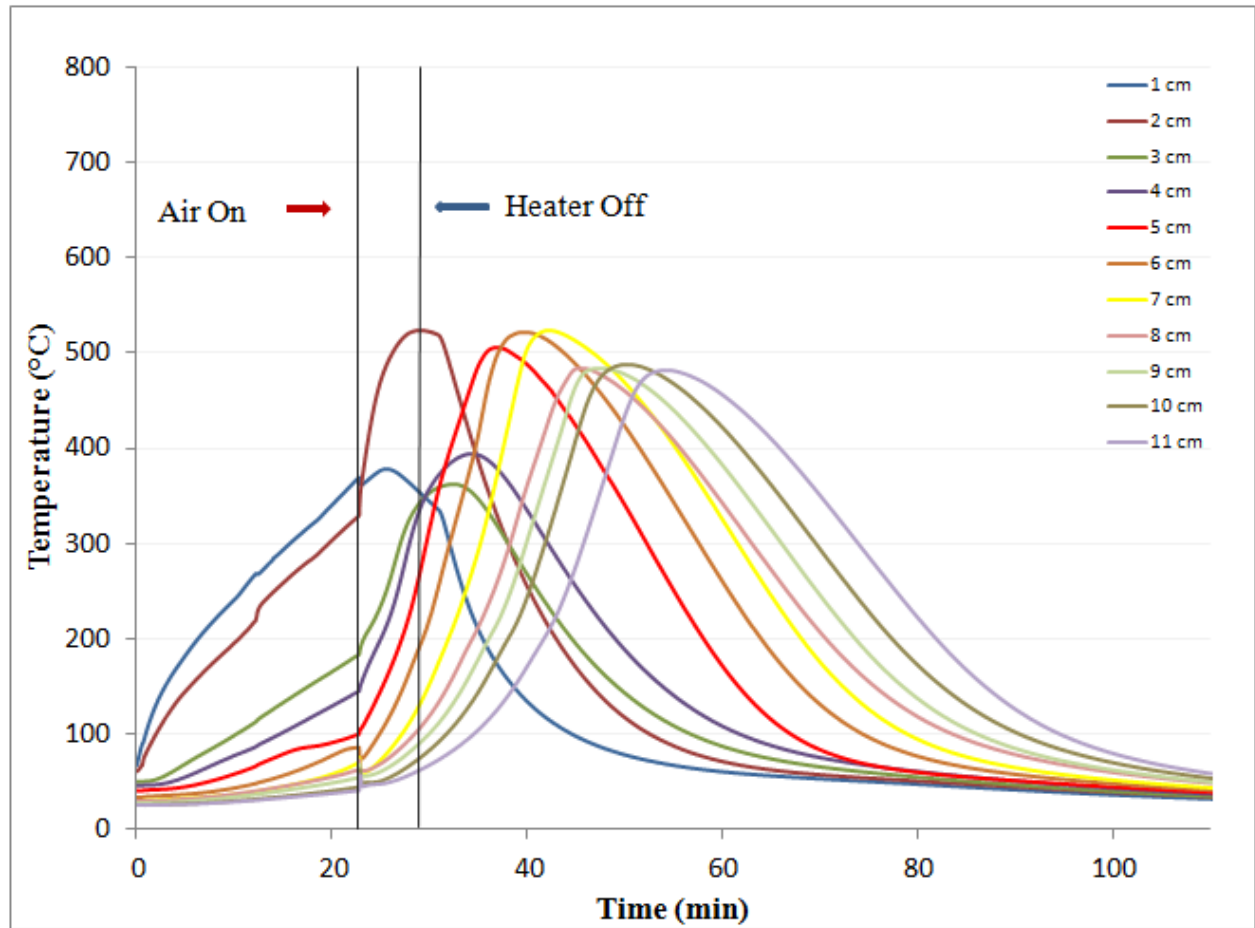
Figure 8: Thermocouple profiles for residual TCE and residual canola oil in sand achieved through pump injection followed by gravity drainage (Experiment 28).

TABLES

Table 1: All Experiments: Initial Conditions and Key Results

Category	Experiment No.	Oil Type	S_{TCE}	mg/kg	S_{OIL}	mg/kg	Analysis	Average Peak Temp °C	Average Propagation Velocity cm/min	SS / NS / UNK
			Initial Conditions						**Results**	
			TCE		Oil					
Oil Type	1	**Canola**	10%	40000	15%	42000	Yes	543	0.56	SS
	2	**Corn**	10%	40000	15%	40500		641	0.75	UNK
	3	**Soybean**	10%	40000	15%	43000		647	0.68	UNK
	4	**Sunflower**	10%	40000	15%	40000		555	0.65	SS
	5	**Peanut**	10%	40000	15%	41500		535	0.64	SS
	6	**Olive**	10%	40000	15%	39000		585	0.63	UNK
	7	**Biofuel**[*]	10%	40000	15%	39500		426	NA	NS
Oil/TCE Concentration	8	Canola	**0%**	**0**	**15%**	**42000**	Yes	552	0.53	SS
	9	Canola	**5%**	**20000**	**15%**	**42000**		567	0.63	SS
	10	Canola	**15%**	**60000**	**15%**	**42000**		558	0.6	SS
	11	Canola	**20%**	**80000**	**15%**	**42000**		538	0.57	SS
	12	Canola	**30%**	**120000**	**15%**	**42000**	Yes	553	0.56	UNK
	13	Canola	**45%**	**180000**	**15%**	**42000**		635	0.77	UNK
	14	None	**10%**	**40000**	**0%**	**0**	Yes	407	NA	NS
	15	Canola	**10%**	**40000**	**5%**	**14000**		536	0.61	SS
	16	Canola	**10%**	**40000**	**10%**	**28000**		572	0.63	SS
	17	Canola	**10%**	**40000**	**20%**	**56000**	Yes	547	0.58	SS
	18	Canola	**0%**	**0**	**25%**	**70000**		549	0.62	SS
	19	Canola	**10%**	**40000**	**2%**	**5600**		579	0.49	UNK
	20	Canola	**15%**	**60000**	**2%**	**5600**		590	0.65	UNK
	21	Canola	**20%**	**80000**	**2%**	**5600**		567	0.42	UNK
	22	Canola	**20%**	**80000**	**5%**	**14000**		542	0.59	SS
Emulsified Oil	23	**EVO-A**	0%	0	15%	25000		539	0.50	SS
	24	**EVO-B**	0%	0	15%	25000		539	0.54	UNK
	25	**EVO-C**	0%	0	15%	27000		547	0.61	SS
	26	**EVO-B**	10%	40000	15%	25000		523	0.52	UNK
	27	**EVO-C**	10%	40000	15%	27000	Yes	565	0.63	SS
Oil Injection	28	**Canola (Injected TCE)**	9%	36000	14%	39200	Yes	477	0.42	SS
	29	**Injected Canola (Resident TCE)**	10%	40000	14%	39200		518	0.44	SS
	30	**EVO-C (Injected TCE)**	9%	3600	14%	24000		441	0.37	SS

Notes: *Methyl Soyate, S_{TCE} = saturation of TCE, S_{OIL} = Saturation of Oil, **Analysis** = sand & gas analysis performed, **SS** = self-sustaining, **NS** = non-self-sustaining, **UNK:** sustainability unknown, **NA** = not applicable.

Table 2: Emulsified Vegetable Oil (EVO) Compositions

	EVO-A	EVO-B	EVO-C
Oil [ml]	Canola 60.00	Canola: Methyl Soyate 40.00: 20.00	Canola 65.00
Span60 [ml]	13.84	13.84	11.00
Ethly Lactate [ml]	2.12	2.12	0.00
Water[ml]	24.04	24.04	24.00
Total[ml]	100.00	100.00	100.00

Note: Densities - Span 60: 1.00 g/ml, Ethyl Lactate: 1.036 g/ml, Water: 0.998 g/ml.

Table 3: Number of Moles of VOCs Observed by Sand and Gas Analysis

Experiment No. TCE: Oil (%)	1(a) 10:15	1(b) 10:15	12 30:15	14 10:00	17 10:20	27 10:15	28 9:14
Initial TCE	1.31	1.40	4.30	1.32	1.29	0.84	1.21
Gaseous TCE: Preheating Phase	9.6E-6	6.1E-5	6.2E-3	7.6E-6	1.4E-7	2.2E-4	7.8E-6
Gaseous TCE: Combustion Phase	8.2E-1	8.9E-1	3.7E0	7.4E-1	7.7E-1	5.5E-1	8.7E-1
Gaseous TCE: Cooling Phase	1.9E-1	1.4E-1	4.3E-1	5.8E-2	2.1E-1	3.3E-2	2.6E-2
TCE in Sand: 10 – 7.5 cm height	0	0	0	0	0	0	0
TCE in Sand: 7.5 – 2.5 cm height	0	0	0	0	0	0	0
TCE in Sand: 2.5 – 0 cm height	0	0	0	0	0	0	0
TCE in Sand: 0 – 2cm (below heater)	2.1E-2	2.5E-2	5.4E-2	9.1E-4	2.7E-2	8.6E-4	0
Gaseous PCE: All Phases	1.9E-3	2.0E-3	2.5E-3	1.9E-3	1.9E-3	1.2E-3	1.0E-3
Phosgene: All Phases	3.0E-9	4.0E-9	NA	NA	NA	NA	NA
Volatilized TCE (Sum for All Phases)	1.01	1.03	4.14	0.80	0.98	0.58	0.90
Observed TCE (Volatilized Plus All Sand)	1.03	1.06	4.19	0.80	1.01	0.58	0.90
TCE Volatilized (%)	77	74	96	61	76	69	74
TCE Combusted (%)	21	24	3	39	22	31	26

Note: Uncertainty on all gas and sand TCE mass values: $\pm$ 0.001